

### **Report on:**

# Scientific Review of

# **British Columbia CSST**

## **Soil Standards Derivation Protocol**

## Submitted to: Ministry of Environment October 2005



Submitted by: Science Advisory Board for Contaminated Sites in British Columbia



Science Advisory Board for Contaminated Sites in British Columbia

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#### **PREFACE**

The analysis provided in this report is intended to support a larger objective. The SAB was asked by the Ministry of Environment (formerly Ministry of Water, Land and Air Protection) to –

- (i) conduct a scientific review of the 1996 Contaminated Sites Standards Taskgroup (CSST) protocols for deriving environmental standards under the BC Contaminated Sites Regulation (BC CSR), and
- (ii) propose revisions based on technical/scientific advances, and in cases where a gap existed in the previous guidance.

The formal objectives of the overall project are -

"Review with an aim to providing the Ministry with detailed recommendations to update and revise the Ministry's existing CSST soil standards derivation protocol.

The project will include consideration of screening risk assessment scenarios and approaches, in additions to the development of exposure scenarios and derivation equations for the newly defined "Wildlands" and Condominium land uses. This project also to include consultation with the broader contaminated sites stakeholder community of any recommended revisions or newly developed components proposed for the revised soil standards derivation protocol."

This report comprises a portion but not the entirety of the protocols review [item (i) above]; in support of future recommendations on revisions to the derivation protocols for soil standards under the British Columbia Contaminated Sites Regulation [item (ii)].

The review project involved oversight by an SAB Task group – co-chaired by Jean Cho, PhD, Dennis Konasewich, PhD, and Jim Malick, PhD - that was instrumental in advising on the direction and critical issues in the review. The SAB recognizes and appreciates the in-depth technical review provided by Golder Associates Limited, as summarized in this report. Readers should note, however, that the views expressed within the report may not necessarily reflect the views of the SAB or the Ministry of Environment. At the time of release of this report, work on revisions to the Contaminated Soil Standards Derivation Protocols for British Columbia was beginning in earnest.

Any recommendations on revisions to the Protocols may require the consideration of issues that were beyond the scope of the Golder review: for example, a desire for consistency in technical/scientific objectives across various levels of application of generic to highly site-specific guidance on contaminated sites assessment and remediation, albeit with reduced uncertainty and an allied reduced conservatism for increasingly site-specific determinations. In addition, this report in a few cases may not adequately reflect a consensus on preferred technical approaches, as reflected in peer review comments received during or subsequent to the finalization of the report. As one example see the comment by Professor Mayer, Attachment 1. It is the expectation of SAB that further work will be required on some technical issues and proposed approaches toward achieving a stronger scientific consensus. Such issues may include, but might not be limited to (i) prediction of soil – groundwater partitioning of metals/metalloids or other contaminants; (ii) requirements for obtaining soil vapour data for volatile contaminants; and (iii) soil standards for wildlands land-uses.



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#### **Acknowledgement**

The SAB appreciates the financial support of the Ministry of Environment in the form of conditional grants that allowed the SAB to undertake the development of Screening Risk Assessment tools for approved professionals. The SAB also acknowledges and appreciates support under the Conditional Grant Program that facilitated the review of the CSST Soil Standard Derivation Protocols.

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### Report on:

### SCIENTIFIC REVIEW OF BRITISH COLUMBIA CSST SOIL STANDARDS DERIVATION PROTOCOL

Submitted to:

Science Advisory Board for Contaminated Sites in British Columbia

Department of Chemistry, University of Victoria PO Box 3065, Stn CSC Victoria, BC V8W 3V6

04-1412-228

July 2005



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#### **REPORT ON**

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#### PREFACE

This report, prepared by Golder Associates Ltd. (Golder) for the Science Advisory Board for Contaminated Sites in British Columbia (SABCS), is a scientific review of the B.C. Ministry of Environment Contaminated Sites Standards Task Group (CSST) soil standards derivation protocol. The current CSST soil standards derivation protocol (the "CSST protocol") was issued in 1996.

The scope of the review focuses on scientific issues for derivation of soil standards based on potential risk to human and ecological receptors. The review is not intended to address policy issues, although instances where policy and science overlap are identified for consideration by the appropriate decision makers. While comprehensive, the review was not intended to be exhaustive, and focused on exposure scenarios and issues deemed to be of relatively high priority, based on consultation with SABCS. Furthermore, this report is not intended to be a protocol for derivation of soil standards, although elements of this work will be useful for this purpose.

The review included the existing exposure scenarios defined by the CSST protocol (e.g., human health direct contact pathways; groundwater pathways [protection of aquatic life, drinking water, irrigation watering, livestock watering]; toxicity to soil invertebrates and plants, and livestock ingesting soil and fodder). Two new exposure pathways were considered: inhalation of vapour intrusion in buildings, as well as toxicity to small mammals and birds. Two new land use categories were considered: high density urban residential (for locations such as high-rise apartments or condominiums) and wildlands.

The regulatory context for the review of CSST standards is that the application of standards is the first step in the evaluation of contaminated sites, and that if standards are exceeded, there are further screening level and detailed risk assessment tools that can be applied for the assessment of contaminated sites. It is thus important that soil standards be reasonably conservative, based on relatively simple approaches and models that are applicable to a broad cross-section of sites recognizing that, when needed, there is the option for higher level assessment.

This document was authored by Peter Chapman, Ph.D., Ian Hers, Ph.D., Blair McDonald, M.E.T., R.P.Bio., Christine Thomas, M.Sc. and Reidar Zapf-Gilje, Ph.D. of Golder Associates Ltd. External peer review comments were provided by Anne Fairbrother, Ph.D. of the USEPA and Mark Richardson, Ph.D. of Health Canada. Review comments were provided by members of the SABCS CSST Review Task Group and the BC Ministry of Environment.

The findings and recommendations are based on the current state of the science. As the practice of risk assessment advances, there will be new developments for soil standard protocol development, contaminant transport modeling, and assessment of exposure and risk to human and ecological receptors. These new advances should be incorporated into future updates to the protocol, as warranted.

#### LIST OF ACRONYMS

BAF	Bioaccumulation factor
BCE	British Columbia Environment
BCWLAP	British Columbia Ministry of Water, Land and Air Protection
BW	Body weight
CCME	Canadian Council of Ministers of the Environment
COPC	Contaminant of potential concern
CSST	Contaminated Sites Standards Task Group
DAF	Dilution attenuation factor
DTPA	Diethylenetriaminepentaacetic acid
ECL	Effect concentration low
ECO-SSL	Ecological soil screening level
EC <sub>X</sub> -NL	Effective concentration resulting in a X% decrease, but not lethal
ERA	Ecological risk assessment
ESSD <sub>X</sub>	Estimated species sensitivity distribution concentration corresponding to
	the Xth percentile
ET	Exposure term
EU	European Union
FIR	Food ingestion rate
HC <sub>X</sub>	Hazardous concentration resulting in a Xth percentile
IRIS	Integrated Risk Information System
K <sub>d</sub>	Partition coefficient
K <sub>OW</sub>	Octanol water partition coefficient
LC <sub>X</sub>	Lethal concentration resulting in a X% decrease
LOEAL	Lowest observed adverse effect level
LOEC	Lowest observed effect concentration
MATC	Median acceptable test concentration
NOAEL	No observed adverse effect level
NOEC	No observed effect concentration
NRC	National Research Council
ORNL	Oak Ridge National Laboratory
PAH	Polycyclic aromatic hydrocarbon
PBPK	Physiologically based pharmacokinetic
PCBs	Polychlorinated biphenyls
PDMS	Polydimethylsiloxane
QSAR	Quantitative structure activity relationship
R <sub>f</sub> C	Reference concentration
$R_{\rm f}D$	Reference dose
RFP	Request for Proposal
SAF	Soil allocation factor
SABCS	Science Advisory Board for Contaminated Sites; SAB
SSD	Species sensitivity distribution
SSL	Soil screening level
TDI	Tolerable daily intake
TEC	Threshold effect concentration
TRV	Toxicity reference value
USEPA	United States Environmental Protection Agency
WQG	Water quality guideline

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#### 1.0 INTRODUCTION

The Science Advisory Board for Contaminated Sites in British Columbia (SABCS) contracted Golder Associates Ltd (Golder) to conduct a scientific review of the B.C. Ministry of Water, Land and Air Protection's (BCWLAP) Contaminated Sites Standards Task Group (CSST) soil standards derivation protocol. The current CSST soil standards derivation protocol (the "CSST protocol") was issued in 1996 (BCE, 1996). SABCS requested a scientific review to address the following questions:

- Is the current CSST protocol scientifically sound? Have there been significant scientific developments in the last decade that should be incorporated into the CSST protocol?
- To the extent that the CSST protocol (or its associated default toxicological and/or hydrogeological parameter values) may not be scientifically sound or up-to-date, how should the protocol or the default parameter values of the protocol be revised or replaced? Specific recommendations to improve its scientific viability were requested.
- Are there exposure scenarios that are not adequately addressed by the CSST protocol? If so, how should these exposure scenarios be addressed?

#### 1.1 Scope of Review

The scope of the scientific review was developed in consultation with SABCS based on: a) the original Request for Proposal (RFP) dated October 6, 2004, b) Golder's response to the SABCS RFP, and, c) an initial kick-off meeting held January 21, 2005 between representatives from the Golder study team, SABCS, and BCWLAP. The scope of this review was limited by the following considerations:

- To the extent considered practical and appropriate, proposed revisions to the CSST protocol need to be harmonized with the contaminated site soil and water guideline derivation protocols of the Canadian Council of Ministers of the Environment (CCME).
- This review was not intended to provide an exhaustive analysis of derivation methodologies from all jurisdictions; rather, the review focused on differences between the existing methodology (BCE, 1996) and selected recent guidance documents (CCME, 2005; USEPA, 2003a). Guidance documents from other jurisdictions were reviewed on a case-by-case basis.

- The review was limited to those scientific concepts and approaches that were found to be sufficiently developed and/or validated to a level appropriate for regulatory use. This consideration was intended to act as a "reality check" on any proposed modifications to the existing CSST protocol.
- A review of policy decisions inherent in the existing derivation methodology was not included, except in those instances where policy decisions may be influenced by the findings of the technical review. We have identified instances where policy and science overlap for consideration by the appropriate decision makers.

The following high priority review tasks were identified based on the original RFP and input from SABCS during the initial kick-off meeting:

- Propose defined exposure scenarios and derivation protocols for deriving new soil standards, if appropriate, for Wildlands and for High-Density Urban Residential settings such as high-rise apartments and condominiums.
- Propose methods to derive standards to address human exposure to soil- or groundwater-derived contaminants in indoor air via soil vapour intrusion into buildings.
- Propose methods to derive standards to address wildlife exposure to soil-derived contaminants (if the scientific review demonstrates that inclusion of such standards is defensible and appropriate).

The regulatory context for the review of CSST standards is that the application of standards is the first step in the evaluation of contaminated sites, and that if standards are exceeded, there are further screening level and detailed risk assessment tools that can be applied for the assessment of contaminated sites. It is important that soil standards be reasonably conservative, based on relatively simple approaches and models that are applicable to a broad cross-section of sites, recognizing that, when needed, there is the option for higher level assessment.

While not the focus of this assessment, it is essential that the broader implications of this review in relation to other regulatory guidance and standards in British Columbia be recognized. The scientific concepts, assumptions and approaches, where appropriate, should be consistent within the regulatory guidance and tools for assessment of contaminated sites.

#### 1.2 Report Organization

The existing CSST protocols include derivation methods for a broad variety of land uses, human and environmental receptors, and environmental media, which resulted in a scientific review that, by necessity, covered a diverse variety of technical issues. We have opted to organize our scientific review by major topics such as matrix pathways, or proposed new land use classifications. A number of technical issues were applicable to multiple Schedule 5 matrix pathways (e.g., groundwater modeling), and therefore, are presented as separate sections. Our report is organized as follows:

- Section 1: Introduction and project overview.
- Sections 2-3: Technical issues common to multiple matrix standards. Section 2 provides recommendations regarding the groundwater models, while Section 3 provides a review of receptor parameters that are common to multiple human health matrix standards.
- Sections 4-6: Human health matrix standards. Section 4 provides recommendations regarding evaluation of soil vapour intrusion into buildings and development of standards for vapour inhalation. Section 5 provides a review with respect to drinking water standards (which share elements with the groundwater model review in Section 2), while Section 6 addresses standards for the ingestion of contaminated soil.
- Sections 7-10: Environmental matrix standards. Section 7 is focused on standards for the protection of soil invertebrates and plants. Section 8 provides recommendations for a derivation methodology for the protection of small mammals and birds. Section 9 provides a review of potential changes to soil standards for the protection of groundwater flow to surface water to aquatic life (which share elements with the groundwater model review in Section 2). Section 10 provides a review with respect to the livestock ingesting soil and fodder standards.
- Section 11: This section summarizes matrix standards that were not included in this scientific review since the scope for this project was insufficient to address these scenarios.
- Section 12: This section describes the proposed scenario for the High Density Urban Residential land use, and provides recommendations regarding the application of selected matrix standards.
- Section 13: This section describes the proposed scenario for the Wildlands land use, and provides recommendations regarding the application of selected matrix standards.
- Section 14: References consulted in the preparation of this scientific review.

#### 2.0 GROUNDWATER MODELS

The groundwater model adopted by CSST was an integral part of the protocol used to back-calculate matrix soil standards for the protection of groundwater. This section of the report evaluates the groundwater fate and transport model used for this purpose. To simplify the discussion, the groundwater model adopted by CSST, as described in the CSST protocol, is referred to as the "CSST model" (BCE, 1996). Groundwater models adopted or proposed by other agencies are also reviewed. This includes a model by USEPA used to develop soil screening levels (SSLs), as documented in the USEPA "*Soil Screening Guidance*" (USEPA, 1996), henceforth referred to as the "USEPA model", a groundwater model proposed by the Science Advisory Board (SAB) of British Columbia, as documented in the Screening Risk Assessment Level 2 protocol (SAB, 2004), henceforth referred to as the "SRA-2 model", and a groundwater model proposed by CCME, as documented in their draft "*Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines*", (CCME, 2005), henceforth referred to as the "CCME model".

#### 2.1 Review of Selected Groundwater Models

#### 2.1.1 CSST Groundwater Model

Matrix soil standards for the protection of groundwater were derived using a groundwater transport model that simulates the movement of a contaminant from the soil to the groundwater, and the subsequent movement of the contaminant in the groundwater to a receptor. The model was developed by BC Environment, with the assistance of Golder Associates Ltd., and was based on the framework described in the draft USEPA "Soil Screening Guidance" (USEPA, 1994).

Contaminant transport is modeled through four chemical/physical compartments, consisting of: (i) contaminant partitioning between soil, soil pore air, and soil pore water; (ii) contaminant leachate movement and attenuation through the unsaturated soil zone; (iii) contaminant leachate mixing with the groundwater, and (iv) contaminant movement and attenuation through the saturated groundwater zone to a receptor. Using this model, soil-groundwater protective standards were derived for the protection of drinking water, livestock watering, irrigation watering and use by aquatic life.

The unsaturated zone transport ((ii), above) mixing of leachate of with groundwater (iii) and contaminant transport in the aquifer (iv) can be characterizing using a Dilution Attenuation Factor (DAF), which is the ratio between the leachate concentration at the contamination source and the groundwater concentration at the receptor. A leachate

concentration that is protective of groundwater is back-calculated by multiplying the groundwater standard for a given constituent by the DAF.<sup>1</sup>

Exhibits containing the model equations and default parameters for the CSST groundwater model are provided in Appendix II. The four chemical/physical compartments are described below.

#### Unsaturated Zone Chemical Partitioning

A linear distribution coefficient is used to describe the partitioning between the sorbed and aqueous phases (" $K_d$  model"). The partitioning of non-polar organic chemicals is a function of the organic carbon partitioning coefficient ( $K_{oc}$ ) of the contaminant and the amount ("fraction") of organic carbon ( $f_{oc}$ ) in the soil. For weakly ionizing organic chemicals, such as pentachlorophenol, partitioning in the model is additionally influenced by the pH of the soil.

The CSST protocol recognized that the partitioning of inorganic constituents was considerably more complex than for organic compounds, being additionally dependent on factors such as pH, sorption to clays, organic matter, iron oxides, oxidation/reduction conditions, major ion chemistry and the chemical form of the metal. However, to simplify the partition model, the distribution coefficients ( $K_d$ ) used in the model were calculated as a function of pH, and as a function of an idealized soil with assigned physical and chemical characteristics. A detailed review of the CSST approach used to derive metal  $K_d$ 's and issues for prediction of metals partitioning is provided in Appendix I.

#### Unsaturated Groundwater Zone

The unsaturated zone groundwater transport model is a one-dimensional model for advection, dispersion, sorption, and first-order decay. The matrix soil standards were developed based on the default assumption that contamination is in contact with the saturated zone. Therefore, unsaturated zone processes are effectively "turned off" in the calculation of the matrix numerical soil standards.

#### Groundwater Mixing Zone

A groundwater mixing zone model is used to represent the dilution of leachate entering groundwater at the interface between the unsaturated zone and saturated zone. The mixing model is based on a mass-balance approach and considers the infiltration of leachate into the groundwater and mixing of chemicals in leachate within groundwater flowing through the aquifer, beneath the contamination source area.

<sup>&</sup>lt;sup>1</sup> The dilution attenuation factor (DAF) is different from the dilution factor (DF), defined in the CSST model, which is limited to mixing of leachate with groundwater.

The mixing depth is calculated using an equation (Appendix II, Exhibit 6) that considers both vertical dispersion of the contamination along the length of the source area and mixing due to the downward velocity of the infiltrating leachate. The equation can, under certain circumstances, calculate a mixing zone thickness greater than the aquifer thickness (assumed to be 5 m for generic guideline development); if this occurs, the mixing depth should be set at the aquifer thickness.

#### Saturated Zone Transport

The groundwater model includes the Domenico and Robbins transient analytical equation to evaluate lateral saturated zone transport to a downgradient receptor. The analytical equation simulates one-dimensional uniform groundwater flow, three-dimensional dispersion, sorption and first-order decay. For the development of soil standards, no vertical dispersion was allowed and it was assumed that the distance to the receptor (well, surface water body) was 10 m.

The saturated zone transport model requires that a saturated zone biodegradation rate be defined. For organic chemicals, the half-life chosen was obtained from literature values where the half-life was equal to "50 percent of anaerobic rate low (highest number of days)" (Appendix II, Table B-2). For non-degrading chemicals (metals, PCB's), the model runs did not allow for contaminant decay.

Since the saturated zone transport equation is time-dependent, the maximum concentration of the chemical at the receptor would be expected to occur at some time in the future, depending on the groundwater velocity and the retardation and decay of the chemical. Since source-depletion was not considered in the development of soil standards, the predicted concentration of the chemical at the receptor will eventually become stable. The default time used to calculate the downgradient concentration for derivation of the CSR Schedule 5 matrix soil standards was set at 2,200 years (personal communication, Mr. George Szefer, MWLAP, April 29, 2005). The CSST protocol documentation indicated a default time of 100 years (Appendix II, Exhibit 7). The rationale for the default travel time selected is not documented. As discussed in Section 2.2.7 of this report, model simulations with a travel time of 2,200 years indicate that this is sufficient time for quasi-steady state conditions to develop for most Schedule 5 chemicals, with the exception of a few metals and higher molecular weight organics.

#### Rationale for Use of CSST Groundwater Model

As described in BCE (1996), "BC Environment recommended its four component model because:

• the major transport processes are represented;

- the major variables affecting each of the transport components are included, can be identified, and can be modified;
- physical and chemical effects are considered;
- model assumptions and criteria derivations are "transparent";
- the model can be calibrated;
- the model performs with reasonable accuracy using a small set of input parameters;
- the accuracy and reliability of the model increases as site specific information increases;
- the model can be used with assumed site characteristics or use site specific data; and,
- the model is scientifically based and defensible.

Attenuation within the model is essentially confined to adsorption-desorption reactions (partitioning), dilution (mixing between contaminated leachate and groundwater), biological degradation (for organics only) and dispersion".

#### CSST Groundwater Model Assumptions

BCE (1996) indicates that the CSST groundwater model was based on assumptions "generally typical of the climatic conditions of the lower Fraser River and Vancouver, and assumed groundwater characteristics typical of those found within the Fraser River sands of the Fraser River delta area. Other assumptions include:

- the site is medium sized (between  $1,500 \text{ m}^2$  and  $12,000 \text{ m}^2$ );
- the total volume of contaminated soil is less than 450 cubic metres (5 m x 30 m x 3 m);
- the depth to groundwater is not more than three (3) metres;
- the distance to the receptor is at least 10 metres;
- the soil is physically and chemically homogeneous;
- the organic content of the soil is at least 0.6 percent;

- the moisture content is uniform throughout the unsaturated zone;
- the porosity of the soil is 30 percent, and 10 percent of the pore volume is water filled;
- the infiltration rate is uniform throughout the unsaturated zone;
- flow in the unsaturated zone is assumed to be one dimensional and downward only, with dispersion, retardation and biological degradation;
- the contaminant is not present as a free product phase (i.e., a non-aqueous phase liquid);
- the maximum concentration in the leachate is equivalent to the solubility limit of the chemical in water under the defined site conditions;
- the aquifer is unconfined;
- the groundwater flow is uniform and steady;
- co-solubility and oxidation/reduction effects are not considered;
- dispersion includes both mechanical dispersion and diffusion, and is assumed to occur in the longitudinal and horizontal transverse directions only;
- mixing of the leachate with the groundwater is assumed to occur through mixing of leachate and groundwater mass fluxes; and,
- dilution by groundwater recharge down gradient of the source is not included.

#### Water Quality Standards Used to Derive Soil Standards

The groundwater transport model derives soil concentration standards to ensure that the contaminant concentrations in the groundwater discharging and in contact with a receptor are less than or equal to established substance-specific water quality criteria for the receptor (i.e. aquatic life) or water use (i.e. irrigation watering, livestock watering or drinking water) of concern. BCE (1996) indicated that for the aquatic life pathway, surface water quality criteria were used to back-calculate soil standards. However, BCE policy was revised shortly after the publication of the above documents in that the surface water criteria was replaced with the water standard applicable to groundwater. The "groundwater" standard is typically 10 times greater than the surface water criteria, under the assumption that a minimum 10-fold dilution of groundwater would occur at the

discharge point to the surface water body. In summary, the applicable matrix soil standards (CSR Schedule 5) were derived using the following water standards:

- Groundwater flow to surface water used by aquatic life: CSR Schedule 6 AW Standard;
- Groundwater used for livestock watering: CSR Schedule 6 LW Standard;
- Groundwater used for irrigation watering: CSR Schedule 6 IW Standard; and,
- Groundwater used for drinking water: CSR Schedule 6 DW Standard.

The above water standards are evaluated in Section 5.0 of this report.

#### 2.1.2 CCME

The draft CCME protocol (CCME, 2005) provides methodology for the derivation of soil guidelines for the protection of (i) potable (drinking) water, (ii) groundwater used for agricultural uses (livestock watering and irrigation), and (iii) freshwater life in nearby surface water. The CCME groundwater model is the "CSST 1996 groundwater model" developed by the British Columbia Contaminated Sites Soil Taskgroup (CSST). While the model is identical, the CCME values for some input parameters are different than those assumed by CSST. In addition, CCME includes separate input parameters for coarse- and fine-grained soils.

The allowable concentration of the chemical in groundwater at the receptor is the appropriate water quality guideline for the pathway. For the aquatic life pathway, CCME (2005) assumes a 10 m separation distance between the contamination source and the surface water body. For the development of generic guidelines, it is assumed that a water well or livestock dugout could be installed at the edge of (or even within) the boundaries of the remediated area. Therefore, no saturated zone transport is assumed, and instead the receptor concentration is assumed to be equal to the concentration in groundwater after mixing of leachate with groundwater for the water well or dug out pathways.

The CCME protocol only applies to organic compounds due to the highly site-specific nature of partitioning for inorganic chemicals and the lack of generalized modeling techniques appropriate for inorganic substances. The CCME protocol indicates that "where groundwater pathways may be of concern for sites contaminated by metals, these pathways should be addressed on a site-specific basis; this would likely include measurement of metals in groundwater at the source and/or at the point of exposure." The CCME protocol concludes that "generalized techniques for evaluating the partitioning and transport of inorganic substances that are appropriate for generic guidelines are not expected to be developed in the foreseeable future".

#### 2.1.3 USEPA Soil Screening Guidance

The USEPA Soil Screening Guidance (1996) provides a methodology for deriving soil screening levels (SSLs) for the protection of groundwater (drinking water). The SSLs are intended as a tool to facilitate prompt identification of contaminants and exposure areas of concern. USEPA (1996) indicates that SSLs can be used as Preliminary Remediation Goals (PRGs) provided that appropriate conditions are met (i.e., conditions found at a specific site are similar to conditions assumed in developing the SSLs).

The development of soil leachate SSLs is based upon a two-step process. The first step is the development of a Dilution Attenuation Factor (DAF). The DAF accounts for leachate mixing and attenuation in the aquifer. A leachate concentration that is protective of groundwater is back-calculated by multiplying the groundwater standard for a given constituent by the DAF. That leachate concentration is then used to back-calculate a SSL that is protective of groundwater using a simple linear equilibrium soil/water partition equation. For the generic SSL approach, default parameter values are used for all non-chemical specific parameters. At sites that are not adequately represented by the default values and where more site-specific data are available, it may be more appropriate to use the site-specific SSL model.

USEPA (1996) selected a dilution attenuation factor (DAF) of 20 to account for contaminant dilution and attenuation during transport through the saturated zone to a receptor well. The USEPA selected a DAF of 20 using a "weight-of-evidence" approach that considered the results of modeling conducted using two models: (i) the USEPA Composite Model for Leachate Migration with Transformation Products (EPACMTP), developed by the Office of Solid Waste (OSW), and (ii) the SSL dilution model, described below. The models were run using inputs based on data from 300 groundwater sites across the USA.

The default DAF of 20 represents an adjustment from the DAF of 10 presented in the December 1994 draft Soil Screening Guidance (USEPA, 1994) to reflect a change in default source size from 30 acres to 0.5 acre. A DAF of 20 is protective for contamination sources up to 0.5 acre in size, although analysis by USEPA indicates that it can be protective of larger sources, as well. The default DAF assumes that contamination is located above the water table.

The EPACMTP is a model for one-dimensional leachate transport in the unsaturated zone, mixing of leachate with groundwater, and three-dimensional transport in groundwater. Linear- and non-linear sorption and decay processes are included in the model. The model includes a Monte Carlo module, which generates model parameters from probability distributions representative of conditions across the USA. The key assumptions for generating the default DAF were:

- (i) The drinking water well is located next to the contamination source (no horizontal separation distance for transport).
- (ii) There is no chemical attenuation through sorption or decay.
- (iii) The well intake is located between 15 and 300 feet below the water table, thus providing for mixing of contaminants within the aquifer.

Probabilistic modeling was conducted assuming varying inputs for contamination source size, location of the well relative to the plume, and hydrological parameters (e.g., infiltration, groundwater flow rate, dispersivity).

The USEPA also evaluated dilution between leachate at a soil contamination source, and groundwater at a receptor using a mass-balance model that only incorporated dilution through mixing of leachate below the water table beneath the contamination source area. The SSL dilution model is identical to that incorporated in the CSST groundwater model, except that a slightly different model is used for calculation of the mixing zone depth. The USEPA mixing depth model is consistent with that used in the MULTIMED model (Sharp-Hansen et al., 1990) and the EPA CMTP model.

The USEPA protocol applies to both organic and inorganic chemicals. The partitioning model used by USEPA to assess inorganic chemicals is described in detail in Appendix I.

#### 2.1.4 Screening Level Risk Assessment 2 (SRA-2) Soil and Groundwater Module

In October 2004, the SAB prepared a draft report entitled Screening Level Risk Assessment 2 (SRA-2) Soil and Groundwater module, which presents a proposed protocol for screening level risk assessment in British Columbia. The *Soil Module* is designed to evaluate the potential for unsaturated zone contaminant migration from soil to groundwater, and the *Groundwater Module* is designed to evaluate the potential for contaminant migration in groundwater to a down-gradient receptor. The purpose of the protocol is to provide practitioners a tool to estimate the receptor concentration for screening risk assessments. While the protocol is not intended to back-calculate soil standards, there are useful concepts in the protocol that are described below.

The SRA-2 soil and groundwater modules cannot be applied if any of the following precluding factors exists:

- Soil or groundwater contamination occurs in fractured bedrock;
- The contaminant of potential concern (COPC) is an ionizing organic compound and the soil pH is either less than 4.9 or greater than 8.0;

- The COPC is an inorganic element or compound; and,
- Potentially mobile non-aqueous phase liquid (NAPL) exists in soil or groundwater.

The SRA-2 Soil Module for organic chemicals uses the same linear distribution coefficient (" $K_d$  model") as that in the CSST groundwater model. The Soil Module can not be used for inorganic compounds, but instead leaching tests are proposed to evaluate unsaturated zone leaching of inorganic constituents. The rationale for excluding inorganic chemicals is that metal release and mobility is highly variable and influenced by numerous site specific processes. There is large variability in measured  $K_d$  values, and comparisons between model-predicted and measured  $K_d$  values suggest that it is difficult to describe this natural variability with generic values, even if pH-dependency is included.

The SRA-2 Groundwater Module includes several precluding factors, which indicate the Module cannot be used if any of the following are true:

- the receptor is a water supply aquifer (i.e., DW, IW, LW) *and* the groundwater plume has traveled beyond the property boundary;
- the distance between the contaminated site and a potential receptor is less than 30 m; and,
- the compound in question decays to harmful daughter products that have been detected in groundwater (e.g., transformation of certain chlorinated solvent compounds).

Some of the above factors relate to science policy decisions and do not necessarily pertain to the validity of the model.

The SRA-2 Groundwater Module incorporates a dilution model for mixing of leachate with groundwater beneath the contamination source, and a groundwater transport model, for simulating solute transport with groundwater away from the contamination source zone. The groundwater mixing model is identical to the USEPA Soil Screening Guidance (1996) mixing model. The groundwater transport model uses a one-dimensional solution by Bear (1979) to the first-order reactive transport equation. The model is a steady-state solute transport model, and only accounts for longitudinal dispersion, and assumes that there is no lateral or vertical dispersive spreading of the plume.

The context for the SRA-2 groundwater tool is screening level risk assessment. There is the option to use more sophisticated groundwater models in a subsequent detailed risk assessment phase.

#### 2.2 Comparison and Evaluation of Groundwater Models

#### 2.2.1 Model Scenario

The CSST model scenario for development of the CSR matrix soil standards makes certain assumptions on the size and location of the contamination source and distance, selects a representative site for estimation of hydrogeological properties (e.g., Fraser River sand deposits; site located in the Fraser River delta area) and distance from the contamination source to the receptor (i.e., 10 m).

The size of the contamination source does not affect the model predictions, as discussed in Section 2.2.7 of this report. The location of the soil contamination source, assumed to be directly above the water table, is considered reasonably conservative. While there would be less mixing of contaminants leaching from impacted soil below the water table, the typical approach for this particular scenario is to evaluate regulatory compliance on the basis of groundwater quality monitoring.

The influence of hydrogeological conditions on model predictions is addressed in the sections below. Overall, the assumptions related to Fraser River sand properties and location (Lower Mainland) may be reasonably conservative. It is noted that many of the contaminated sites in British Columbia are located within the Lower Mainland.

A distance of 10 m to the receptor (i.e., surface water body, well) is considered reasonable for most contaminated sites in BC.

#### 2.2.2 Model Framework and Approach

The CSST and CCME groundwater model frameworks are identical, each consisting of a four-component analytical model.

While certain elements of the CSST and USEPA groundwater models are similar, the USEPA only considered one groundwater scenario (transport to a receptor well) and used a different modeling approach (multiple models and a weight-of-evidence approach) to select a single default dilution attenuation factor (DAF equal to 20) for all chemicals of concern. The USEPA selected a default DAF of 20 based on a comprehensive modeling effort that involved the use of two different models and selection of input parameters using a probabilistic approach. The USEPA conducted simulations for a variety of site sizes and combinations of input parameters based on field data from hundreds of sites from across the USA. The approach has undergone a relatively extensive review including a review by the USEPA Science Advisory Board.

The SRA-2 protocol is designed as a tool to facilitate derivation of site specific standards, and comprises two distinct modules ("Soil and Groundwater Modules") for evaluation groundwater flow to a surface water body. The main differences between the CSST and SRA-2 models are that the SRA-2 model (i) incorporates the use of leaching tests to evaluate metals partitioning, (ii) does not include unsaturated zone transport, and (iii) assumes steady state conditions for groundwater (saturated zone) transport. As described in the SRA-2 report, the BC SAB also recommended as part of their review that a DAF of 20 be adopted for a receptor well scenario. At this time, it is recommended that a four-component model be retained for both the drinking water and aquatic life scenarios, since different approaches for the two scenarios (i.e., DAF of 20 for water-well scenario and four-component model for aquatic life scenario) will result in inconsistent standards, as described in Section 2.2.3 below.

Although the CSST protocol and SRA-2 groundwater models are used for different purposes, the models should generally be consistent in their formulation and non-site specific model input parameters. Certain aspects of the CSST protocol review could be useful for refinement of the SRA-2 model and development of supplementary modeling tools to SRA-2.

#### Recommendations

Retain a multi-component analytical model consisting of (i) unsaturated zone partitioning, (ii) groundwater mixing, and (iii) saturated zone transport; however, consider refinements to the model and input parameters described in the sections below. Unsaturated zone transport does not affect the calculation of soil standards based on the current model scenario; therefore, at least for purposes of generic standard derivation, the unsaturated zone component could be removed from the model framework.

#### 2.2.3 Implications of Adopting the USEPA DAF Approach

The implications of adopting the USEPA DAF approach are discussed both in terms of implications for soil standards for protection of drinking water, and consistency between the water-well and aquatic life scenarios.

The DAFs for individual chemicals and pH conditions, calculated using the current CSST model and inputs, are both greater than and less than the USEPA DAF of 20. A fixed DAF of 20 for the groundwater flow to a drinking water well scenario could result in either higher or lower soil standards depending on the soil-water partitioning coefficient ( $K_d$ ), biodegradation half-life (for organics) and transport simulation time. Compared to a DAF of 20, in general, higher standards would be predicted for compounds with lower soil-water partition coefficients and moderate to high half-lives (e.g., benzene,

trichloroethylene, tetrachloroethylene, pentachlorophenol) while lower standards would be predicted for compounds with higher soil-water partition coefficients (e.g., benzo(a)pyrene). For several metals, lower standards would be predicted at higher pH (corresponding to higher  $K_d$ 's), assuming transient conditions (e.g., 2,200 years).

Considering the extensive analysis and review the USEPA approach has been subjected to, adopting the USEPA DAF potentially has merit; however, there are implications if a different approach (i.e., CSST model) is used for the groundwater flow to surface water scenario. For example, for benzo(a)pyrene, adopting a DAF of 20 would result in a soil standard for the protection of drinking water of 4 mg/kg. In contrast, using the CSST model there would be no soil standard possible for the protection of aquatic life (i.e., "NS" designation in the Contaminated Site Regulation) based on a higher DAF and groundwater concentration above the solubility limit. Different modeling approaches should not be used for the drinking water and surface water scenarios when significant differences in standards could result that are not supported based on science. Therefore, the USEPA DAF approach is not recommended at this time, and instead a multi-component model consistent with the current CSST approach is recommended.

#### 2.2.4 Applicable Chemicals

The CSST and USEPA protocols are applied to both inorganic and organic chemicals.

The CCME groundwater protocol only applies to organic chemicals since it is not considered appropriate by CCME at this time to develop generic nation-wide guidelines for metals due to the variability and uncertainty in partitioning relationships for metals.

The SRA-2 protocol takes a similar approach to CCME as the model only applies to organic chemicals. Site-specific leaching tests are proposed for inorganic chemicals to quantify partitioning in the unsaturated zone between soil and water.

#### 2.2.5 Unsaturated Zone Partitioning

Non-ionizing Organics

**Model Characteristics**: The CSST protocol, USEPA and CCME protocols use the same model for unsaturated zone partitioning of non-ionizing hydrophobic organics:

$$C_{t} = C_{w} / \rho_{b} * (K_{oc} * f_{oc} + \theta_{w} + \theta_{a} * H')$$
(2.1)

where  $C_t$  is the total soil concentration (mg/kg),  $C_w$  is the soil-water concentration (mg/L),  $K_{oc}$  is the organic carbon-water partition coefficient (L/kg),  $f_{oc}$  is the fraction organic carbon (dimensionless),  $\theta_w$  is the water-filled porosity (dimensionless),  $\theta_a$  is the air-filled porosity (dimensionless), H' is the Henry's Law constant (dimensionless) and  $\rho_b$  is the bulk dry density (kg/L).

The linear equilibrium partitioning model based on organic carbon content is widely used for non-ionizing organics. Numerous studies have shown that sorption of organics by soils is highly correlated with the organic matter content (e.g., Chiou et al. 1979, Hassett et al. 1980), provided the  $f_{oc}$  is above a critical level. USEPA (1996) suggests that when  $f_{oc}$  is below about 0.001, adsorption to inorganic mineral surfaces becomes important. For most non-ionic organics, sorption is a linear function of equilibrium solution concentration up to 60 percent to 80 percent of its water solubility (Hassett and Banwart 1989).

**Model Input Parameters:** The non-specific chemical input parameters to equation 2.1 assumed by CSST, USEPA and CCME protocols are different, as shown below.

	f <sub>oc</sub>	$\theta_{\rm w}$	$\theta_{a}$	ρ <sub>b</sub> (kg/L)	K' benzene $(K_{oc} = 62, H'=0.23)^3$	K' TCE (Koc = 94, H'=0.42) <sup>3</sup>	K' Naphthalene (K <sub>oc</sub> = 1200 H'=0.0198) <sup>3</sup>
CSST	0.006	0.1	0.2	1.75	0.50	0.71	7.3
USEPA <sup>1</sup>	0.002	0.3	0.13	1.5	0.46	0.65	2.6
CCME <sup>2</sup>	0.005	0.119	0.241	1.7	0.44	0.52	6.1

**TABLE 2.1:** Comparison of Model Inputs for Non-Ionizing Organic Chemicals

1. USEPA (1996)

2. CCME (2005), coarse-grained soil

3. Source of the  $K_{oc}$ 's are SRA-2 Appendix C, Table C-1

The CCME defaults for organic carbon are based on "review of organic carbon contents of various Canadian subsoils undertaken in support of the CWS-PHC (CCME, 2000)", while the water- and air-filled porosities were chosen to be "representative of typical sand (coarse-grained) soil".

To further evaluate the effect of differing input parameters on the partitioning calculations, equation 2.1 is re-formulated, as follows:

$$K' = K_{oc} * f_{oc} + (\theta_w + \theta_a * H'/\rho_b)$$
(2.1)

The back-calculated soil standard increases linearly as K' increases. The fraction organic carbon has the greatest effect on the K' parameter. As shown in Table 2.1, there is little difference in K' calculated using the CSST and CCME defaults.

The inputs for the CSST protocol were based on Fraser River sand, where information was available. To provide preliminary data on fraction organic carbon, Golder reviewed information where organic carbon testing was conducted on Fraser River sand at three sites. The  $f_{oc}$  for twenty samples varied between 0.00065 and 0.0083, with a median

value of 0.003. The test methods for organic carbon varied (loss on ignition organic matter content converted to  $f_{oc}$ , Leco analyzer); therefore, the organic carbon values are approximate. While this data set would suggest a lower organic carbon content based the on results for Fraser River sand, it is suggested that the groundwater model should apply to varying hydrogeologic environments. Also there would likely be differences in organic carbon content for near-surface unsaturated soils compared to deeper aquifer material. Therefore, it may be appropriate to utilize different  $f_{oc}$  values for the unsaturated and saturated zones.

The water-filled porosity in the unsaturated zone will vary as a function of soil type and infiltration rate. Water-retention models can be used to estimate water contents for different soil types. The estimated water contents using the Van Genuchten model and model curve-fitting parameters by Schaap and Leij (1998) are shown in Table 2.2.

		Van Genuchten Parameters			Predicted Porosity & Water Contents			
						Residual Water	Field	
	Bulk Density	$\alpha_1$	N	M	Total Porosity	Content	Capacity	
SCS Soil Type	(g/cm <sup>3</sup> )	(1/cm)	(unitless)	(unitless)	$\theta$ (cm <sup>3</sup> /cm <sup>3</sup> )	θ <sub>r</sub> (cm <sup>3</sup> /cm <sup>3</sup> )	$\theta_{fc}$ (cm <sup>3</sup> /cm <sup>3</sup> )	
Clay	1.43	0.01496	1.253	0.2019	0.459	0.098	0.33	
Clay Loam	1.48	0.01581	1.416	0.2938	0.442	0.079	0.26	
Loam	1.59	0.01112	1.472	0.3207	0.399	0.061	0.24	
Loamy Sand	1.62	0.03475	1.746	0.4273	0.390	0.049	0.10	
Sand	1.66	0.03524	3.177	0.6852	0.375	0.053	0.055	
Sandy Clay	1.63	0.03342	1.208	0.1722	0.385	0.117	0.28	
Sandy Clay Loam	1.63	0.02109	1.330	0.2481	0.384	0.063	0.23	
Silt	1.35	0.00658	1.679	0.4044	0.489	0.050	0.28	
Silty Clay	1.38	0.01622	1.321	0.2430	0.481	0.111	0.32	
Silty Clay Loam	1.37	0.00839	1.521	0.3425	0.482	0.090	0.31	
Silt Loam	1.49	0.00506	1.663	0.3987	0.439	0.065	0.30	
Sandy Loam	1.62	0.02667	1.449	0.3099	0.387	0.039	0.17	
Arithmetic Mean	1.52				0.43	0.073	0.24	

 Table 2.2

 Predicted Soil Water Contents Using Van Genuchten Model

The total porosity values in Table 2.2 are relatively high and bulk density values are low, since tests were conducted on near-surface agricultural soils. During dry periods, the unsaturated zone water contents in uncovered areas will tend to be between the residual water content and field capacity. Based on the data in Table 2.2, the water- and air-filled contents assumed by CSST are considered reasonable for sandy soils. The CSST unsaturated zone bulk dry density is somewhat high and could be reduced to  $1.7 \text{ g/cm}^3$ .

#### Recommendations

Adopt the  $K_{oc}$  values for non-ionizing organics listed in SRA-2 Appendix C, Table C-1. It is noted that for several compounds, the  $K_{oc}$  values proposed by SAB in the SRA-2 report are significantly different than the CSST values.<sup>2</sup> The source of most SRA-2  $K_{oc}$  values are those given in USEPA (1996).

Revise the unsaturated zone bulk dry density to  $1.7 \text{ g/cm}^3$ , consistent with the value assumed by CCME.

Consideration could be given to adjusting the fraction organic carbon; however, further evaluation of this parameter for different hydrogeologic environments is recommended before any changes are made. Since partitioning is sensitive to  $f_{oc}$ , an alternative would be to develop multiple soil standards based on  $f_{oc}$  ranges and to provide the option for testing of site soil samples for  $f_{oc}$ .

#### **Ionizing Organics**

The  $K_{oc}$  for an ionizing organic chemical will depend on the soil pH. The CSST protocol derived a pH-dependent  $K_d$  isotherm for pentachlorophenol (PCP). As part of SRA-2, the method used to derive  $K_d$  values for PCP was revised slightly based on the equations below, derived by Schwarzenbach et al. (2002), and analysis conducted by Mr. Don Burnett, Morrow Environmental, Burnaby, BC. For PCP, the  $K_{oc}$  values were derived using the following equations:

$$K_{oc} = K_{oc_{non-ionic}} f_i + K_{oc_{ionic}} (1 - f_i)$$
(2.2)

where

$$\log K_{oc_{non-ionic}} = 0.82 \log K_{ow} + 0.14$$

$$K_{oc_{ionic}} = 0$$

$$f_i = \frac{1}{1 + 10^{(pH - pKa)}}$$
(2.3)

The ionic  $K_{oc}$  values were obtained from Schwarzenbach et al. (2002). The pKa and  $K_{ow}$  values used were obtained from Table 8.5.1.1, found on the MWLAP web site at:

http://wlapwww.gov.bc.ca/wat/wq/BCguidelines/chlorophenols/bcchlorophenol-111.htm#P43552\_674574.

<sup>&</sup>lt;sup>2</sup> The USEPA (1996)  $K_{oc}$ 's are as follows (CSST values in parentheses): Benzene – 62 (83.2), Ethylbenzene – 200 (1096.5), Toluene – 140 (302), Xylenes – 200 to 310 (389), benzo (a) pyrene - 970,000 (891,251), naphthalene – 1,200 (1,288.2), pyrene – 72,444 (68,000), tetrachloroethylene – 260 (158.5), trichloroethylene – 94 (107.2).

The revised PCP  $K_{oc}$  is compared to the values used in the CSST protocol (SSS model) and USEPA protocol in Figure 2.1. As shown, the revised  $K_{oc}$  values are slightly lower compared to the CSST protocol.



Figure 2.1: K<sub>oc</sub> as a Function of pH for PCP (from SAB, 2004)

#### Recommendation

Adopt the ph-dependent  $K_{oc}$  isotherm for pentachlorophenol derived by SAB, as documented in SRA-2.

#### **Inorganic Chemicals**

Three approaches for estimation of unsaturated zone partitioning are evaluated: (i) the use of measured total soil concentrations and model-predicted  $K_d$  partitioning coefficients, (ii) an empirical approach where  $K_d$ 's are obtained from laboratory or field tests, and (iii) an approach where leaching tests are used to estimate unsaturated zone pore-water concentrations. Each approach is discussed below.

 $K_d$  Partitioning Model: The CSST and USEPA use the same model for unsaturated zone partitioning of inorganic chemicals:

$$C_t = C_w / \rho_b * (K_d + \theta_w + \theta_a * H^2)$$
(2.4)

where  $K_d$  is the soil-water partition coefficient (except for mercury, the Henry's Law constant is assumed to be zero). The approach used by CSST and USEPA, as documented in the Soil Screening Guidance (USEPA, 1996), to derive pH-dependent  $K_d$  values is discussed in detail in Appendix I. A summary of this discussion is provided below.

The "USEPA Model" (USEPA, 1996) approach involved the use of the MINTEQ2A geochemical speciation model to generate pH-dependent isotherms for barium, beryllium, cadmium, chromium (III), mercury, nickel, silver and zinc due to the inherent difficulty in determining a generic  $K_d$  value. For many metals, sorption characteristics are highly dependent on the pH. The pH is also a parameter that can be readily measured in the field; therefore, a pH-dependent approach is practical for generic soil standard application. There are several other important geochemical parameters that influence metals sorption, including hydrous ferric oxide (HFO) content, organic matter content, the presence of clay minerals, redox conditions, major ion chemistry, and chemical speciation of the metal.

The USEPA MINTEQ2A modeling exercise assumed sorbent surfaces were limited to HFO and particulate organic matter (POM), and assumed constant values for these parameters based on mid-range values measured at sites across the USA. For HFO, a limited dataset of six measurements was used to derive model input values. Other important assumptions were (i) system equilibrium was assumed, (ii) the redox state of the system was not considered because of the lack of reliable data when the isotherms were modeled, (iii) metal competition was not considered, and (iv) the background porewater chemistry input into MINTEQ2A was defined based on 13 chemical constituents that commonly occur in groundwater.

For arsenic (III), chromium (VI), selenium and thallium, experimental pH-dependent isotherms based on the properties of Wisconsin sand aquifer material were used to generate  $K_d$  values. The USEPA did not provide  $K_d$  values for lead and copper.

The USEPA subsequently developed the "**3MRA model**" system (Multimedia, Multipathway and Multireceptor Risk Assessment) in response to the 1995 Hazardous Waste Identification Rule (HWIR). The 3MRA system is a series of models for screening-level assessment of human and ecological health risks resulting from chronic exposure to contaminants. The 3MRA model includes isotherms that are used to predict soil-water metals partitioning.

As part of 3MRA, the MINTEQA2 model was used to develop concentration-dependent partition coefficients for various combinations of four key parameters ("master variables") affecting metal sorption (pH, HFO, POM and labile organic matter (LOM)). Representative values for master variables were calculated for conditions representing the saturated and unsaturated soil zones.

The approach for modeling partition coefficients adopted for 3MRA was considered by USEPA to be an improvement upon the 1996 USEPA SSL approach for a number of reasons including: (i) thermodynamic data were updated within the MINTEQA2 thermodynamic database making it possible to model the behavior of several additional metals, including arsenic (III), arsenic (V), antimony, beryllium, chromium (VI), cobalt, selenium and vanadium; (ii) the database of hydrous ferric oxide sorption reactions was expanded to include sorption reactions for arsenic, antimony, beryllium, chromium (VI), cobalt, selenium and vanadium; and (iii) the mid-range HFO content was decreased by a factor of 10, which was considered warranted based on comparisons of MINTEQA2 estimates of  $K_d$  with literature values.

**Empirical Data and Parametric Relationships**: An alternate approach to the USEPA or 3MRA approach would be to rely completely on empirical data to determine  $K_d$ 's for use in partitioning models. As discussed above, the USEPA Model used a partial empirical approach for four metals based on limited data. There are more recent compilations of laboratory data where larger data sets are analyzed. For example, Sauvé et al. (2000) compiled data from 70 studies where there were both analyses of metals in leachate (batch tests, centrifugation) and total metals content. The results and statistical analysis for four metals (cadmium, copper, lead and zinc) are provided in Figure 2.2. As shown, there is a weak correlation between  $K_d$  and pH; however, the  $K_d$ 's vary over two to three orders-of-magnitude. Sauvé et al. (2000) found that a parametric model based on the solution pH, soil organic matter and total metal content yielded improved predictions of dissolved metal concentrations than just the pH.



**FIGURE 2.2:** Empirical K<sub>d</sub> Values Compiled by Sauvé et al. (2000). Purple symbols are CSST values, orange symbols are USEPA SSL values.

The CSST and USEPA  $K_d$ 's are compared to the empirical  $K_d$ 's compiled by Sauvé et al. (2000) for cadmium and zinc (Figure 2.2). For these two metals, the comparison indicates the CSST and USEPA  $K_d$ 's are near the low end of the empirical  $K_d$  range at lower pH; however, as pH increases, the CSST and USEPA  $K_d$ 's become less conservative when compared to the empirical  $K_d$ 's.

Leaching Tests and Pore-Water Standards: A third possible approach would be to use leaching tests and to compare pore-water leachate concentrations to generic pore-water standards protective of the groundwater pathway, similar in concept to the approach recommended by SAB for SRA-2. The analysis of additional soil samples using leaching tests, such as the Synthetic Precipitation Leaching Procedure (SPLP) (EPA SW-846 Method 1312), would be required. The advantage of this approach is that leaching tests potentially provide for a more direct indication of metals that may be released to the unsaturated zone, and also measure desorption of metals, which is important since the leaching of metals can be affected by aging and weathering of soils.

The State of New Jersey recently released a protocol (March 11, 2005) for the use of leaching tests (SPLP) to determine soil remediation criteria (see Appendix C of Appendix I). Replicate soil samples are analyzed for leachable and total metal concentrations. One option given is to directly compare the metals concentrations in leachate to the target pore-water concentration, which in New Jersey is the target groundwater concentration divided by a generic dilution attenuation factor (DAF) of 12. A second option is to back calculate a soil cleanup criteria based on the observed correlation between leachable and total metal concentrations. The New Jersey guidance also includes a correction factor to adjust leachate test results when metals are weakly sorbed and when the test dilution for the SPLP test (20 water: 1 solids) could exceed the unsaturated zone dilution.

**Discussion and Recommendations**: There are significant limitations associated with soil-water partitioning coefficients developed using geochemical speciation models for the purpose of generic soil standard development. These limitations include (i) the model only accounts for some of the geochemical processes that result in metals sorption, (ii) there is a wide variation in model-predicted  $K_d$  values, depending on the input parameters adopted, and (iii) model-predicted  $K_d$  values are both greater than and less than reported empirical partition coefficients. However, the empirical tests themselves represent a range of different tests and conditions making direct comparison difficult.

While there are obvious limitations, in our opinion, the use of the USEPA 1996 SSL partition coefficients represents the best available approach for deriving *generic soil standards* for metals at this time. This is reflected in guidance from several other regulatory jurisdictions, which essentially have adopted the USEPA pH-dependent isotherms. Discussions with the experts (Jerry Allison, Allison Geosciences; Robert Truesdale, RTI International) who were instrumental in developing the USEPA and 3MRA guidance over the past decade also indicate for generic standard purposes, it would be difficult to improve upon the USEPA approach, in the absence of site specific data for key geochemical parameters.

The 3MRA isotherms provide additional flexibility through a parameterized approach based on several master geochemical parameters, and also provide MINTEQ2A generated isotherms for several oxy-anions, chemicals for which USEPA previously only provided empirically-derived isotherms for. While the use of the 3MRA approach could be applied when site-specific standards are derived, it is not considered practical for the development of generic soil standards since parameters such as iron oxide and organic matter content are not measured in typical site investigations in British Columbia. The 3MRA approach also does not lend itself readily to generation of pH-dependent isotherms, as described in Appendix I. Also, it is noted that the 3MRA iron oxide contents are considerably lower than those presented in the literature (Battelle, 1989). These lower iron oxide contents may be overly conservative with respect to natural conditions in British Columbia.

The CSST protocol assumed that the  $K_d$  isotherm for copper could be used as a surrogate for lead. This is not considered scientifically defensible, as copper and lead behave differently in natural environments (i.e., copper is considerably more mobile than lead). There is no USEPA isotherm for lead, but there is a 3MRA isotherm for this metal. Neither USEPA nor 3MRA include isotherms for copper. As described below, the 3MRA lead isotherm is used for initial evaluation of lead partitioning. The USEPA SSL  $K_d$ 's for mercury are not recommended since empirical data indicates the USEPA  $K_d$ 's are overly conservative and also do not correctly predict the influence of pH on  $K_d$ (Bright and Telmar, 2003).

From a regulatory perspective, it is desirable that soil-water partitioning models used to develop generic standards are conservative. The USEPA partition model likely underpredicts sorption since not all the processes that contribute to metals sorption are accounted for in the model. Because the USEPA model is based on a set of simplifying assumptions, it is not possible to verify whether or not the USEPA model is intrinsically conservative. Figure 2.2, for example, suggests that the USEPA model is reasonable conservative for zinc but not necessarily conservative for cadmium at a pH of 8. One way to gain further insight on the predictive capability of the groundwater fate and transport model, and indirectly metals partitioning, is to evaluate data for sites where there is soil and near-contaminated source groundwater quality data. It is recommended that the groundwater model be evaluated through analysis of field data from multiple contaminated sites.

In summary, it is recommended that generic pH-dependent soil standards be derived using the USEPA SSL  $K_d$  partition coefficient approach. In addition, it is recommended that pore-water standards for metals be developed as a *complementary* approach, to enable direct comparison of leachable concentrations to pore-water standards since use of leaching tests provides for the most direct indication of possible leaching and impacts to groundwater. To support this option, further evaluation of leaching test protocols and guidance on implementation of this approach for assessment of contaminated sites is
required (e.g., similar in concept to protocol developed by NJDEP, Appendix I). A completely empirical approach based on, for instance, data compiled by Sauvé et al. (2000), is not recommended at this time since the conditions under which tests are conducted vary widely, the data varies over several order-of-magnitude (making selection of a representative empirical value difficult), and since it appears that comprehensive data has been compiled for only a few metals.

## Recommendations

For derivation of soil standards, adopt the partition coefficients recommended by USEPA (1996) for the following metals: antimony; arsenic (III); barium; beryllium; cadmium; chromium (III); chromium (VI); nickel; selenium; silver; thallium; vanadium; and, zinc. It is noted that antimony, barium, beryllium, mercury, nickel, selenium, silver, thallium and vanadium are not currently included in the Schedule 5 matrix standards. The implications for use of USEPA partition coefficients to derive pH-dependent standards for these metals should be further evaluated before any changes to the CSR standards are considered. Such an evaluation goes beyond the scope of this report. The USEPA  $K_d$ 's for mercury are not recommended since empirical data indicates they are overly conservative and do not correctly predict the influence of pH on  $K_d$ .

Develop an isotherm for lead using data in the 3MRA database, assuming iron oxide and organic matter input values identical to those assumed by USEPA in development of SSLs. For comparison to CSST standards, an interim  $K_d$  isotherm was developed using 3MRA predictions for "mid-range" iron oxide and organic matter conditions, with an iron oxide concentration of 0.05 wt% and organic matter concentration of 0.11 wt%.

Using a similar approach to the 3MRA modeling effort, employ the MINTEQA2 thermodynamic database to develop an isotherm for copper assuming inputs identical to those assumed by USEPA in development of SSLs.

Consideration should be given to a regulatory framework that includes pore-water standards and a protocol where the results of leaching tests can be compared to pore-water standards. For metals, pore-water standards and leaching tests would avoid some of the scientific issues and uncertainty associated with the  $K_d$  approach.

To gain further insight on the predictive capability of the metals partitioning model, it is recommended that soil and near-contaminated source groundwater quality data from contaminated sites in British Columbia be evaluated to provide for field-based estimates of groundwater fate and transport, and indirectly partitioning behaviour. **Comparison of CSST and USEPA K\_d's**: The CSST and USEPA SSL's are compared in Table 2.3 for the range of pH values in the CSR standards. All other factors being equal, an increase in  $K_d$  results in an increase in the soil standard.

- The Kd's for arsenic (III) and chromium (VI) are virtually identical within a pH range of 5 to 8.
- For cadmium, the USEPA K<sub>d</sub>'s are slightly lower (however, both the CSST and USEPA the K<sub>d</sub>'s are relatively high).
- For lead, the USEPA  $K_d$ 's, calculated using the provisional 3MRA isotherms, are lower than the CSST  $K_d$ 's, except at a pH of 5.0.
- For zinc, the USEPA K<sub>d</sub>'s are lower than the CSST Kd's, except at a pH of 6.0.

It is noted that for the purposes of calculations in Table 2.3, the mid-point of the pH range was selected for the pH ranges.<sup>3</sup>

<sup>&</sup>lt;sup>3</sup> The protocol followed by MWLAP to derive the CSR soil standards rounded up the pH when selecting the Kd for each pH range in the standards. For example, for a pH range of 6 to 6.5, the Kd for a pH of 6.3 was chosen. For the calculations shown in Table 2.3, the mid-point pH was selected (e.g., 6.25). This difference is not considered significant.

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Table 2.3

	Comparison of soil screening levels calculated with CSST- and USEPA-recommended soil-water partition coefficients														
			1	2	3	4	5	6	7	8	9	10	11	12	13
	CSR Standards			CSST Inputs (Transient Model)					USEPA SSL 1996 (Steady State Model)			ate Model)			
	Receptor		Background	pH for	CSR	рН	CSST	DAF	DAF	Calc. Tox	Calculated	рН	USEPA	Calc. Tox	Calculated
	Groundwater		Soil	Matrix	Matrix	for Kd	1996	@ 100	@ 2200	based Soil	CSST Input	USEPA	SSL	based Soil	USEPA Input
Metal	Concentration'		Concentration <sup>2</sup>	Standard	Standard <sup>3</sup>	Table B-2 <sup>4</sup>	$K_{d}^{4}$	years	years	Standard <sup>°</sup>	Standard <sup>®</sup>	SSL	${\sf K_d}'$	Standard	Standard <sup>®</sup>
	(mg/L)		(mg/kg)		(mg/kg)		(L/kg)			(mg/kg)	(mg/kg)		(L/kg)	(mg/kg)	(mg/kg)
Arsenic	0.05		14.9	N/A	20	5	25.2	3.29	3.29	4.15	19.1	5	27.0	4.45	19.3
111	0.05		14.9	N/A	20	6	27.1	3.29	3.29	4.47	19.4	6	29.1	4.80	19.7
	0.05		14.9	N/A	20	7	29.2	3.29	3.29	4.81	19.7	7	29.5	4.86	19.8
	0.05		14.9	N/A	20	8	31.4	3.29	3.29	5.17	20.1	8	31.6	5.21	20.1
Cadmium	0.0006	9	1.3	<7	2	7	251	125	3.29	0.50	1.8	7	118.9	0.23	1.5
	0.0006		1.3	7 to < 7.5	2.5	7.25	604.5	4.65E+05	3.29	1.2	2.5	7.25	251.2	0.50	1.8
	0.0006		1.3	7.5 to 8	25	7.75	2792.5	Out of range	9.13	15	17	7.75	1631.2	3.2	4.5
	0.0006		1.3	>= 8	150	8	4597	Out of range	49.2	136	137	8	4466.8	8.8	10
Chromium	0.09		58.9	N/A	65	N/A	N/A	N/A	N/A	N/A	N/A	5	1995.3	591	650
111	0.09		58.9	N/A	65	N/A	N/A	N/A	N/A	N/A	N/A	6	211348.9	62580	62639
	0.09		58.9	N/A	65	N/A	N/A	N/A	N/A	N/A	N/A	7	2511886.4	743770	743828
	0.09		58.9	N/A	65	N/A	N/A	N/A	N/A	N/A	N/A	8	4466835.9	1322630	1322689
Chromium	0.01		58.9	N/A	60	5	30.5	3.29	3.29	1.01	59.9	5	30.7	1.01	60
VI	0.01		58.9	N/A	60	6	23.3	3.29	3.29	0.77	59.7	6	29.9	0.99	60
	0.01		58.9	N/A	60	7	17.8	3.29	3.29	0.59	59.5	7	18.0	0.59	59
	0.01		58.9	N/A	60	8	13.6	3.29	3.29	0.45	59.3	8	13.9	0.46	59
Copper	0.09	10	74	<5.0	90	5	50.1	3.42	3.29	14.9	88.9	N/A	N/A	N/A	N/A
	0.09		74	5.0 to 5.5	100	5.25	89.7	4.98	3.29	26.6	101	N/A	N/A	N/A	N/A
	0.09		74	5.5 to 6	200	5.75	359.5	1511	3.29	106	180	N/A	N/A	N/A	N/A
	0.09		74	6 to <6.5	1500	6.25	2029.5	Out of range	5.15	940.70	1015	N/A	N/A	N/A	N/A
	0.09		74	>=6.5	30000	6.5	5012	Out of range	74	33380.30	33454	N/A	N/A	N/A	N/A
Nickel	1.1		N/A	N/A	100 to 500	N/A	N/A	N/A	N/A	N/A	N/A	5	17.4	63.2	63.2
	1.1		N/A	N/A	100 to 500	N/A	N/A	N/A	N/A	N/A	N/A	6	38.9	141.0	141
	1.1		N/A	N/A	100 to 500	N/A	N/A	N/A	N/A	N/A	N/A	7	87.1	315	315
	1.1		N/A	N/A	100 to 500	N/A	N/A	N/A	N/A	N/A	N/A	8	1883.6	6817	6817
Lead	0.11	11	108.6	<5.5	150	5.5	158	16.7	3.29	57.20	166	5.5	280	101.4	210
	0.11		108.6	5.5 to 6	250	5.75	359.5	1494	3.29	130.12	239	5.75	700	253.4	362
	0.11		108.6	6 to <6.5	2000	6.25	2029.5	Out of range	5.15	1149.74	1258	6.25	3000	1085.7	1194
	0.11		108.6	>=6.5	40000	6.5	5012	Out of range	74	40798.15	40907	6.5	10200	3691.4	3800
Zinc	0.9	12	138.1	<6.0	150	6	7.45	3.29	3.29	22.23	160	6	37.6	111.5	250
	0.9		138.1	6 to <6.5	300	6.25	45.65	3.37	3.29	135.34	273	6.25	43.4	129	267
	0.9		138.1	>6.5 to <7	1500	6.75	362.5	1650	3.29	1073.53	1212	6.75	61.3	182	320
	0.9		138.1	>=7	3000	7	1000	Out of range	6.06	5454.31	5592	7	75.0	222	360

Notes:

1. Receptor groundwater concentration is CSR AW freshwater standard (Schedule 6), unless otherwise noted.

2. Background soil concentration is that referenced in CSR matrix soil standard (Schedule 4).

3. CSR Schedule 5, freshwater standard

4. Table B-2 Overview of CSST Procedures for the Derivation of Soil Quality Matrix Standards for Contaminated Sites.

5. Tox Based Soil Standard =  $C_g * DAF * (K_d * \theta_u/\rho_b)$  where  $C_g$  is groundwater concentration, DAF = dilution attenuation factor (3.29),  $\theta_u$  is water-filled porosity (0.1),  $\rho_b$  = bulk dry density (1.75)

6. Calc. CSST Input Standard = Tox. Based Standard + Background Soil Conc. (freshwater standard)

7. USEPA Soil Screening Guidance (USEPA, 1996) cadmium, chromium III, zinc, mercury, nickel (Figure 11), Arsenic (III), chromium (VI) (Figure 10). For lead the approximate interpolated values obtained from 3MRA isotherms using a using a mid-range HFO (0.05 % wt) and mid-range POM (0.11% wt) for a dissolved lead concentration of 0.06 mg/L were used.

8. Calc. USEPA Input Standard = Tox. Based Standard + Background Soil Conc. (freshwater standard)

9. Based on correspondance from George Szefer, April 8, 2005

10. Based on hardness equal H>200, default value in SSS model, March 2005 version

11. Based on hardness equal H>200<300, default value in SSS model, March 2005 version

12. Based on hardness equal H>100<200, based on footnote 7 in Schedule 5 for zinc.

#### 2.2.6 Unsaturated Zone Transport

The BCE (1996) and CCME (2005) unsaturated zone models are identical. However, for the purpose of calculating soil standards or guidelines, the thickness of soil between the contamination zone and water table is taken to be zero; therefore, unsaturated zone processes are not considered. The SRA-2 model does not include unsaturated zone transport.

Further evaluation of unsaturated zone transport processes is on-going by the SAB in a separate project. If there are findings from this evaluation that have implications for the model used for generic soil standard development, the recommendation below should be updated, as warranted.

#### Recommendation

For clarity, eliminate unsaturated zone transport from the CSST model, subject to findings of on-going evaluation by SAB.

#### 2.2.7 Mixing of Leachate with Groundwater

Groundwater Mixing Model

The CSST (BCE 1996), USEPA (1996), SRA-2 (2004) and CCME (2005) models for mixing of leachate with groundwater are based on identical mass-balance models for dilution of leachate below a contamination source zone:

$$C_{w} = C_{gw} (1 + Z_{d} V / I X)$$
(2.5)  

$$C_{w} = C_{gw} DF$$
(2.6)

where  $C_w$  is the leachate concentration in the unsaturated zone (mg/L),  $C_{gw}$  is the groundwater concentration at the down-gradient boundary of the source zone (mg/L),  $Z_d$  is the average thickness of the mixing zone (m), V is the Darcy velocity in groundwater (m/year), I is the infiltration rate (m/year), X in the length of contaminated soil source parallel to groundwater flow (m), and DF is the dilution factor due to mixing of leachate with groundwater (dimensionless).

Different equations are used for calculation of the mixing depth, as outlined below:

CSST and CCME:

$$\begin{array}{ll} Z_d = r + s & (2.7a) \\ r = 0.01X & (2.7b) \\ s = d_a \; \{1 - \exp(2.178 X I/V d_a))\} & (2.7c) \end{array}$$

USEPA

$$Z_d = r + s$$
 (2.8a)  
 $r = (0.0112 X^2)^{0.5}$  (2.8b)

$$s = d_a \{1 - \exp[(-XI)/(Vd_a)]\}$$
 (2.8c)

SRA-2

$$Z_{d} = r + s$$
(2.9a)  
r = 0 044 X<sup>1.23</sup> (2.9b)

$$s = d_a \{1 - \exp[(-XI)/(Vd_a)]\}$$
 (2.9c)

where r is the mixing depth available from dispersion and diffusion (m), s is the mixing depth available due to the infiltration rate and groundwater flow rate (m), and  $d_a$  is the aquifer thickness (m).

The reason for the difference in the mixing depth (r) calculated by USEPA and SRA-2 is that different equations were used to estimate the longitudinal dispersivity. The SRA-2 equation for longitudinal dispersivity is based on Neuman (1990) and was considered by SRA-2 to be a better model for short transport distances.

The above mixing models are compared by calculating the DF using the CSST default input parameters (X = 5 m, I = 0.55 m/year,  $d_a = 5$  m, V = 12.6 m/year).

	CSST	USEPA	SRA-2
$Z_d(m)$	0.5	1	0.53
Dilution Factor	3.31	5.61	3.43

**TABLE 2.4:** Comparison of Dilution Factors forDifferent Groundwater Mixing Models

The revised SRA-2 mixing model results in a four percent increase in the back-calculated soil standard compared to the CSST model.

The groundwater mixing zone equation is based on the assumption that the chemical is distributed evenly throughout a "mixing zone". As noted in CCME (2005), in reality the concentration of the chemical would not be constant through this zone; however, further mixing would be expected at the point of exposure within a well or surface water body. Therefore, the mixing zone approach is considered to be a reasonable approximation for purposes of generic standard development.

# Recommendation

Adopt the revised SRA-2 groundwater mixing model for derivation of soil standards.

# Groundwater Mixing Model Inputs

CSST (BCE 1996) and CCME (2005) use different inputs for the mixing zone equation (USEPA can not be readily compared since a probabilistic approach was taken). The DF calculated using the SRA-2 groundwater mixing model, using the CSST and CCME inputs is provided in Table 2.5.

	X (m)	I (m/year)	d <sub>a</sub> (m)	K (m/year)	i	V (m/year)	DF
CSST	5	0.55	5	N/A	N/A	12.6	3.43
CCME	10	0.28	5	320	0.05	16*	6.25

<b>TABLE 2.5:</b>	Comparison of Dilution Factors for
Different G	coundwater Mixing Models Inputs

\* calculated

The reason for the higher CCME DF compared to CSST is primarily a lower infiltration rate (I) and to a lesser extent, longer contaminated source length (X), which results in a greater mixing depth. For both CSST and CCME, the infiltration rate was calculated using a simple water balance model where the infiltration is equal to the precipitation minus the sum of the surface runoff and evapotranspiration. The assumed CSST precipitation is the approximate mean precipitation at Vancouver International Airport. The CSST protocol does not give a rationale for the surface runoff and evapotranspiration. The CCME recharge is based on data for Halifax, Nova Scotia. The CSST and CCME contaminated source lengths are based on the "typical dimension" of a contaminated site.

The CSST recharge rate is based on a simple model that does not take into consideration hydrological variations and the properties of soil. Estimation of percolation of water within the unsaturated zone is complex. API (1996) describes 13 different empirical methods and models that can be used to estimate recharge for input into environmental site assessments. Two common models that can be used for groundwater recharge estimation are (i) water balance models (HELP, SESOIL), and (ii) numerical models based on the Richards equation (VS2DT, HYDRUS). Water balance models couple climatic and hydrological data with a simple model for unsaturated zone groundwater flow. Numerical models based on Richard's equation provide for more realistic simulation of unsaturated flow processes, but generally do not have as extensive capabilities in terms of climatic and hydrological inputs.

Recharge can also be estimated from rainfall infiltration measurement data. In the SAM model (GSI, 1997), infiltration data from 101 sandy soil sites in 18 geographic regions in the United States was analyzed, as compiled by Stephens & Associates (API, 1996). To

obtain a high-range estimate of infiltration, a regression curve was fitted to mean annual precipitation and net infiltration measurements such that 80 percent of the measured infiltration rates would fall below the curve. The "80% regression curve" was considered to provide a reasonably conservative estimate of infiltration rates and leachate impacts in most sandy soil conditions, and is expressed, as follows:

$$I = 0.0018 P^2$$

where I is the mean annual net infiltration (cm/year), P is the mean annual precipitation (cm/year). This equation and the mean precipitation assumed in the CSST protocol results in a net infiltration rate of 0.18 m/year (compared to 0.55 m/year assumed by CSST).

Site specific infiltration rates are dependent on climatic conditions and soil properties, which are highly variable within British Columbia. For generic soil standard purpose, it is difficult to select representative model input values. An infiltration rate of 0.55 m/year appears to be somewhat high compared to that assumed by CCME and the 80% percent value (0.18 m/year) based on US empirical data; however, climatic conditions within coastal British Columbia area are wet, therefore justifying a higher infiltration rate.

The contaminated site source length of 10 m is considered reasonable based on typical contaminated site size.

## Recommendation

At this time, no change to the infiltration rate is proposed. However, consideration should be given to more scientifically-based estimation of the recharge rate. This could consist of use of models such as HELP and VS2DT and inputs corresponding to several climatic zones within BC.

It is recommended that a contaminated site source length of 10 m be adopted, consistent with the CCME protocol.

## 2.2.8 Saturated Zone Transport

The CSST and CCME saturated zone models are identical. The CSST and CCME models are a transient analytical solution for one-dimensional flow, three-dimensional dispersion, sorption and first-order decay. The assumed input parameters are also identical, except that CCME (2005) assumes that a water well or irrigation dugout is located at the edge of the contamination source zone whereas CSST assumes a 10 m separation distance between the contamination source and receptor. For the aquatic life

pathway, both CSST and CCME (2005) assume a 10 m separation distance. A different analytical model was proposed for SRA-2, which unlike CSST and CCME (2005), is not designed for soil standards development. The SRA-2 model is a steady state analytical solution for one-dimensional flow, one-dimensional dispersion and first-order decay.

**Dispersion**: Model simulations using the CSST model indicate that for approximate steady state conditions, transverse (lateral) dispersion does not result in significant concentration attenuation at 10 m from the source. This is expected based on the source size and relatively small transport distance.

**First Order Decay Constant**: The first-order decay constant can have a significant affect on the DAF for organic chemicals where a half-life was assumed. Predicted concentrations as a function of down-gradient distance and time are calculated for benzene (half-life 365 days), toluene (half-life of 105 days) and benzo (a) pyrene (1059 days) (Figures 2.3 to 2.5). The simulations at 100 years indicate a saturated zone DAF (i.e., excluding groundwater mixing) of 1.40 for benzene, 6.6 for toluene, and very high DAF (53 orders-of-magnitude) for benzo (a) pyrene. For inorganic chemicals, no decay was assumed.

The combination of decay (half-life) and sorption ( $K_{oc}$ ) has a significant effect on contaminant transport. A review of these parameters is recommended, particularly in the context of development of generic soil standards.



Predicted Benzene Attenuation using CSST Saturated Zone Model



Figure 2.4 Predicted Toluene Attenuation using CSST Saturated Zone Model



Figure 2.5 Predicted Benzo (a) Pyrene Attenuation for CSST Saturated Zone Model

The CSST half-lives were intended to be representative of anaerobic conditions. Since publication of the CSST protocol in 1996, there have been numerous published studies that present decay constants. An in-depth discussion of estimation and selection of representative decay constants goes beyond the scope of this report; a few key issues are discussed below. Biodegradation rates are highly chemical and site dependent. For certain chemicals (e.g., benzene), biodegradation, in some cases, will not occur under anaerobic conditions. For some chlorinated solvent chemicals, depending on the type of biotransformation, a co-substrate or hydrogen donor must be present at sufficient concentrations for reactions to occur. It is also important to recognize that rate constants in the literature represent a range of types of studies. The most reliable studies for estimation of conservative rate constants are generally field studies where biodegradation rate sufficient to models, as opposed to studies where bulk attenuation rates representative of biodegradation, dispersion and sorption are derived. A compilation of rate constants for BTEX published by Newell et al. (2002) is provided in Figure 2.6.



**FIGURE 2.6:** Biodegradation rate constants (λ) and Bulk Attenuation Rate Constants (k) for BTEX compounds from the literature (adapted from Rifai and Newell, 2001)

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The 25<sup>th</sup> percentile decay constant may be a reasonable value for soil standard development purposes. For initial comparison purposes, the 25<sup>th</sup> percentile decay constants by Suarez and Rafai (1999) are compared to the CSST and SRA-2 decay constants in Table 2.6.

	T <sub>1/2</sub> Benzene (days)	T <sub>1/2</sub> Toluene (days)	T <sub>1/2</sub> Ethylbenzene (days)	T <sub>1/2</sub> m-xylene (days)
CSST	365	105	114	183
SRA-2 (Table 2)	N/A	530	850	930
25 <sup>th</sup> Suarez and Rafai (1999)	N/A	600	2000	690

# **TABLE 2.6:** Comparison of BTEX Chemical Half-lives for First-Order Biodegradation

Although further review of decay constants should be conducted, some of the CSST constants appear to be non-conservative.

**Simulation Transport Time**: The CSST default simulation time was set at 2,200 years. The rationale for selecting a default time of 2,200 years is not clear, although intuitively one would expect, for a travel distance of 10 m, steady state or near steady state conditions after this time period. Approximate steady state conditions do occur for most matrix chemicals; however, for several organics and metals with high  $K_d$  values, steady state conditions are not predicted at 2,200 years due to their high sorption potential. For chemicals without decay, at steady state conditions, no attenuation within the saturated zone is predicted. For chemicals with both sorption and decay, some attenuation would be predicted at steady state conditions.

## Recommendations

Retain the 10 m separation distance between the contamination source and the receptor for the saturated zone model for all water uses.

It is recommended that a steady state model be adopted for a number of reasons. First, the model is relatively sensitive to the  $K_d$  chosen; since there is significant uncertainty in  $K_d$ , it is considered more appropriate to eliminate the influence of  $K_d$ , at least for purposes of generic standard development. Second, it appears that from the travel time chosen, the intent was to simulate approximate steady state conditions. Third, adopting a steady state model would eliminate the very large differences in dilution attenuation factors based on pH variation, and would increase transparency of the protocol used to derive standards.

A more in-depth review of decay constants should be conducted. When complete, representative values based upon this review should be selected for input into the model. For consistency, identical parameters should be selected for both the groundwater model used to back-calculate soil standards and SRA-2.

The combination of decay (half-life) and sorption ( $K_{oc}$ ,  $f_{oc}$ ) have a significant effect on model-predicted organic groundwater concentrations at 10 m from the source. Once representative half-lives have been selected, it is recommended that the steady state model be run to evaluate the effect of these two parameters. The simulation results, together with the mixing model results, should be used to derive example soil standards. The results should be carefully assessed to evaluate whether incorporation of these fate and transport processes is reasonable for generic soil standard development purposes.

# 2.2.9 Implication of Proposed Changes for Metals Standards

The implications of proposed changes to partitioning coefficient (USEPA SSL  $K_d$ 's) and the use of a steady state model are evaluated for metals through comparison of example soil standards for protection of the aquatic life pathway calculated (i) using the CSST metal partitioning coefficients and transient model, and (ii) USEPA SSL partitioning coefficients and steady state model (Table 2.3). The soil standards in Table 2.3 are developed for pH ranges recommended in the CSR matrix standards (Schedule 5). The soil standard was back-calculated using Equation 2.10, as follows:

$$C_{t} = C_{w} * DAF * \left\{ K_{d} + \left(\frac{\theta_{w}}{\rho_{b}}\right) \right\}$$
(2.10)

The CSST DAF was estimated using the transient groundwater transport model and CSST input parameters, assuming a default time of 2,200 years. For most chemicals and pH values, using this time results in a DAF of 3.29. For comparison purposes, the DAF calculated assuming a default travel time of 100 years is also presented (this DAF is not used for standard calculation purposes). Consistent with the approach used for the CSR standards (footnotes in Schedule 5), the example soil standards are equal to the sum of the soil-based standard and the background soil concentration.

For metals that were considered by both CSST and USEPA (1996b), the comparisons indicate the following:

- The example soil standards for arsenic (III) and chromium (VI) are virtually identical within a pH range of 5 to 8.
- For cadmium, the CSST and example USEPA soil standards are similar at low pH, but at higher pH, the USEPA soil standards are lower.
- The example lead soil standards calculated using provisional 3MRA isotherms, are slightly greater than the CSST standard for at pH less than 5.5, but are less than the CSST standards above pH 5.5.
- The example zinc soil standards, calculated using the USEPA  $K_d$  values, are slightly greater than the CSST derived standard at pH less than 6.0, but are less than the CSST standards above a pH of 6.0.

The USEPA  $K_d$  values and example soil standards for chromium (III) and nickel, which re not included as matrix soil standards in the CSST protocol, are also provided in Table 2.3.

As indicated above, the soil standards are equal to the sum of the toxicologically based standard and background soil concentration. The implicit assumption for this calculation protocol is that soils with background metals concentration will not leach metals to groundwater. This may a reasonable assumption at near neutral pH for relatively insoluble heavy metals in weathered soils. However, this assumption may be less appropriate for lower pH conditions and/or where there are mineralized conditions that result in elevated background groundwater concentrations. A more conservative approach would be to cap the lower limit of the standard as the greater of the background soil concentration and risk-based soil concentration. This would result in lower standards for several metals at low pH (e.g., arsenic, lead and zinc).

#### 2.2.10 NAPL Issues

The CSST protocol partitioning equation for organics is limited to three phases (sorbed, aqueous and vapour) and does not address partitioning from a non-aqueous phase liquid (NAPL) source. A three-phase partitioning model is conservative since it does not incorporate an upper bound for soil to pore-water partitioning. A more accurate representation of organic partitioning is one in which concentrations in pore-water can not exceed an upper limit based on solubility considerations for partitioning from the NAPL phase. The partitioning model commonly used to describe dissolution of chemicals from NAPL is based on an effective solubility concept, where the maximum concentration in groundwater is equal to the mole fraction multiplied by the pure-chemical solubility.

It is recommended that the CSST protocol be revised to include a check based on solubility considerations assuming a single chemical is present (no co-solubility effects). The check would involve comparison of the back calculated acceptable pore-water concentration to the pure-chemical solubility. If the pure-chemical solubility is exceeded, then no soil standard would be possible for that chemical. An example is provided below for toluene:

- Solubility = 530 mg/L;
- DAF = 22.6;
- Acceptable concentration in groundwater at receptor (marine water) = 3.3 mg/L;
- Acceptable pore-water concentration at contamination source = 74.6 mg/L; and,
- Acceptable pore-water concentration < solubility; soil standard is possible.

It is expected that for most organic chemicals, the solubility check will indicate that the acceptable pore-water concentration is less the chemical solubility.

#### Recommendation

Include a check based on solubility considerations assuming a single chemical is present (no co-solubility) effects. If the acceptable pore-water concentration at the contamination source exceeds the pure-chemical solubility, then no soil standard would be possible for that chemical.

### 2.2.11 Groundwater and Surface Water Mixing

The CSR soil standards were derived using a "groundwater" standard that is typically 10 times greater than the surface water criteria, under the assumption that a minimum 10-fold dilution of groundwater would occur at the discharge point to the surface water body.

Evaluation of the mixing and interaction of groundwater with surface water has in recent years received greater attenuation and study. The processes are complex, are highly site specific and involve consideration of numerous factors, including hydrogeology, hydrology and climate, and ecology. In particular, the biogeochemical processes within the upper few centimeters in sediments found beneath most surface water bodies (hyporheic zone) can have a profound effect on pore-water and surface water chemistry. New tools and concepts have been developed to assist in evaluating groundwater and surface water interaction, with considerable focus on processes within the hyporheic zone. Some of the recent studies highlight the variability in groundwater discharge zones based on site specific conditions.

Due to the complexity and site specific nature of groundwater and surface water interaction, it is difficult to take the factors described above into account when developing generic criteria. Based on a brief review of regulatory guidance, little was found in terms of approaches to developing generic criteria based on groundwater and surface water mixing concepts, although there is some guidance for site specific evaluations, including consideration of flux concepts (i.e., consideration of groundwater mass flux relative to capacity for dilution with receiving surface water bodies), variation in physical-chemical and biological properties of contaminants, and habitat considerations. It is noted that both the State of Massachusetts (GW-3 Standards) and USEPA (Environmental Indicator Supplemental Guidance CA 750) adopted a dilution factor of ten between groundwater and surface water criteria. No change is recommended for the dilution factor that was adopted for the CSST protocol in BC.

#### Recommendation

Retain a dilution factor of ten between groundwater and surface water criteria.

#### 2.2.12 Groundwater Model Protocol Documentation

Mr. Chris Neville of S. S. Papadopulos & Associates, Inc. of Waterloo, Ontario was retained by SAB in Fall of 2004 to review the site-specific standard (SSS) model, which is the model that was adopted by CSST for derivation of soil standards. As part of his review, Mr. Neville provided comments on groundwater model documentation, which are provided below.

# Comments on Groundwater Model Document by Mr. Chris Neville

In the existing site-specific standard (SSS) model documentation, there are multiple tables describing parameters. Two condensed tables of (1) user-specified model parameters and (2) internal model parameters would help the user to quickly identify the data requirements and to better understand the operation of the model. The default values and acceptable ranges of parameters could be included in these two tables. In addition, there is no need for the same parameter to be described in each of the four components of the model. However, in cases where there is an unsaturated and saturated version of the same parameter, the two parameters should been retained.

The presentation of the four equations describing the four components of the model would be simplified if presented together along with the two equations for decay (see last page of this appendix). A schematic of these four pathways being modeled would improve user understanding. In this schematic is would be helpful to highlight that the parameter  $C_w$  (contaminant concentration in groundwater at receptor) is set at the applicable water quality standard. An explanation of the Linked Parameter Sets (A, B, C) is also suggested.

List of Specific Parameter and Equation Errors in Help File

The following is a list of specific errors in the documentation. In all cases, the equations programmed in the SSS model are nevertheless correct, while the documentation is incorrect.

- 1. The definition of d (depth from surface to uncontaminated groundwater surface) is incorrect. In general, the groundwater surface will not be uncontaminated and the correct definition should be d = depth from the ground surface to the water table.
- 2. The water-filled porosity  $n_u$  is the same as the value specified in the soil/leachate partitioning model. This fact should be made clear to the user.
- 3. The calculated value of  $K_d$  is the same as the value specified in the soil/leachate partitioning model. This fact should be made clear to the user.
- 4. The parameter  $D_{1/2US}$  is not the average number of frost-free days in a year; rather, it is the average number of days during which there is frost. The SSS graphical interface has the following definition for the parameter *FFD*: "Number of days when ground surface < 0°C". This is correct.
- 5. The equation in the documentation for the unsaturated/saturated mixing zone model is incorrect (Equation 2 should contain  $Z_d$  not  $Z_m$ ).

- 6. The definition of *I* is incorrect. Evapotranspiration (ET) should be added to runoff (RO) rather than subtracted from it.
- 7. The infiltration rate *I* in the saturated zone model is the same as the value specified in the unsaturated zone model. The apparent differences reflect only the fact that in the unsaturated zone model the value is specified in units of m/yr, while in the mixing zone unsaturated/saturated model the value is converted to units of m/s. The second definition is therefore redundant.
- 8. The explanation in the Help file of the air filled porosity,  $n_a$  is not correct. The documentation states that  $n_a=n-n_u$ , when in fact the air and water filled porosities are specified independently by the user and no consideration is given to n, the total porosity.
- 9. The thickness of the aquifer,  $d_a$ , specified in the unsaturated/saturated mixing zone model is not used in the saturated groundwater zone model calculations. In the groundwater model, the contamination beneath the source is assumed to extend across the full thickness of the aquifer. This fact should be made clear to the user.
- 10. It should be noted that the Darcy groundwater flux V in the mixing zone is the same as the value specified in the groundwater flow equation. The groundwater flux in the mixing zone will, in general, be better characterized than the groundwater flux in the downgradient groundwater flow regime. Therefore, if the downgradient groundwater flux is set as a constant in the model, the mixing zone groundwater flux should remain a variable that can be changed to reflect site conditions.
- 11. The decay constant in the saturated zone,  $L_S$ , should be a factor of the half-life in the saturated zone,  $t_{1/2S}$ , rather than the half-life in the unsaturated zone,  $t_{1/2US}$ .
- 12. Only one parameter symbol should be used for the dry bulk density of the soil.  $r_b$  is used in the interface and for consistency in Table 1. In other words, the Greek symbol  $\rho_b$ , should be replaced.

The use of footnotes is problematic. The footnotes in the text appear to be part of other decimal numbers making it very hard to decipher what the footnote at the end of the page is pertaining to. Footnotes should be removed and the footnote text should be incorporated into the tables.

## 2.3 Summary of Recommended Changes

A summary of the recommended changes to the groundwater model are provided below. Where applicable, the implication of the change on the current matrix soil standard is also provided (i.e., increase in the standard, no change in the standard, decrease in the standard).

- 1. Retain a multi-component analytical model consisting of (i) unsaturated zone partitioning, (ii) groundwater mixing, and (iii) saturated zone transport for all receptor scenarios; however, consider refinements to the model and input parameters as described in this section of the report and summarized below (no change in standard). Adopting the USEPA DAF of 20 for the receptor well scenario is not recommended at this time.
- 2. Since unsaturated zone transport does not affect the calculation of soil standards based on the current model scenario; for clarity, eliminate the unsaturated zone component from the CSST protocol, subject to findings of on-going evaluation of unsaturated zone transport by SAB (no change in standard).
- 3. Adopt the K<sub>oc</sub> values listed in SRA-2 Appendix C, Table C-1.
- 4. Adopt the pH-dependent K<sub>oc</sub> isotherm for pentachlorophenol derived by SAB, as documented in SRA-2 (slight decrease in soil standards).
- 5. Revise the unsaturated zone bulk dry density to 1.7 g/cm<sup>3</sup> input into the organic chemical partitioning equation, consistent with the value assumed by CCME (slight increase in the soil standards).
- 6. Consideration could be given to adjusting the fraction organic carbon used for the organic chemical partitioning equation; however, further evaluation of this parameter for different hydrogeologic environments is recommended before any changes are made. Since partitioning is sensitive to  $f_{oc}$ , an alternative would be to develop multiple soil standards based on  $f_{oc}$  ranges and to provide the option for testing of site soil samples for  $f_{oc}$ .
- 7. Adopt the revised SRA-2 groundwater mixing model for derivation of soil standards (slight increase in the standards).
- For derivation of soil standards, adopt the partition coefficients recommended by USEPA (1996b) for the following metals: antimony; arsenic(III) (no change in soil standards); barium; beryllium; cadmium (increase in soil standards); chromium(III) (increase in soil standards); chromium (VI) (no change in soil standards); cyanide;

nickel; selenium; silver; thallium; vanadium; and, zinc (decrease in soil standards, in most cases). It is noted that antimony, barium, beryllium, mercury, nickel, selenium, silver, thallium and vanadium are not currently included in the Schedule 5 matrix standards. The implications for use of USEPA partition coefficients to derive pH-dependent standards for these metals should be further evaluated before any changes to the CSR standards are considered. Such an evaluation goes beyond the scope of this report. The USEPA  $K_d$ 's for mercury are not recommended since empirical data indicates they are overly conservative and do not correctly predict the influence of pH on  $K_d$ .

- 9. Develop an isotherm for lead using data in the 3MRA database, assuming iron oxide and organic matter input values identical to USEPA SSL defaults. An interim  $K_d$ isotherm was developed using 3MRA for "mid-range" iron oxide and organic matter conditions, with an iron oxide concentration of 0.05 wt% and organic matter concentration of 0.11 wt%.
- 10. Using a similar approach to the 3MRA modeling effort, employ the MINTEQA2 thermodynamic database to develop an isotherm for copper, assuming iron oxide and organic matter input values identical to USEPA SSL defaults.
- 11. Consideration should be given to a regulatory framework that includes pore-water standards and a protocol where the results of leaching tests can be compared to pore-water standards. For metals, pore-water standards and leaching tests would avoid some of the scientific issues and uncertainty associated with the K<sub>d</sub> approach.
- 12. To gain further insight on the predictive capability of the metals partitioning model, it is recommended that soil and near-contaminated source groundwater quality data from contaminated sites in British Columbia be evaluated to provide for field-based estimates of groundwater fate and transport, and indirectly partitioning behaviour
- 13. At this time, no change to the infiltration rate used to calculate groundwater mixing is proposed. However, consideration should be given to more scientifically-based estimation of the recharge rate. This could consist of use of models such as HELP and VS2DT and inputs corresponding to several climatic zones within BC.
- 14. It is recommended that a contaminated site source length of 10 m be adopted for the groundwater mixing model, consistent with the CCME protocol (slight increase in the soil standards).
- 15. Retain the 10 m separation distance between the contamination source and the receptor for the saturated zone model for all water uses.

- 16. Consideration should be given to adopting the SRA-2 steady state analytical model for saturated zone transport since the intent of the CSST model was to simulate steady state conditions and since dispersion does not affect the model simulations for a transport distance of 10 m (decrease in soil standards in some cases).
- 17. A comparison of literature half-lives for biodegradation suggests that some of the CSST half-lives assumed for organic chemicals may not be conservative. A more indepth review of decay constants should be conducted. When complete, representative values based upon this review should be selected for input into the model. For consistency, identical parameters should be selected for both the groundwater model used to back-calculate CSR soil standard and SRA-2.
- 18. The combination of decay (half-life) and sorption ( $K_{oc}$ ,  $f_{oc}$ ) have a significant effect on model-predicted organic groundwater concentrations at 10 m from the source. Once representative half-lives have been selected, it is recommended that the steady state model be run to evaluate the effect of these two parameters. The simulation results, together with the mixing model results, should be used to derive example soil standards (i.e., similar to metals Table 2.3 described earlier). The results should be carefully assessed to evaluate whether incorporation of these fate and transport processes is reasonable for generic soil standard development purposes.
- 19. The CSST protocol should be revised to include a check based on solubility considerations assuming a single chemical is present (no co-solubility) effects. If the acceptable pore-water concentration at the contamination source exceeds the pure-chemical solubility, then no soil standard would be possible for that chemical.
- 20. Make the documentation changes to the groundwater protocol suggested by Mr. Chris Neville of S.S.Papadopulos & Associates, Inc. of Waterloo, Ontario.

# 3.0 HUMAN HEALTH PROTECTIVE STANDARDS – GENERAL CONSIDERATIONS

The potential direct and indirect exposure pathways typically considered in the development of human health soil quality standards, along with the general contaminant classes for which they are evaluated, are:

- Intake of contaminated soil (soil ingestion, dermal contact and dust inhalation) applies to all contaminant classes with the exception of volatiles for the dust inhalation pathway;
- Inhalation of soil contaminants in indoor air applies only to volatile contaminants; and,
- Groundwater used for drinking water applies to only to soluble contaminants.

The existing CSST protocol has derivation procedures for the intake of contaminated soil and groundwater used for drinking water, but not for the indoor inhalation pathway. However, the CSST is considering revising the protocol to include the indoor inhalation pathway. The proposed derivation process for the inhalation pathway is described in detail in Section 4.0. Sections 5.0 and 6.0 review the existing CSST protocol for derivation of soil standards for ingestion of groundwater used for drinking water and intake of contaminated soil, and provides recommendations where warranted.

A discussion of the process for deriving soil quality guidelines for each of the direct and indirect exposure pathways identified above has been provided in separate sections. However, there is some overlap in the derivation process for all three exposure pathways. Areas where there is overlap are discussed in the following section.

# 3.1 General Considerations

The derivation of human health soil quality guidelines typically involves consideration of the following:

- Classification of contaminants as a threshold (non-carcinogenic) or non-threshold (carcinogenic) contaminant;
- Identification of the acceptable level of risk associated with exposure to contamination at sites;
- Determination of a critical human toxicity reference value (TRV) representative of a defined acceptable toxicological hazard or risk posed by a chemical;
- Definition of appropriate critical human receptors for the specified land uses;

- Development of defined exposure scenarios for the specific land uses; and,
- Integration of exposure scenarios and toxicity information with CSST policy decisions to calculate soil quality standards.

The above process was used to derive the Contaminated Sites Regulation matrix soil standards (Schedule 5).

## 3.1.1 Contaminant Classification

Environmental contaminants are classified according to their potential carcinogenicity and mutagenicity based on the quantity, quality and nature of the available toxicological and epidemiological studies. Agencies such as Health Canada, US EPA Integrated Risk Information System (IRIS; http://www.epa.gov/iris/index.html) and the International Agency on Research for Cancer (IARC; <u>http://www.iarc.fr/ENG/Databases/index.php</u>) have developed classification schemes for substances. The existing CSST protocol recommended supporting Health Canada carcinogenic classification when available. However, no official Health Canada TRVs were available prior to the release of the protocol. Therefore, the existing CSST protocol relied on the IARC and US EPA IRIS for carcinogenic classification. CCME (2005) relied on Health Canada to classify contaminants according to their potential carcinogenicity and mutagencity to humans.

#### Recommendation

The existing classification of contaminants for which there are matrix standards should be reviewed to see whether new information is available that would indicate a need for re-classification of a contaminant.

## 3.1.2 Level of Protection

For non-threshold contaminants, it is assumed that there is some probability of harm to human health at any level of exposure. Consequently, it is not possible to determine a dose below which adverse effects do not occur. The philosophy of Health Canada (2004a) is such that human exposure to non-threshold contaminants should be reduced to the lowest levels deemed reasonably feasible. CCME (1996) agrees in principle with the Health Canada philosophy and adopted the position that contaminated site related risks arising from exposure to non-threshold agents should be at least remediated to levels within the range of  $1 \times 10^{-4}$  to  $1 \times 10^{-7}$ . The soil quality guidelines derived by CCME (2005) reflect incremental risk levels from soil of both  $1 \times 10^{-5}$  and  $1 \times 10^{-6}$ , as these were the target incremental risk levels specified by most Canadian jurisdictions. In BC, the CSST adopted an incremental risk level of  $1 \times 10^{-5}$  for deriving soil quality standards for human health.

For threshold contaminants, it is common to ascribe some allowable proportion of the total exposure from a contaminated site to the soil or water media. Considering the five sources to which people are exposed (i.e., air, water, soil, food and consumer products), 20% is typically apportioned for both the soil and water media. Both CCME (2005) and the existing CSST protocol adopted the default value of 20% of the Residual Tolerable Daily Intake (RTDI) or Tolerable Daily Intake (TDI), respectively, for threshold substances. This means, for example, if a matrix soil standard is calculated for intake of soil, the TDI is multiplied by a soil allocation factor (SAF) of 0.2 to account for exposure via other exposure media. If defensible contaminant-specific evidence exists demonstrating that the contaminant does not occur in a given medium, CCME (2005) indicated that apportionment may be increased from 20% to a value given by:

SAF = 100% / (number of applicable exposure media)

Depending on the physical and chemical properties of a substance, it may not be present in all of the media. For example, a high molecular weight hydrocarbon has low solubility and volatility and as a result the contribution of the air and water pathways to exposure may be insignificant. In this case, a SAF of 33% may be appropriate based on three applicable exposure pathways (soil, food and consumer products). In order to provide consistent guidance on when to include or exclude the air and water media in the calculation of the SAF, the following cut-offs should be used:

- Soluble or Non-Soluble As recommended by CCME (2005), any substance for which a published water quality guideline is available in Canada can be considered soluble. For substances with no published water quality guidelines, if the pure phase solubility is equal to or greater than a derived concentration for the protection of potable groundwater or livestock watering, then the contaminant is considered to be soluble.
- Volatile or Non-Volatile A similar procedure would be followed as outlined in Section 4.2.4 regarding determining whether a substance is volatile or not. The only exception would be that the attenuation factor would not be included in the equation.

For a number of substances, Health Canada has derived estimated daily intake (EDIs) which represent the daily exposure of a chemical due to normal background exposure (i.e., not including exposure from a contaminated site). The EDI takes into account exposure from various media including ambient air, indoor air, soils, house dust, drinking water, food, and consumer products for the general Canadian population. We considered using the EDI to provide information on the distribution of a substance among the various media at a contaminated site. However, the EDI is not necessarily reflective of the distribution of a substance at a contaminated site because the apportionment of a substance in soil, water or air will be related to its physical and chemical properties,

rather than background estimates. However, the EDI can be used to show which media account for the majority of the background exposure and thus which media can not be discounted.

#### Recommendation

Consider allowing for increasing the apportionment for soil, where appropriate. In order to provide consistent guidance on when to include or exclude the air and water media in the calculation of the SAF, the guidelines recommended above regarding solubility and volatility of a substance should be used. When available, the EDI should be consulted to see which media account for the majority of the background exposure and thus which media can not be discounted.

#### 3.1.3 Toxicity Reference Values

The existing CSST protocol indicated that when available, human health toxicity reference values (TRVs) were taken from CCME Ecological and Human Health Assessment documents (e.g., Canadian Soil Quality Guidelines for Pentachlorophenol: Environmental and Human Health [CCME 1997]). However, the CCME assessment documents were not available prior to the release of the existing CSST protocol and therefore, TRVs from other sources were consulted following the hierarchy shown, as discussed in detail by Fox (1995):

## 1. Health Canada

- US EPA Integrated Risk Information System (IRIS), or US EPA - Health Effects Assessment Summary Tables (HEAST) or US Department of Health and Human Services – Agency for Toxic Substances and Disease Registry (ATSDR) or World Health Organization (WHO)
- 3. Open scientific literature or special purpose derivations

A review of the existing matrix standards indicates that the majority of the TRVs used in the derivation process were taken from US EPA IRIS. Since issuing the CSST protocol, CCME and more recently Environment Canada have published assessment documents for all 28 of the substances for which CCME has derived soil quality guidelines. Furthermore, Health Canada has recently published TRVs for a variety of contaminants (Health Canada 2004b). For threshold contaminants, Health Canada derives a Tolerable Daily Intake (TDI) or Tolerable Concentration (TC) and for non-threshold contaminants, oral and inhalation slope factors have been derived.

The CCME (2005) protocol follows a similar hierarchy to the existing CSST protocol where Health Canada is the first choice, followed by US EPA and WHO. However, CCME does not allow for use of TRVs derived from the open scientific literature or special purpose derivations. CCME recommends that if a soil quality guideline is derived using TRVs specified by an agency other than Health Canada, or a guideline developed in the absence of any human health toxicity benchmarks, is considered to be a provisional guideline.

The US EPA hierarchy of human health TRVs was recently revised (US EPA 2003; OSWER Directive 9285.7-53) to the following: 1) US EPA IRIS; 2) US EPA Provisional Peer Reviewed Toxicity Values; and 3) Other toxicity values, including other US EPA sources such as HEAST, ATSDR, and National Center for Environmental Assessment (NCEA) provisional values and non US EPA sources (e.g., California EPA toxicity values). The revised hierarchy replaces that presented in Risk Assessment Guidance for Superfund, Volume I, Part A Human Health Evaluation Manual (US EPA 1989).

# Recommendation

The CSST hierarchy for selection of TRVs is considered appropriate, and is similar to that proposed by CCME. Using the hierarchy adopted, determine whether new scientific information is available that supports changing the TRV. Calculate updated matrix soil standards using any TRVs that are revised as a result of this process.

# 3.1.4 Receptor Selection and Assumptions

The selection of sensitive receptors is linked to land use considerations and is primarily dependent on the ages of the human receptors reasonably expected to be associated with those land uses. It is widely accepted that children (toddlers) are much more likely to come into contact with and ingest greater amounts of soil and dust each day then adults. Combine these higher rates with a lower average body mass and this puts a child more at risk from contaminated soil than an adult. This is why a child (toddler) is considered a more sensitive receptor than an adult in most scenarios. The CSST protocol, Health Canada (2004a) and CCME (2005) all assume the same typical age categories for receptors shown in Table 3.1.

For non-threshold substances, an adult is typically the critical receptor for all land uses and exposure is assumed to be continuous over 70 years. For threshold substances, exposure is typically averaged over the most sensitive life stages. Generally, the toddler stage (six months to four years) is considered the most sensitive. Both the existing CSST protocol and CCME (2005) used an adult receptor for developing standards for nonthreshold substances and a toddler for threshold substances. However, for both non-

threshold and threshold contaminants, the existing CSST protocol and CCME (2005) indicate if a different age group is determined to be more sensitive, then this more sensitive age group should be used as the receptor.

The receptor assumptions used in the existing CSST protocol were a combination of values taken from Angus Environmental (1991), Newhook (1992) and MENVIQ (1992) and were identical to the values recommended in the original CCME (1996) protocol. Health Canada (2004a) recently revised their human receptor assumptions to reflect the current state of knowledge. The values recommended by Health Canada (2004a) were adopted by CCME (2005). A comparison of the existing receptor assumptions used in the CSST protocol to the recently revised values adopted by CCME (2005) and Health Canada (2004a) is provided in Table 3.1. Further details on the sources (i.e., scientific study) that each parameter selected by CCME/Health Canada is based on are provided in Appendix I of the CCME (2005) protocol document.

Age Classes (years)	Infant (0-0.5)	Toddler (0.6-4)	Child (5-11)	Teen (12-19)	Adult (20+)
Body Weight – BW (kg)	7 (8.2)	13 (16.5)	27 (32.9)	57 (59.7)	70 (70.7)
Air Inhalation Rate – IR (m <sup>3</sup> /day)	2 (2.1)	5 (9.3)	12 (14.5)	21 (15.8)	23 (15.8)
Water Ingestion Rate - WIR (L/day)	0.75 (0.3)	0.8 (0.6)	0.9 (0.8)	1.3 (1.0)	1.5 (1.5)
Soil Ingestion Rate – SIR (kg/day)	0.00002 (0.00002)	0.00008 (0.00008)	0.00002 (0.00002)	0.00002 (0.00002)	0.00002 (0.00002)
Skin Surface Areas <sup>2,3</sup> – SA (m <sup>2</sup> )	0.30	0.26	0.41	0.43	0.43
Hands	(0.032)	(0.043)	(0.059)	(0.080)	(0.089)
Other	(0.146)	(0.258)	(0.455)	(0.223)	(0.250)
Dermal Loading to Skin – DL (kg/m <sup>2</sup> – event)	0.01	0.01	0.01	0.01	0.01
Hands	(0.001)	(0.001)	(0.001)	(0.001)	(0.001)
Other	(0.0001)	(0.0001)	(0.0001)	(0.0001)	(0.0001)

**TABLE 3.1:** Human Receptor Characteristics Adopted by CSST (BCE 1996) and CCME (2005)/Health Canada (2004a)<sup>1</sup>

1. The values not in brackets represent the CSST (BCE 1996) values, the values in brackets represent the values adopted by CCME (2005) and Health Canada (2004a).

2. BCE (1996) assumed total body is exposed for the infant; head, arms, hands, lower legs for toddler and child; and head, arms, and hands for teens and adults. Soil dermal contact rate (SR) = SA x DL.

3. CCME/Health Canada assume arms are exposed for adults and teens; arms and legs are assumed to be exposed for infants, toddlers and children. Soil dermal contact rate (SR) =  $(SA_{hands}xDL_{hands}+SA_{other}xDL_{other})x$  event/day (where event/day = 1).

### Recommendation

The receptor characteristics in the existing CSST protocol should be revised to reflect the above human health characteristics adopted by Health Canada and CCME.

## 3.1.5 Exposure Period

The amount of time a receptor spends on site is linked to the land use. The exposure period depends on the frequency, duration and intensity of the exposure assumed for the land use. The sensitive receptors, exposure period and exposure pathways that were assumed for each land use in the existing CSST protocol are provided in Table 3.2.

# **TABLE 3.2:** Human Health Exposure Assumptions For Each Land UseBased On Existing CSST Protocol

	Agricultural	Residential/ Parkland	Commercial	Industrial <sup>1</sup>
Sensitive Receptor	toddler (TC) adult (NTC)	toddler (TC) adult (NTC)	toddler (TC) adult (NTC)	Not applicable
Exposure Term (ET)	$\begin{array}{c} TC - 1.0^2 \\ NTC - 1.0^4 \end{array}$	$TC - 1.0^{2}$ NTC - 1.0 <sup>4</sup>	$TC - 0.33^{3}$ NTC - 0.33 <sup>5</sup>	Not applicable
Direct Soil Exposure Pathways	Ingestion dermal contact dust inhalation	ingestion dermal contact dust inhalation	ingestion dermal contact dust inhalation	Not applicable
Indirect Soil Exposure Pathways	groundwater indoor inhalation <sup>6</sup>	groundwater indoor inhalation	groundwater indoor inhalation	groundwater

Notes:

TC – Threshold Contaminant

NTC - Non-Threshold Contaminant

1. Soil intake standards are not derived for the industrial land use scenario as the CSST recognized that issues relating to soil quality for human health protection on industrial sites are the mandate and responsibility of WCB.

2. Exposure Term for TC for Agricultural, Urban Parkland and Residential Land Use: 24hr/d x 7d/wk x 52wk/yr x 3.5yr/3.5yr

3. Exposure Term for TC for Commercial Land Use: 12hr/24hr x 5d/7d x 48wk/52wk x 3.5 yr/3.5yr

- 4. Exposure Term for NTC for Agricultural, Urban Parkland and Residential Land Use: 24hr/d x 7d/wk x 52wk/yr x 70yr/70yr
- 5. Exposure Term for NTC for Commercial Land Use: 12hr/24hr x 5d/7d x 48wk/52wk x 70yr/70yr
- 6. This pathway was not part of existing CSST protocol but is recommended for inclusion based on this review.

The exposure term (ET) is a modifying factor to account for non-continuous exposure, and referenced in Table 4 of the CSST protocol. Generally, the exposure terms used in the existing CSST protocol for each land use are the same as those used by CCME (2005). The only exceptions are outlined below.

Exposure Term for Non-Threshold Contaminants - CCME (2005) assumes the ET for non-threshold contaminants for all land uses (including commercial) is 1.0 since the exposure period (i.e., 10 hrs/day, 5 d/wk, 48 wk/yr for 30 to 40 years over a lifetime) exceeds the likely latency period for most carcinogens. Assuming an ET of 1.0 for non-threshold substances for the agricultural and residential land use scenarios is fairly standard for guideline development purposes. However, assuming an ET of 1.0 for the commercial land use scenario is a fairly conservative assumption, as this assumes that a worker is exposed for their entire life expectancy. The existing CSST protocol assumes an ET of 1.0 for agricultural and residential land use, but uses an ET of 0.33 for commercial land use (see Table 3.2). In the existing CSST protocol, a commercial workers exposure (i.e., 12 hrs/d, 5 d/wk, 48 wk/yr, 70 yrs) to a non-threshold substance was amortized over life expectancy (i.e., 70 yrs), which resulted in a exposure term of 0.33. Changing the exposure term to 1.0 for the commercial land use scenario for non-threshold substances would result in more conservative soil standards (approximately 3 times lower). It is worth noting that CSST did not adopt this approach when it was initially recommended in the original protocol (CCME 1996).

Health Canada is currently looking into the validity and defensibility of amortization for carcinogenic substances. Until that time, Health Canada (2004a) currently recommends averaging daily exposure (i.e.,  $hrs/d^4$ , d/wk, wk/yr, total yrs exposed to site) over the life expectancy. If cancer risks are estimated for adults, then the 56 year duration of adulthood (i.e., 20 to 75 years) should be used for life expectancy. If cancer risks are estimated on the basis of lifetime average daily intake, then an average life expectancy of 75 years should be used.

Considering that CSST did not adopt the approach when it was initially recommended in the original protocol (CCME 1996) and considering that the Health Canada (2004a) approach is more in line with the existing CSST approach, no change is recommended at this time. However, further evaluation of exposure amortization may be warranted upon completion of the Health Canada study.

**Hours Per Day Exposure Term** - CCME (2005) does not consider hours per day exposure for soil ingestion or dermal contact, consistent with Health Canada (2004a) recommendations, since soil ingestion and dermal contact are not expected to occur at a uniform rate throughout the day. The CCME (2005) recommends only applying the hours per day exposure to the dust/air inhalation pathway. For the ingestion and dermal pathways, the CCME commercial ET is 0.66 (5 days/7 daysx48 weeks/52 weeks).

The existing CSST protocol currently incorporates hours per day exposure for the soil ingestion, dermal contact and dust inhalation pathways. If hours per day is excluded from the calculation for the soil ingestion and dermal contact pathways, the only

<sup>&</sup>lt;sup>4</sup> Hours per day exposure would only be applicable for the dust/air inhalation pathways.

noticeable change would be for the commercial land use scenario, which was the only land use to assume a less than 24 hour exposure term<sup>5</sup>. The exposure term would increase from 0.33 to 0.66, which would result in a two times more conservative soil standard for the soil ingestion and dermal contact pathways.

CCME assumes a receptor spends 10 hrs/day on a commercial site and CSST assumes 12 hrs/day. This slight difference in exposure time translates into an exposure term of 0.27 versus 0.33 for CCME and CSST, respectively. The slight difference in hours per day exposure is only applicable for the inhalation pathways, if the hours per day exposure term is removed for the other pathways (see above paragraph).

Sensitive Receptor for Threshold Contaminants at Commercial Sites - The CSST commercial standard for threshold contaminants is based on a toddler receptor, which is a conservative assumption, but typically a standard assumption for guideline derivation purposes. Toddlers are unlikely to be present at commercial sites for appreciable periods of time. While a toddler is assumed to ingest four-times more soil than a child, the conditions under which toddlers would ingest significant quantities of soil (i.e., direct contact with exposed dirt) would be unlikely at most commercial sites. While in residential "back-yards", toddlers could quite readily come into contact with soil, unrestricted contact with soil at commercial sites with unpaved dirt surfaces would be infrequent. For the commercial scenario and threshold contaminants, a more realistic sensitive receptor may be a child receptor. We recognize that for most commercial sites an adult would be the most appropriate receptor; however; the commercial scenario is not defined to preclude children and therefore, it would not seem conservative enough to adopt the adult as the sensitive receptor. Therefore, we recommend adopting a child as the sensitive receptor for the commercial scenario. However, it is important that the commercial land use standard is defined to exclude any commercial scenarios where children or toddlers could be present for appreciable periods of time (e.g., daycare at commercial site, community centres, and hospitals). For commercial scenarios where toddlers or children could be present, the more conservative residential standards should be applied.

As indicated in the above section, removing the hours per day exposure term for the soil ingestion pathway for the commercial scenario would result in a 2 times decrease in the soil standard. If the sensitive receptor for a commercial scenario is changed from a toddler to a child, the implication for the standard can be evaluated through use of a factor (F) that combines the receptor characteristics and exposure term, as follows:

Current CSST protocol:  $F_{toddler} = 13 \text{ kg} / (8x10^{-5} \text{ kg/day } x 0.33) = 4.9x10^{5} \text{ day}$ 

Proposed CSST protocol:  $F_{child} = 32.9 \text{ kg} / (2x10^{-5} \text{ kg/day x } 0.66) = 2.5x10^{6} \text{ day}$ 

<sup>&</sup>lt;sup>5</sup> Agricultural, Residential and Urban Park land use scenarios all assumed the receptor was present 24 hr/day. Therefore, if the hours per day exposure term is removed, the overall exposure term does not change (see Table 3.2).

The implication is that instead of the intake standard decreasing by a factor of 2 times, it would increase by a factor of 5 times for commercial sites.

**Industrial Land Use** - The CCME (2005) protocol also includes derivation of a human health soil intake guideline for industrial land use whereas the CSST protocol does not. The existing CSST protocol did not develop soil intake standards for the industrial land use exposure scenario as CSST recognized that issues relating to soil quality for human health protection on industrial sites are the mandate and responsibility of the Workers Compensation Board of British Columbia (WCB). It is fairly common practice in site investigations and risk assessment in B.C. to apply the commercial land use standards for soil intake to a site classified for industrial land use. This is a highly conservative practice as the sensitive receptor for an industrial setting is an adult whereas in a commercial setting the sensitive receptor for a threshold contaminant is a toddler. Considering that adults consume one quarter of the soil typically consumed by children and have about four times the body mass to distribute chemicals, an industrial land use standard would generally be higher than those generated for other land uses (including commercial).

# Recommendations

Assuming an exposure term of 1.0 for non-threshold contaminants (i.e., CCME approach), regardless of the land use, is considered an overly conservative assumption. Considering that CSST did not adopt this approach from CCME when it was initially recommended in the original protocol (CCME 1996) and considering that the Health Canada (2004a) approach is more in line with the existing CSST approach, no change is recommended at this time. Further evaluation of exposure amortization may be warranted upon completion of the Health Canada study

As recommended by Health Canada (2004a) and CCME (2005), the hours per day exposure term should not be applied to the soil ingestion and dermal contact exposure pathways as soil ingestion and dermal contact are considered to be independent of the time spent outdoors in contact with contaminated soil. For both of these pathways, 100% of the daily unintentional intake of contaminated soil should be assumed to come from the site, regardless of the number hours spent on site. Inhalation exposures should still be derived based on the number of hours spent on the contaminated site.

BCMWLAP should engage in discussions with WCB to determine whether issues relating to soil quality for human health protection on industrial sites are the mandate and responsibility of the Workers Compensation Board of British Columbia (WCB) or BCMWLAP.

Consideration should be given to adopting a less conservative sensitive receptor (child versus toddler) for the commercial land use scenario for threshold contaminants. This change is contingent on an appropriate designation of the commercial land use scenario.

# 4.0 HUMAN HEALTH PROTECTION: VAPOUR INHALATION

The migration of volatile chemicals into indoor air through soil vapour intrusion is an exposure pathway that was not part of the existing CSST protocol. The development of regulatory criteria or standards for this pathway is considered important since experience at contaminated sites has indicated the potential for unacceptable human health risk resulting from soil vapour intrusion. The scope of the evaluation presented below is the protection of human health based on chronic health risks due to long-term exposure to vapours. It does not address potential safety hazards associated with landfill gases such as methane.

There have been significant recent developments for regulatory guidance for the soil vapour intrusion pathway, including guidance prepared by USEPA (2003), Golder (2004) ("Health Canada" guidance) and Science Advisory Board for Contaminated Sites (SABCS) in British Columbia (SAB, 2004). Golder Associates has been integrally involved in the development of guidance for these agencies.

The proposed framework and protocol for deriving standards presented in this chapter is generally consistent with that proposed by the Science Advisory Board (SAB) of British Columbia, as documented in the Screening Risk Assessment (SRA) Level 1 and 2 protocols (SAB, 2004a,b). The proposed SRA approach for vapour intrusion (VI) was presented during a workshop on July 16, 2004, and the SAB SRA VI report was completed in Fall 2004.

## 4.1 Review of Soil Vapour Guidance

Regulatory guidance for soil vapour intrusion developed by the Canadian Council of Ministers of Environment (CCME), US Environmental Protection Agency (USEPA), Health Canada (Golder, 2004) and SAB (SRA-VI) are reviewed below.

Integral components of regulatory guidance for the vapour intrusion pathway are (i) partitioning equations used to estimate vapour concentrations, based on concentrations in soil or groundwater, (ii) prediction of vapour transport and indoor vapour concentrations, and (iii) procedures used to estimate potential human health risk based on predicted indoor air concentrations.

The vapour transport component can be quantified through use of a vapour attenuation factor ("alpha"), which is the ratio of the indoor air concentration divided by soil vapour concentration at the point of interest (i.e., "ppbV/ppbV" or dimensionless ratio). The soil vapour concentration can either be measured or estimated from the concentration in groundwater. The vapour attenuation factor is the inverse of the dilution factor, which is used by CCME to describe vapour intrusion.

There are three different types of vapour attenuation factors or alpha's:

*Groundwater-to-indoor air alpha*: This alpha is based on the soil vapour concentration estimated from groundwater data (i.e., using Henry's Law constant) and represents chemical transport through both the capillary fringe immediately above the water table and higher regions of the unsaturated zone.

*Soil vapour-to-indoor air alpha*: This alpha is based on the measured soil vapour concentration within the unsaturated zone and represents transport through the unsaturated zone. If the soil vapour concentration is estimated for a soil contamination source above the water table, then the soil vapour-to-indoor air alpha is the appropriate factor to apply for estimation of the indoor air concentration.

*Subslab vapour-to-indoor air alpha*: This alpha is based on the measured subslab vapour concentration measured immediately below a building foundation and represents primarily transport through the foundation.

## 4.1.1 CCME CWS-PHC (2000)

The Canadian Council of Ministers of the Environment (CCME) established generic soil standards for the vapour intrusion pathway as part of the Canada Wide Standards for Petroleum Hydrocarbon Compounds (CWS-PHC) (June 2000). The CCME framework was based on the US Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) approach, although some modifications to the fractions and toxicity reference values were made. Soil standards were developed for the F1 and F2 fractions for residential and commercial land use scenarios. These F1 and F2 fractions correspond to alkane equivalent carbon ranges between n-C6-10 (F1) and >n-C10-16 (F2). The Johnson and Ettinger (J&E) model was used to calculate the vapour attenuation ratio used to derive the standards.

The CCME CWS-PHC (2000) guidance for vapour intrusion is similar to that proposed in the draft CCME "*Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines*" (2005). Additional details on the model and assumptions used to derive soil standards are provided below.

## 4.1.2 CCME Protocol (2005)

The CCME guidance provides a method for estimating a soil quality guideline for a broad range of volatile organic compounds (VOCs) based on migration of subsurface soil vapour into buildings. Contamination of indoor air by volatilization from contaminated soil is considered by CCME to be "a critical pathway of exposure for volatile organic chemicals."

The migration of soil vapours into indoor air is considered to be a function of several factors including soil type, depth or distance of contamination from the building foundation, type of building foundation, the building air exchange rate, and building dimensions. The indoor air concentration is estimated using the one-dimensional analytical model developed by Johnson and Ettinger (1991). For purposes of generic guideline development, steady state conditions are assumed, and depletion of the contaminant source is not considered. The soil gas advection rate into the building is calculated using the Perimeter Crack Model, which estimates the soil gas flow rate to a drain, intended to approximate a crack in the floor/wall seam. The soil vapour concentration is calculated using a linear partitioning model that assumes equilibrium conditions between contaminants adsorbed to soil particles, dissolved in soil pore water, and in the vapour phase within the soil pores.

The key input parameters assumed by CCME (2005) for the J&E model are summarized below:

**Depth to Contamination ("diffusional path length"):** For purposes of generic guideline development, it is assumed that the soil-borne contamination is a minimum of 30 cm (0.3 m) from the building foundation.

**Indoor to outdoor pressure differential** ( $\Delta P$ ): For residential dwellings, a building depressurization of 4 Pa was assumed based on an approximate annual pressure differential data from CMHC. For commercial and industrial buildings, a lower default negative pressure differential of 2 Pa was selected because of "forced, calibrated air exchange designed into heating systems, and due to the more regular and routine movement of building occupants into and out of the structure."

*Soil permeability to soil gas flow:* The soil gas permeability of soil beneath a building foundation was assumed to be  $1 \times 10^{-8}$  cm<sup>2</sup> for coarse-grained soil, and  $1 \times 10^{-10}$  cm<sup>2</sup> for fine-grained soil. For comparison, USEPA (2003) suggests that typical soil gas permeability's are within the following ranges:

- Medium sand:  $1.0 \times 10^{-7}$  to  $1.0 \times 10^{-6}$  cm<sup>2</sup>
- Fine sand:  $1.0 \times 10^{-8}$  to  $1.0 \times 10^{-7}$  cm<sup>2</sup>
- Silty sand:  $1.0 \times 10^{-9}$  to  $1.0 \times 10^{-8}$  cm<sup>2</sup>
- Clayey silt:  $1.0 \times 10^{-10}$  to  $1.0 \times 10^{-9}$  cm<sup>2</sup>

**Building air exchange rate:** A building air change rate of  $1 \text{ hr}^{-1}$  is assumed for a residential scenario, while an air change rate of  $2 \text{ hr}^{-1}$  is assumed for a commercial scenario.

*Building mixing height:* A building mixing height of 4.88 m is assumed for a residential scenario, while a height of 3 m is assumed for a commercial scenario.

**Building footprint area:** A building footprint of  $150 \text{ m}^2$  is assumed for a residential scenario, while an area of 300 m<sup>2</sup> is assumed for a commercial scenario.

Under the CCME protocol, the allowable indoor air concentration originating from soil contamination is the reference concentration ( $R_fC$ ) or tolerable concentration (TC) minus the background indoor air concentration for threshold substances, or the risk-specific concentration (RSC) for non-threshold substances.

# 4.1.3 USEPA Draft Vapour Intrusion Guidance (2003)

The USEPA recently published draft guidance for the vapour intrusion pathway (USEPA, 2003) that enable derivation of screening groundwater and soil vapour criteria for a residential land use scenario. The USEPA guidance embodies a three-tiered approach, as follows:

**Preliminary Screening**: This step involves qualitative screening of sites to evaluate the potential for vapour intrusion, and to identify site conditions that warrant immediate assessment and possible mitigation.

*Secondary Screening*: This step involves the use of generic or semi-site-specific vapour attenuation factors to determine acceptable concentrations in groundwater or soil vapour (i.e., groundwater or soil vapour criteria) based on target risk levels and standard equations for estimating health risk. The USEPA approach is to calculate criteria using look-up tables of specified vapour attenuation factors based on 1/3 order-of-magnitude increments.

*Site Specific Screening*: This step involves the site specific use of a model to predict indoor air concentrations. There is a strong emphasis on the use of direct measurements (subslab vapour, indoor air) to confirm model predictions as part of a site specific assessment.

The semi-site-specific attenuation factors are provided in look-up charts ("alpha charts") for four US Soil Conservation Soil (SCS) soil types and varying depth to contamination source. The generic vapour attenuation factors are as follows:

• Subslab vapour-to-indoor air alpha: 0.1;

- Soil vapour-to-indoor air alpha: 0.01<sup>6</sup>;
- Groundwater-to-indoor air alpha: 0.001.

The semi-site-specific vapour attenuation factors were developed using the Johnson and Ettinger (1991) model; however, empirical data were used to ensure that the model-derived values were reasonable. The model-predicted results were compared to measured attenuation factors from chlorinated solvent-impacted sites, and there has been debate concerning the appropriateness of these attenuation factors for chemicals that biodegrade aerobically. The semi-site-specific attenuation factors are up to 14 times lower than the generic attenuation factors for groundwater and up to 77 times lower for soil vapour (i.e., depending on the depth and soil type).

The USEPA is currently preparing updated guidance that will likely include changes to the above generic attenuation factors. In addition, the alpha charts will be supplemented by a constrained version of the J&E model where users will be able to vary a limited number of parameters, within certain ranges, to estimate health risk and calculate groundwater and soil vapour criteria.

4.1.4 Draft Health Canada and SRA-2 VI Guidance

The draft Health Canada (HC) and SAB SRA-2 VI guidance for screening level risk assessment are similar and provide a protocol for estimation of potential human health risk from vapour intrusion for both residential and commercial land use scenarios. Although the protocol includes methods for soil, groundwater and soil vapour concentration data, preference is given to use of groundwater and soil vapour media for screening level risk assessment, with use of soil data being strongly discouraged. The methodology described can also be used to derive screening groundwater and soil vapour criteria.

The draft HC and SAB SRA-2 VI guidance follow a similar tiered evaluation framework for screening level risk assessment (SLRA) as the USEPA guidance, comprising Preliminary and Secondary Screening steps (Figure 4.1). The vapour intrusion SLRA guidance consists of two tiers. The first tier, Preliminary Screening, is a qualitative screening step to categorize sites according to their potential for vapour intrusion, to determine whether the assessment should proceed to the second tier, and to identify site conditions that warrant immediate assessment and possible mitigation. The second tier, Secondary Screening, consists of a screening-level quantitative risk assessment where representative semi-site specific vapour attenuation factors are used to estimate indoor air concentrations, which, in turn, are used to predict health risk. The semi-site specific

<sup>&</sup>lt;sup>6</sup> In context of USEPA guidance, the soil vapour-to-indoor air alpha is applicable when the vapour measurement is below 5 foot depth below the building slab.
vapour attenuation factors are based on the results of model predictions using the Johnson and Ettinger (J&E) model. The look-up charts for the semi-site specific vapour attenuation charts were developed with the Johnson and Ettinger model using benzene as a representative chemical; however, empirical data was used to validate to model results. The user selects the vapour attenuation factor that is most relevant using site specific information such as depth to contamination, building type (residential and commercial) and soil type (coarse- and fine-grained).



FIGURE 4.1: Flow Chart for Health Canada SLRA Vapour Intrusion Guidance

Unlike the USEPA guidance, the HC/SAB guidance does not include generic attenuation factors and instead the user proceeds directly to semi-site-specific attenuation factors. The proposed HC/SAB semi-site specific attenuation factors are slightly lower (by about 30 percent) than the USEPA guidance since different input parameters were used for the J&E model. The HC/SAB guidance also includes several site-specific optional adjustments, when warranted based on site-specific conditions, which reflect contaminant mass flux and source depletion considerations, mixing height for vapour inside the building, and biodegradation of hydrocarbon vapours. The SRA guidance also includes a check for where the risk-based target indoor air concentration are lower than the background indoor air concentration; in such cases, the target indoor air concentration is replaced by the median background concentration.

### 4.1.5 Comparison of CCME, USEPA and HC/SAB Guidance

The CCME, USEPA and HC/SAB vapour attenuation ratios are compared in Table 4.1. A depth to contamination of 1.5 m was chosen to enable comparison to the USEPA semisite specific attenuation factors, since this is the minimum depth for which attenuation factors are provided for the USEPA guidance. The CCME attenuation factor is that given in Table 3.6 of the Canada Wide Standards Scientific Rationale Document (CCME, 2000). As noted in Section 4.1.1, the CCME (2005) protocol assumes an identical model and input parameters as CCME (2000). The USEPA semi-site specific attenuation factors are those provided in Figures 3a and 3b (USEPA, 2003). The HC/SAB attenuation factors are those provided in Figures 3 to 7 (SAB, 2004).

		Groundwater to Indoor Air				Soil Vapour (Soil) to Indoor Air					
		<u>Resid</u>	ential	<u>Comn</u>	nercial	<u>Resid</u>	ential	<u>Comn</u>	nercial		
	Depth	Coarse-	Fine-	Coarse-	Fine-	Coarse-	Fine-	Coarse-	Fine-		
		Grained	Grained	Grained	Grained	Grained	Grained	Grained	Grained		
		(Sand)	(Loam)	(Sand)	(Loam)	(Sand)	(Loam)	(Sand)	(Loam)		
CCME CWS-	1.5 m	N/A	N/A	N/A	N/A	3.7E-05	1.9E-06	2.0E-05	1.4E-06		
PHC (2000)	30 m	N/A	N/A	N/A	N/A	8.9E-06	8.8E-07	6.5E-06	6.9E-07		
USEPA Draft	Generic	1.0E-03	1.0E-03	N/A	N/A	1.0E-02	1.0E-02	N/A	N/A		
VI Guidance (2003)	1.5 m	1.2E-03	1.4E-04	N/A	N/A	2.2E-03	1.4E-03	N/A	N/A		
	30 m	2.7E-04	7.0E-05	N/A	N/A	3.1E-04	1.3E-04	N/A	N/A		
Health Canada Draft	1.5 m	8.3E-04	1.0E-04	1.6E-04	2.5E-05	1.6E-03	1.0E-03	2.5E-04	2.1E-04		
VI Guidance (2004)	30 m	1.9E-04	5.0E-04	4.7E-05	1.3E-05	2.2E-04	9.0E-05	5.2E-05	2.3E-05		

**TABLE 4.1:** Comparison Guidance Vapour Attenuation Factors

The HC/SAB attenuation factors are approximately 30 percent lower that the USEPA factors. The CCME attenuation factors are over one order-of-magnitude less than the HC/SAB factors. For example, for a residential scenario and coarse-grained soil, the CCME attenuation factors are 42 times less than the HC/SAB factors.

The main reasons for the difference between the CCME and HC/SAB attenuation factors are summarized below for the residential scenario. Additional justification for input parameters is provided in SAB (2004):

*Air exchange Rate*: CCME 1 hr<sup>-1</sup>, HC/SAB: 0.35 hr<sup>-1</sup>. The HC/SAB residential air exchange rate was chosen based on extensive literature review of published air change rates (Hers et al., 2001). In regions with relatively cold climates, the recent trend has been to construct "air-tight" houses with reduced ventilation rates to minimize energy consumption and costs (e.g., "R-2000" houses in Canada; Gusdorf and Hamlin, 1995). In Canada, the minimum required ventilation rate under the CSA F326 standard for "*Residential Mechanical Ventilation Systems*" depends on the number and types of rooms in the house but usually works out to about 0.3 air changes per hour.

**Building Mixing Height**: CCME 4.88 m, HC/SAB: 3.66 m. The CCME building mixing height assumes complete mixing over two stories, whereas HC/SAB assumes mixing over one and half stories, since some vapour attenuation would be expected between floors.

Soil Gas Advection Rate: The CCME soil advection rate ( $Q_{soil}$ ) is calculated using the Perimeter Crack Model. For coarse-grained soil, a  $Q_{soil}$  of 0.6 L/min is obtained using the CCME default parameters ( $k_a = 1x10^{-8} \text{ cm}^2$ ,  $r_{crack} = 0.2 \text{ cm}$ ,  $X_{crack} = 49 \text{ m}$ ,  $Z_{crack} = 2.44 \text{ m}$ ,  $\Delta P = 4 \text{ Pa}$ ). For the HC/SAB guidance, the  $Q_{soil}$  value (5 L/min) was directly input into the model and was based on a typical range of about 1 to 10 L/min observed for tracer test data for residential buildings and coarse-grained soils. The Perimeter Crack Model is most sensitive to the soil-air permeability. The CCME default soil-air permeability of  $1x10^{-8} \text{ cm}^2$  is representative of fine sand.

*Soil Moisture*: The CCME water-filled and total porosity is 0.119 and 0.36, respectively. The HC/SAB water-filled and total porosity is 0.055 and 0.375, respectively. The HC/SAB porosities are identical to those assumed by USEPA and are based on a water-retention model for sand assuming relatively dry conditions below a building.

# 4.2 Proposed Protocol for Soil Vapour Intrusion Criteria or Standards

### 4.2.1 General Considerations

Case studies at a number of sites throughout North America have indicated potential unacceptable health risk associated with soil vapour intrusion. In particular, there have been chlorinated solvent-impacted sites where elevated indoor vapour concentrations were well above background levels. This experience indicates that soil vapour intrusion can be a significant potential exposure pathway and that regulatory guidance is warranted.

There are significant challenges associated with development of regulatory guidance for the soil vapour pathway. The pathway is fairly complex, vapour intrusion is highly variable depending on site conditions, and there is a relatively high level of uncertainty associated with predictive models used for this pathway. In particular, the development of a single-valued generic soil or groundwater criteria is challenging from a regulatory perspective since by necessity, generic criteria are conservative to ensure a low occurrence of "false negatives" (i.e., risks are identified as acceptable when, in fact, they are not). This results in many sites as being identified as needing further assessment, but where there is no unacceptable vapour intrusion risk at the site (i.e., high rate of false positives). For the above reasons, there is an increased emphasis on the use of a tiered guidance framework and use of site data and adjustments to generic criteria for more realistic and less conservative evaluation of soil vapour intrusion. The trend is also toward comprehensive, integrated guidance that addresses both screening and detailed risk assessment protocols, and which includes supporting guidance on methodology (e.g., soil vapour sampling).

### Recommendation

If soil vapour intrusion standards are included in the BC regulatory framework, it is considered essential that a readily implementable screening risk assessment protocol be in place to facilitate the derivation of less conservative, site-specific standards, and that protocols be in place for technically defensible methods for soil vapour characterization.

# 4.2.2 Applicable Media

The USEPA vapour intrusion guidance is limited to criteria for soil vapour and groundwater. The draft Health Canada guidance, while including a protocol for estimation of potential risks associated with contamination in soil, groundwater and soil vapour, indicates a strong preference for the use of soil vapour, and to a lesser extent groundwater, for risk assessment purposes.

Soil vapour characterization provides for a more direct measurement of potential vapour intrusion risk since the partitioning calculations are by-passed. Potential limitations associated with soil vapour as a medium for standard development include possibly greater temporal variability compared to concentrations measured in groundwater, and less well-developed protocols for soil vapour characterization compared to groundwater.

Groundwater characterization for evaluation of vapour intrusion studies should provide information on concentrations in groundwater near to the water table. This is because cross-media transfer from groundwater to soil vapour occurs when chemicals in porewater volatilize into soil gas, which occurs in the capillary transition zone above the

water table. Relatively short monitoring well screens situated across the water table are desirable when evaluating the soil vapour intrusion pathway, although a combination of shallow and deeper well screens may be warranted for site characterization purposes, particularly when a DNAPL source is present. A limitation with groundwater as a media for standard development is that partitioning calculations are required to estimate the vapour concentration.

Groundwater standards for the vapour intrusion pathway should only apply when contamination is limited to dissolved constituents in groundwater. In areas where LNAPL is present at the water table or where there is soil contamination above the water table, only soil vapour standards are applicable. The implication is that soil vapour characterization would be required at all sites with LNAPL contamination. Since petroleum hydrocarbon dissolved plumes are typically relatively short and since it is often difficult to distinguish between dissolved and residual NAPL zones, it is debatable whether groundwater standards would be of practical use at many petroleum hydrocarbon sites. In contrast, there are numerous examples of long chlorinated solvent dissolved plumes and therefore, there would be significant areas of these sites where groundwater standards could apply. Consideration could be given to only developing soil vapour standards for petroleum hydrocarbon compounds.

There are significant limitations associated with the use of soil as a medium for standard development purposes, including: (i) soil-vapour partitioning relationships are complex and there is significant uncertainty in the partitioning relationships commonly used; (ii) there is considerable variability in natural organic carbon, which is a sensitive parameter for estimation of vapour concentrations; (iii) soil concentrations tend to exhibit greater small-scale variability than groundwater or soil vapour concentrations; and, (iv) measured soil concentrations may be biased low as a result of sampling methods and volatilization losses. It is noted that when typical default organic carbon fraction values (e.g., 0.006) are used, relatively conservative soil criteria are calculated.

For an existing building scenario, the use of groundwater and soil vapour standards to evaluate potential soil vapour intrusion risks is considered technically sound and practically implementable. For sites under-going re-development or where future development may occur (e.g., Brownfield sites with no buildings), it is recognized that the absence of soil standards may be problematic in that remediation end-points are less well defined when based solely on groundwater and/or soil vapour. For sites undergoing remediation, it may be desirable to derive site specific remediation targets for soil that correspond to the generic or risk-based soil vapour standard, as applicable, to guide the site remediation process. The soil concentration targets can be calculated on a sitespecific basis using partitioning relationships described in the SRA-2 guidance (SAB, 2004b). Development of site specific target concentrations for jar or bag headspace vapour tests may be useful to guide remediation excavations. Post-remediation sampling of groundwater and soil vapour may be warranted to confirm standards have been met.

### Recommendation

For purposes of standard development, applicable media should be limited to groundwater and soil vapour, and should not include soil. However, the contaminated sites regulatory framework should incorporate a process by which site-specific remediation targets may be developed for soil to guide site remediation, where groundwater and/or soil vapour concentrations exceed relevant standards.

Groundwater standards are only applicable when contamination is limited to a dissolved plume in groundwater. If there is LNAPL at the water table or soil contamination above the water table, only vapour standards should apply. The implication is soil vapour characterization would be mandatory at sites with LNAPL or soil contamination.

Since petroleum hydrocarbon dissolved plumes are typically relatively short and since it is often difficult to distinguish between dissolved and residual NAPL zones, it is debatable whether groundwater standards would be of practical use at many petroleum hydrocarbon sites. Consideration could be given to only developing soil vapour standards for petroleum hydrocarbon compounds.

# 4.2.3 Preliminary Screening and Precluding Factors

Two important components of the SRA guidance are Preliminary Screening and evaluation of precluding factors (Figure 4.1). Preliminary Screening is a qualitative screening step where sites are categorized according to their potential for vapour intrusion. No further assessment of the vapour intrusion pathway is required (i) at sites where occupied or future buildings are greater than 30 m from concentrations in soil and/or groundwater that are above background levels<sup>7</sup>, provided that certain conditions are met, or (ii) where the chemical is not of concern based on screening based on volatility and toxicity (see Section 4.2.4). At the opposite end of the spectrum, if there are indications of significant health or safety risk (contamination in sumps or basements, chemical odours indicative of a subsurface vapour source), immediate follow-up action including possible risk mitigation is required.

Under the SRA protocol, all sites that fall between the above scenarios proceed to Secondary Screening; however, precluding factors are initially evaluated to determine whether Secondary Screening is appropriate, or whether the assessment should proceed to detailed risk assessment. These precluding factors are sites with the following characteristics:

<sup>&</sup>lt;sup>7</sup> 30 m lateral or vertical distance

- Very high gas permeability media such as vertically or near vertically fractured bedrock, karst, cobbles or other media with unusually high gas permeability;
- Utility conduits that intersect a vapour contamination source and that are directly connected to the building, and/or; and,
- Buildings with earthen basements.

Although the Health Canada and SAB guidance includes a precluding factor for shallow depth to contamination (less than 1 m), this precluding factor is not applicable for standards development since a separate vapour standard is proposed for shallow depths (see Section 4.2.5).

The proposed protocol for derivation of generic vapour standards utilizes the Secondary Screening attenuation factors assuming conditions considered applicable to most sites (coarse-grained soil, 1 m depth to contamination). The attenuation factors proposed for derivation of standards may not be sufficiently protective for sites with conditions described by the above precluding factors. However, the above precluding factors would likely only apply at a small number of sites. Consideration should be given to including the above precluding factors in the regulation so that users are directed to proceed to detailed risk assessment when these factors apply.

## Recommendations

The regulation accompanying the vapour standards should include the preliminary screening step to identify whether vapour standards apply based on the 30 m rule. This, in concept, would be similar to the procedure followed to determine whether the aquatic life standards apply for groundwater flow to surface water.

The regulation accompanying the vapour standards should include a preliminary screening step to evaluate whether there are indications of significant health or safety risk (contamination in sumps or basements, chemical odours indicative of a subsurface vapour source) where immediate follow-up action including possible risk mitigation is required.

The protocol should recognize that the attenuation factors used for SRA and proposed for the derivation of generic vapour standards may not be protective of all site conditions. The regulation accompanying the vapour standards should identify the site precluding factors which would require a detailed risk assessment to be conducted. The precluding factors could includes sites with the following characteristics:

- Very high gas permeability media such as vertically or near vertically fractured bedrock, karst, cobbles or other media with unusually high gas permeability;
- Utility conduits that intersect a vapour contamination source and that are directly connected to the building, and/or;
- Buildings with earthen basements.

### 4.2.4 Chemical Screening

The HC guidance includes screening step for evaluation of chemical toxicity and volatility to determine whether a chemical is contaminant of potential concern (COPC). The approach taken for the HC guidance was to compare the target indoor air concentration to the maximum theoretical equilibrium soil vapour concentration based on either groundwater-to-vapour (Henry's Law constant) or NAPL-to-vapour (Raoult's Law) partitioning multiplied by a conservative attenuation factor, to determine whether the chemical was toxic and volatile, as follows:

If  $C_{vapour} * \alpha_{screen} > C_{target}$  then chemical is volatile and toxic.

where  $C_{vapour}$  is the maximum predicted soil vapour concentration,  $\alpha_{screen}$  is a conservative attenuation factor, and  $C_{target}$  is the risk-based target indoor air concentration (PAQS<sub>HH-VI</sub> defined below).

The intent of chemical screening is to identify chemicals that should be included for risk assessment purposes. However, it is counterproductive to set too conservative a screen since this will needlessly identify additional chemicals as potentially of concern for vapour intrusion. It is proposed that the  $\alpha_{screen}$  be slightly higher than the upper range empirical subslab-to-indoor air alpha. The subslab alpha is reasonable for this purpose since the closest measurement point to the interior of the building is subslab soil vapour. As discussed in Section 4.2.5, empirical data indicates that 0.01 is a conservative upper bound subslab alpha. Considering the uncertainty in this alpha, a  $\alpha_{screen}$  of 0.02 is proposed.

### Recommendation

A protocol for identifying chemicals of potential concern for vapour intrusion is required. It is recommended that this screening be based on the maximum predicted equilibrium vapour concentration and a conservative alpha factor of 0.02.

### 4.2.5 Proposed Standards and Vapour Attenuation Factors

The proposed regulatory framework for evaluation of soil vapour intrusion is based on three different types of standards depending on depth to the vapour contamination source and measurement point:

**Subslab/shallow soil vapour standards (< 1 m)**: This *empirical* standard would apply when depth to the soil vapour measurement point is less than 1 m below the building foundation.

Soil vapour standards (>=1 m): This model-derived standard would apply when the depth to the soil vapour measurement point is greater than or equal to 1 m below the building foundation. The soil vapour measurement must be above the contamination zone.

*Groundwater standards* (>=1 m): This *model-derived* standard would only apply when there is only dissolved contamination and the depth to the water table is equal to or greater than 1 m below the building foundation.

The vapour intrusion standard implementation framework is shown in Figure 4.2. The proposed generic vapour attenuation factors are provided below in Table 4.2. The source of the generic attenuation factors are shown in Figure 4.3.

	<b>Residential Scenario</b>	<b>Commercial Scenario</b>
Subslab/Shallow Vapour	1E-02	1E-03
Soil Vapour	1.8E-03 <sup>1</sup>	2.5E-04 <sup>1</sup>
Groundwater	8.8E-04 <sup>1</sup>	1.6E-04 <sup>1</sup>

**TABLE 4.2:** Preliminary Vapour Attenuation Factorsfor Standard Development Purposes

Note: 1. Alpha's are for benzene for transport through 1 m of coarse soil; recommend that chemical-specific alpha's be calculated

It is anticipated that the proposed soil vapour standards would require a new matrix table as part of the Contaminated Sites Regulation (CSR), if implemented. The format for a possible matrix table is provided below in Table 4.3. For the groundwater-to-indoor air pathway, inclusion of the vapour pathway would simply require an additional column to the Schedule 6 matrix standards.



FIGURE 4.2: Framework for Generic Soil Vapour Intrusion Standards



FIGURE 4.3: Health Canada/SAB SRA-2 Vapour Attenuation Factor Charts

	Residentia	al	Commercial				
	Subslab/Shallow Soil Vapour (< 1 m)	Soil Vapour (> 1 m)	Subslab/Shallow Soil Vapour (< 1 m)	Soil Vapour (> 1 m)			
Chemical1							
Chemical2							

## **TABLE 4.3**: Example Soil Vapour Matrix Table

## Subslab/Shallow Soil Vapour Standards (< 1 m)

The subslab/shallow soil vapour standard is calculated using a non-chemical specific vapour attenuation factor of 0.01 for residential sites and 0.001 for commercial sites. The rationale for an attenuation factor of 0.01 for residential sites is that empirical data indicates that this is a reasonable upper bound (SAB, 2004; Hers et al., 2005). For commercial sites, there is virtually no empirical data. Therefore, the commercial subslab/shallow vapour alpha is obtained by scaling the residential empirical subslab alpha by the model predicted deeper soil vapour alpha's as follows:

Commercial subslab/shallow alpha = 0.01 \* Commercial soil vapour alpha / Residential soil vapour alpha = 2.5E-04/1.8E-03 = 1.4E-03 (rounded down to 1E-03)

The rationale for the scaling is based on model predictions for the soil vapour to indoor air pathway, which indicate a roughly one order-of-magnitude reduction in alpha. A similar one order-of-magnitude reduction would be expected for the subslab alpha.

The subslab/shallow soil vapour standards apply to soil vapour concentrations measured either below a building foundation or adjacent to the building; however, there are specific requirements for where the soil vapour measurement must be taken. If adjacent to the building, the soil vapour sample should be taken as close to the water table as possible. The soil vapour measurement depth must be at least 0.3 m below the building foundation, and 0.5 m below ground surface, and obtained reasonably close to the building (e.g., within 5 m). Below the building, the soil gas sample may be collected directly below the foundation slab.

Soil Vapour Standard (> 1 m)

The soil vapour standard is calculated using a chemical-specific J&E model-derived attenuation factor assuming a coarse-grained soil and 1 m depth to contamination. The proposed vapour attenuation factor for benzene is given in Table 4.2. The soil vapour standards are about five times less than the subslab/shallow vapour standard. Only about 20 percent of this difference is due to vapour attenuation over 1 m depth. There is a

disjoint in the subslab/shallow and soil vapour standards since greater variability is expected for subslab and shallow soil vapour measurements based on a number of considerations including (i) greater variability in soil types and possible soil disturbance near to building foundations, (ii) environmental factors such as wind, atmospheric pumping and temperature will have a greater effect on shallow soil gas near the building, and (iii) the effect of biodegradation may be variable in shallow regions below and beside the building. The above processes will have less of an influence on deeper soil gas.

Groundwater Standard (> 1 m)

The groundwater standard is calculated assuming transport through both the capillary fringe and the unsaturated zone. Partitioning according to the Henry's law constant is used to estimate the vapour concentration from the concentration in groundwater. It is considered reasonable to limit the groundwater standard to depths greater than 1 m below the foundation to account for possible seasonal water table fluctuations and to allow for a certain thickness of the tension-saturated zone (i.e., capillary fringe), which varies with texture. The alpha value used to develop the example groundwater standard is consistent with the upper bound of the observed Health Canada empirical values.

### Precedence for Application of Standards

Guidance is required on the precedence for application of standards since it is expected that at many sites both groundwater and soil vapour data will be obtained. Soil vapour samples could be obtained at a number of locations including near to the water table and from shallower regions either below or adjacent to the building. Repeat soil vapour sampling may be warranted to evaluate temporal variability.

As discussed in Section 4.2.2, the use of soil vapour measurements is generally preferable since estimation of partitioning from groundwater is not required. However, appropriate protocols must be followed for soil vapour sampling and analysis. It is recommended that soil vapour standards take precedence over groundwater standards. However, if measured groundwater concentrations exceed standards by orders-of-magnitude, and soil vapour concentrations are less than the standards, the site investigation report should address possible reasons for this discrepancy.

# Recommendation

Since soil vapour measurements provide for a more direct indication of potential vapour intrusion risk, it is recommended that soil vapour standards take precedence over groundwater standards, when measurements for both media are available.

### Biodegradation Adjustment

The aerobic biodegradation of hydrocarbon vapours (e.g., BTEX) is well documented (Ostendorf and Kampbell, 1990; Ririe and Sweeney, 1995; Fischer et al., 1996, DeVaull et al., 1997, Hers et al, 2001, DeVaull et al., 2002). Several studies indicate significant attenuation in hydrocarbon vapour concentrations can occur over short vertical intervals. Unfortunately, there is still little information on the influence of buildings on oxygen transport and hydrocarbon vapour profiles below buildings. It is hypothesized that a building could limit the migration of oxygen to below the building thus potentially limiting biodegradation below the building. However, it is also possible that advective soil gas movement or pumping through barometric fluctuations could result in elevated oxygen levels below buildings. In the absence of field data, modeling studies have been used to gain insight on vapour biodegradation, as described below.

The HC guidance includes an adjustment for hydrocarbons which readily biodegrade under aerobic conditions. The justification for the proposed adjustment is empirical data and the results of model predictions. For applicable chemicals, the base alpha is reduced by a factor of 10 when the depth from the foundation to the vapour contamination source is greater than 4 m and there is no significant capping effect beside the building. This depth was roughly based on the results of model predictions using a numerical model for diffusive vapour transport and oxygen-limited first-order biodegradation.

The results of recent numerical modeling by Johnson (2005) of diffusive and advective transport combined with oxygen-limited biodegradation suggest that based on the model assumptions and inputs chosen for a residential scenario, the predicted alpha would be at least 10 times less than the base case alpha (i.e., which assumes no biodegradation) for a vapour contamination source greater than 3 m depth below the building.

The State of New Jersey and Massachusetts are proposing for their vapour intrusion guidance to calculate generic criteria using an alpha that incorporates a 10 times reduction factor for readily biodegradable hydrocarbon compounds (e.g., BTEX) regardless of the depth to contamination.

Aerobic biodegradation is an important process for hydrocarbon vapour attenuation. At this time, there is insufficient scientific basis for incorporation of a biodegradation adjustment for a generic groundwater or soil vapour standard based on a depth to contamination of 1 m, although it may be appropriate to include this adjustment for greater depths. However, a separate set of standards for deeper contamination sources would add to the complexity of the generic standards.

### Recommendation

At this time, it is recommended that no biodegradation adjustment be incorporated in the calculation procedure for soil vapour intrusion standards. Further research into hydrocarbon vapour biodegradation below buildings is recommended. If warranted, the protocol should be revised to incorporate biodegradation for applicable chemicals.

### Chemical Specific Issues

The SRA vapour intrusion protocol is non-chemical specific in that physical-chemical properties are not taken into account when selecting the attenuation factor. As noted in Section 4.1.4, the attenuation factor was derived using physical-chemical properties for benzene, since the diffusion coefficient, which is the only transport parameter influenced by physical-chemical properties, only varies by about a factor of two for most common VOCs. For SRA-2, benzene was assumed as a surrogate chemical for ease of calculations. However, for derivation of generic standards, it would be relatively simple to calculate chemical-specific attenuation factors when deriving groundwater or soil vapour standards.

### Recommendation

It is recommended that chemical-specific properties be used to calculate a chemicalspecific alpha value used to derive groundwater and soil vapour standards.

### 4.3 Soil Vapour Inhalation Standard Risk Equations

The proposed risk equations used to derive soil vapour and groundwater standards for the indoor vapour inhalation pathway are provided in Exhibit 4-1. The proposed protocol for deriving groundwater and soil vapour standards involves up to four steps:

- 1. Calculate target indoor air concentration.
- 2. Adjust target indoor air concentration based on background air concentrations, as warranted.
- 3. Calculate soil vapour standard, using the soil vapour-to-indoor air alpha.
- 4. Calculate groundwater standard, as follows:

- a. Calculate an acceptable soil vapour concentration using the groundwater-toindoor air alpha;
- b. Compare the soil vapour concentration to the maximum theoretical soil vapour concentration based on partitioning from NAPL phase; and,
- c. If the acceptable soil vapour concentration is less than the maximum theoretical concentration, calculate a groundwater standard using the Henry's Law constant partitioning equation (otherwise, no standard possible).

## Exhibit 4-1 - Equations for Soil Vapour Inhalation Standards

### **Calculation Target Indoor Air Concentrations**

Threshold Substances (TC =  $R_fC$ ):

$$PAQS_{HH-VI} = \frac{HQ^T \times TC}{(AF_L)xET_1xET_2}$$

If no TC  $(R_fC)$  is available, can calculate from TDI  $(R_fD)$  as follows:

$$TC = \frac{[TDI] \times BW}{(IR)}$$

Non-Threshold Substances (unit risk (UR)):

$$PAQS_{HH-VI} = \frac{\left[ILCR^{T}\right] \times ED}{\left(AF_{L} \times UR\right) \times AT \times ET_{1} \times ET_{2}}$$

If no UR is available, can calculate from slope factor (SF) as follows:

$$UR = \frac{\left[SF\right] \times IR}{\left(BW\right)}$$

### Adjustment for Background Air Concentration (when warranted)

If  $PAQS_{HH-VI} < C_{background air}$  then  $PAQS_{HH-VI} = C_{background air}$ 

### **Calculation of Example Soil Vapour Standard**

The shallow soil vapour standard (< 1 m depth) is calculated as follows:

$$PSVQS_{HH-VI} = \frac{PAQS_{HH-VI}}{a_{SV}}$$

The deep soil vapour standard (> 1 m depth) is calculated as follows:

$$PDVQS_{HH-VI} = \frac{PAQS_{HH-VI}}{a_{DV}}$$

## Calculation of Example Groundwater Standard

The maximum theoretical vapour concentration is then calculated based on the maximum value for the predicted equilibrium concentration based on Henry's Law constant (i.e., dissolved source), and the predicted concentration based on Raoult's Law (i.e., NAPL source) and then compared to the back calculated vapour concentration based on the groundwater alpha. If the maximum possible vapour concentration is less than the back calculated vapour concentration is less than the back calculated vapour concentration, no groundwater standard is possible.

Maximum theoretical  $C_{vapour}^{Max}$  = Maximum [ UCF1 \* X \*  $C_{solubility}$  \* H', UCF2 \* X \* VP / RT ]

$$C_{vapour}^{\quad Gdw} = \frac{PAQS_{HH-VI}}{a_G}$$

If  $C_{vapour}^{Max <} C_{vapour}^{Gdw}$  then no standard possible.

If a groundwater standard is possible, it is calculated as follows:

$$PGQS_{HH-VI} = \frac{PAQS_{HH-VI}}{1000*a_{c}*H'}$$

where,

PAQS <sub>HH-VI</sub>	= Preliminary human health air standard $(mg/m^3)$
PSVQS <sub>HH-VI</sub>	= Preliminary human health shallow soil vapour standard $(mg/m^3)$
PDVQS <sub>HH-VI</sub>	= Preliminary human health deep soil vapour standard $(mg/m^3)$
PGQS <sub>HH-VI</sub>	= Preliminary human health groundwater standard (mg/L)
HQ <sup>T</sup>	= Target hazard quotient (recommend 0.5)
ILCR <sup>T</sup>	= Target incremental lifetime cancer risk $(1x10^{-5})$
$\alpha_{SV}$	= Shallow soil vapour-to-indoor air alpha (dimensionless)
$\alpha_{DV}$	= Deep soil vapour-to-indoor air alpha (dimensionless)
$\alpha_G$	= Groundwater-to-indoor air alpha (dimensionless)
$TC(R_fC)$	= Tolerable concentration $(mg/m^3)$
$TDI(R_fD)$	= Tolerable daily intake (mg/kg-day)
UR	= Unit risk factor $(mg/m^3)^{-1}$
Slope factor	= Slope factor $(mg/kg-day)^{-1}$
TRV	= toxicity reference value (mg/kg bw day)
BW	= body weight (kg)
IR	= air inhalation rate $(m^3/d)$
AF <sub>L</sub>	= absorption factor for lung (unitless)

ET <sub>1</sub>	= exposure term 1 (unitless) – days per week/7 x weeks per yr/52
$ET_2$	= exposure term 2 (unitless) – hours per day/24
VP	= vapour pressure (atm)
Х	= mole fraction (dimensionless)
R	= Boltzman constant (m <sup>3</sup> -atm/K-mole)
Т	= Temperature (K)
H'	= Henry's Law constant (dimensionless)
C <sub>solubility</sub>	= Pure-phase solubility (mg/L)
UCF1	= Unit conversion factor 1 $(L/m3)$
UCF2	= Unit conversion factor 2 (1000 mg/g)

**Exposure Term for Non-Threshold Contaminants** – The exposure term for non-threshold compounds includes the component related to the fraction of time exposed ( $ET_1$  and  $ET_2$ ) and amortization of less than a lifetime exposure over a lifetime (ED/AT).

CCME (2005) assumes the ET for non-threshold contaminants for all land uses (including commercial) is 1.0 since the exposure period exceeds the likely latency period for most carcinogens as indicated in Section 3.0.

The PQRA guidance by Health Canada (2005) assumes the ET for non-threshold contaminants for residential land use is 1.0. For commercial land-use, the ET is 0.24 based on ET<sub>1</sub> equal to 0.71 (5 days/7 days) and ET<sub>2</sub> equal to 0.33 (8 hours/24 hours). For the residential and commercial scenarios, Health Canada current policy is not to allow amortization for less than a lifetime of exposure for residential, commercial or industrial exposures (ED/AT = 1). As indicated in Section 3.0, Health Canada is currently evaluating their policy on amortization for carcinogenic substances.

While the CSST protocol did not directly address inhalation of vapours, for the dust inhalation pathway, the ET's were 1.0 for the residential scenario and 0.33 for the commercial scenario.

**Exposure Term for Threshold Compounds** – The exposure term for threshold compounds is the fraction of time exposed ( $ET_1$  and  $ET_2$ ).

CCME assumes an exposure term of 0.33 for threshold contaminants based on  $ET_1$  equal to 0.71 (5 days/7 days) and  $ET_2$  equal to 0.42 (10 hours/24 hours).

Health Canada (2005) assumes the ET for threshold contaminants are 1.0 for residential land use and 0.24 for commercial land-use, as indicated above for non-threshold substances.

While the CSST protocol did not directly address inhalation of vapours, for the dust inhalation pathway, the ET's were 1.0 for the residential scenario and 0.33 for the commercial scenario.

Adjustment of Target Indoor Air Concentration for Background – For a few chemicals, target indoor air concentrations are less than typical background indoor air concentrations. For example, for benzene and a residential scenario, the target air concentration (PAQS<sub>HH-VI</sub>) is  $3 \mu g/m^3$  for an acceptable lifetime cancer risk of  $1 \times 10^{-5}$  and unit risk of 0.0033 mg/m<sup>3</sup> (Health Canada, 2005). Published background concentrations of benzene in indoor air are at similar levels to the unit risk factor. For example, the reported median indoor benzene concentration was 5.4  $\mu g/m^3$  for a large indoor air quality study (757 homes) conducted by Health Canada (Otson and Davis, 1993). It is recommended that the target risk-based indoor air concentration, if lower, be replaced with the background air concentration (e.g., median value from literature) since it is not considered practical to regulate to levels below background. An initial survey of Reference Concentrations (R<sub>f</sub>C) and Unit Risk (UR) factors for volatile chemicals suggest that there are only a few chemicals where the acceptable risk-based air concentrations (based on HQ=1; cancer risk =  $1 \times 10^{-5}$ ) are on the same order as typical background concentrations.

Acceptable Risk Levels - The identification of acceptable risk levels is a policy decision; the discussion below is intended to provide background information on the approach taken by regulatory jurisdictions.

The USEPA Soil Screening Guidance (USEPA, 1996) acceptable risk levels are a lifetime cancer risk of  $1 \times 10^{-6}$  for carcinogens and a hazard quotient of 1 for noncarcinogens. For carcinogens, "USEPA believes that setting a  $1 \times 10^{-6}$  risk level for individual chemicals and pathways generally will lead to cumulative risks within the  $1 \times 10^{-4}$  to  $1 \times 10^{-6}$  range for the combinations of chemicals generally found at Superfund sites." For non-carcinogens, it was considered difficult to address additive effects since HQs should only be added for those chemicals with the same toxic endpoint and/or mechanism of action. USEPA also considered possible apportionment to adjust the HQ as a percentage of a regulatory health-based level that is allocated to the source and pathway being regulated to account for non site related exposures to other media. Apportionment was not applied since "USEPA has traditionally focused on quantifying exposures to a receptor that are clearly site-related and has not included exposures from other sources ..."

The HC guidance assumes a hazard quotient of 0.2 and acceptable lifetime cancer risk of  $1 \times 10^{-5}$ . Although not explicitly addressed, the rationale for a HQ of 0.2 is understood to be based on a similar concept to the soil allocation factor used for direct contact pathways where the HQ is adjusted to reflect apportionment for other potential background exposure sources.

For the vapour inhalation pathway, there can be significant indoor sources of volatile chemicals from various sources including consumer products, building materials and emission sources. For some chemicals, there can also be relatively significant outdoor ambient sources. It is expected that other sources of volatiles (e.g., soil, groundwater, consumer products) would be small in comparison to indoor and outdoor sources. A reasonable apportionment factor may be 0.5 for non-carcinogens.

**Check Based on Maximum Theoretical Vapour Concentration:** As indicated in Exhibit 4.1, the derivation procedure for groundwater includes a check to determine whether the back-calculated soil vapour concentration based on the groundwater alpha and target indoor air concentration (PAQS<sub>HH-VI</sub>) exceeds the maximum theoretical vapour concentration. If this is the case, it is not possible to calculate a standard. The maximum theoretical vapour concentration is that predicted for either groundwater-to-vapour partitioning based on Henry's Law constant using the effective solubility, or NAPL-to-vapour estimated from Raoult's Law using the effective vapour pressure. Except for petroleum fractions (i.e., CCME F1, F2), the effective solubility is equal to the purephase solubility and effective vapour pressure is equal to the pure-phase vapour pressure (i.e., mole fraction equal to one).

### Recommendations

Assuming an exposure term of 1.0 for non-threshold contaminants (i.e., CCME approach), regardless of the land use, is considered an overly conservative assumption. Instead the exposure terms proposed by Health Canada (with slight modification) is recommended. The following exposure terms are proposed and would apply to both threshold and non-threshold compounds:

Residential =  $ET_1 X ET_2 = 7 \text{ days}/7 \text{ days } x 52 \text{ weeks}/52 \text{ weeks } x 24 \text{ hrs}/24 \text{ hrs} = 1.0$ Commercial =  $ET_1 X ET_2 = 5 \text{ days}/7 \text{ days } x 48 \text{ weeks}/52 \text{ weeks } x 10 \text{ hrs}/24 \text{ hrs} = 0.27$ 

Further evaluation of exposure amortization may be warranted upon completion of the Health Canada study.

It is recommended that the target risk-based indoor air concentration, if lower, be replaced with the median background air concentration based on a survey of literature values.

### 4.4 Example Soil Vapour Intrusion Standards

Example standards are calculated for selected chemicals for the soil vapour intrusion pathway (Table 4.4). For VPH and LEPH, the example standards are calculated using the protocol adopted from Golder (1995), while for the F1 and F2, the methodology outlined in the CCME CWS-PHC (CCME, 2000) are used. The toxicity reference values were obtained from CCME (2000). The surrogate chemicals and toxicity reference values are provided in Table 4.5. There are several issues associated with criteria development for petroleum hydrocarbon compounds; evaluation of these issues goes beyond the scope of this document. It is noted that the State of Washington and USEPA Region 9 are developing soil vapour intrusion guidance for total petroleum hydrocarbon (TPH) fractions.

Date Printed: June 17, 2005

# Table 4.4

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### Example Standards for Vapour Intrusion Pathway

Media	Alpha	Naphthalene	Benzene	TCE	Xylenes	n-Hexane	VPH	LEPH	F1	F2
Toxicity Reference Factors	•	•			-					
UR (mg/m <sup>3</sup> )-1		-	3.30E-03	6.09E-04	-	-	-	-	-	-
TC (mg/m <sup>3</sup> )		4.9E-02	-	-	1.80E-01	2.00E-01	*	*	*	*
Residential										
Exposure Term		1	1	1	1	1	1	1	1	1
PAQS <sub>HH-VI</sub> (mg/m <sup>3</sup> )		4.9E-02	5.00E-03	1.64E-02	1.8E-01	2.0E-01	*	*	*	*
Groundwater (ug/L)	8.80E-04	7424	44	85	1461	81	175	50	38	22
Soil Vapour (mg/m <sup>3</sup> )	1.80E-03	27	2.8	9.1	100	111	236	129	670	311
Commercial										
Exposure Term		0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27
PAQS <sub>HH-VI</sub> (mg/m <sup>3</sup> )		1.81E-01	1.12E-02	6.08E-02	6.67E-01	7.41E-01	*	*	*	*
Groundwater (ug/L)	1.60E-04	No Criteria	540	1727	29762	1653	3500	No Criteria	22500	No Criteria
Soil Vapour (mg/m³)	2.50E-04	726	45	243	2667	2963	6037	3426	17704	8333
CSR AW Fresh Std (ug/L)		10	4000	200	NS	NS	1500	500	N/A	N/A
CSR AW Marine Std (ug/L)		10	1000	200	NS	NS	1500	500	N/A	N/A
CSR Gdw DW Std (ug/L)		NS	5	50	300	NS	NS	NS	N/A	N/A

Note:

1. For benzene, the example standard for residential scenario is calculated by replacing the risk-based air concentration with the background concentration (5 ug/m<sup>3</sup>)

2. UR = unit risk factor, TC = tolerable concentration (RfC), NS = no standard, N/A = not applicable, \* = see Table 4.5

For groundwater-to-indoor air, the example standards are compared to the Contaminated Sites Regulation aquatic life (AW) and drinking water standards (DW). For benzene, VPH and LEPH, the example vapour standards for the residential scenario are significantly less than the CSR AW standards. The example TCE vapour standard is slightly (about 2 times) less than the CSR AW standard. For the chemicals selected, the CSR DW standards were less than the example residential vapour standards. The example groundwater standards for vapour inhalation do not include adjustment for potential mass flux limitations, which can be important, as further discussed below.

I able 4.5       04-1412-22         Physical-Chemical Properties and Toxicity Reference Values											-1412-228		
Fraction											Fraction Avg	Avg	
	Parameter	Surrogates	Tolerable Concentration	Molecular Weight	Vapour Pressure	Henry's Law Constant	Henry's Law Constant	Solubility	Log (Koc)	Mass Fraction	Molecular Weight	Mole Fraction	
			(mg/m3)	(g/mole)	(atm)	(atm-m3/mole)	(dimensionless)	(mg/L)	(cm3/g)	(-)	(g/mole)	(-)	
MWLAP	VPH	n-Hexane	0.18	86.17	8.89E-01	1.20E-01	2.81E+00	1.80E+01	1.77	0.6	N/A	0.6	
		Toluene	3.8	92	3.73E-01	6.60E-03	2.70E-01	5.30E+02	2.26	0.4	N/A	0.4	
MWLAP	LEPH	Naphthalene	0.049	128.19	4.90E-04	4.80E-04	7.50E-03	1.00E+02	3.08	0.2	N/A	0.2	
		Decane	3.1	142.3	1.73E-03	1.87E-01	7.99E+00	5.20E-02	5.29	0.8	N/A	0.8	
CCME	F1	C7-C8 Aromatic	0.4	92	3.80E-02	6.49E-03	2.77E-01	1.80E+03	2.40	0	100	0	
		C8-10 Aromatic	0.2	120	6.30E-03	1.20E-02	5.13E-01	6.50E+01	3.20	0.09	100	0.075	
		C6-8 Aliphatic	18.4	100	6.30E-02	1.20E+00	5.13E+01	5.40E+00	3.60	0.55	100	0.55	
		C8-10 Aliphatic	1	130	6.30E-03	1.90E+00	8.12E+01	4.30E-01	4.50	0.36	100	0.28	
CCME	F2	C10-12 Aromatic	0.2	130	6.30E-04	3.40E-03	1.45E-01	2.50E+01	3.40	0.09	180	0.12	
		C12-16 Aromatic	0.2	150	4.80E-05	1.30E-03	5.56E-02	5.80E+00	3.70	0.11	180	0.13	
		C10-12 Aliphatic	1	160	6.30E-04	2.90E+00	1.24E+02	3.40E-02	5.40	0.36	180	0.41	
		C12-16 Aliphatic	1	200	4.80E-05	1.25E+01	5.34E+02	7.60E-04	6.70	0.44	180	0.40	

. . .

Note: Temperature-corrected to 12 degrees Celcius (Method 1, Golder 2004), source of physical-properties for F1 and F2 fractions are CCME CWS-PHC.

### 4.5 Contaminant Mass Flux Check

When contamination is limited to dissolved chemicals migrating in groundwater, the only source of vapours are chemicals that volatilize from groundwater. The available mass that could potentially volatilize under steady state conditions is controlled by the mass flux in groundwater flowing below the building. The development of the proposed alpha factors in Section 4.2.5 did not take into consideration possible mass flux considerations and instead assumed that the available mass in groundwater matches or exceeds the volatilization rate represented by the attenuation factor, regardless of the attenuation factor volatilization rate. Mass flux limitations are particularly important for chemicals with high Henry's Law constants (e.g., aliphatic hydrocarbon compounds).

The HC guidance includes a simple mass flux check to ensure that the predicted indoor air concentration, for the selected attenuation factor, is not unrealistic based on the available mass flux. The mass flux check is applicable when there is only a dissolved contamination source and requires an estimate of the Darcy velocity (specific discharge). The mass flux check is based on an analytical model that couples groundwater transport and unsaturated zone transport (Figure 4.4). The model assumptions are somewhat arbitrary, but considered reasonably conservative in that they are unlikely to over predict the influence of mass flux limitations. The mass flux check assumes that all dissolved chemicals within the top 1 m of groundwater flowing below the entire width of the building will volatilize and enter the building (i.e., leaving no chemicals in groundwater down-gradient of the building). In reality, dissolved plumes only loose a small portion of their mass through volatilization. In addition, it is assumed that the groundwater chemicals are not attenuated through biodegradation. For the HC guidance, if the predicted mass flux through volatilization is greater than the available mass flux in groundwater, then the predicted indoor air concentration is reduced (i.e., scaled) based on the available mass flux.



**FIGURE 4.4:** Conceptual Model for Groundwater Mass Flux Adjustment

For generic standards development, application of a mass flux check requires that a Darcy velocity be assumed. Although velocities will vary depending on site conditions, for initial evaluation of the potential significance of mass flux limitations, a Darcy velocity of 500 m/year is assumed. This velocity is unlikely to be exceeded at most contaminated sites is British Columbia. For this Darcy velocity, the mass flux adjustment is applicable to LEPH, F1 and F2. The adjusted groundwater concentrations (unadjusted values in parentheses) are as follows:

- LEPH: 840 ug/L (50 ug/L)
- F1: 51 ug/L (38 ug/L)
- F2: 50 ug/L (22 ug/L)

### Recommendation

A mass flux adjustment should be considered if groundwater standards are included for petroleum hydrocarbon compounds. Alternately, if groundwater standards were not to be included for petroleum hydrocarbons (as suggested in Section 4.2.2), mass flux limitations and overly conservative (low) groundwater standards would not be an issue.

### 4.6 Summary of Recommendations

The recommendations provided in the above sections are summarized below:

- 1. If soil vapour intrusion standards are included in the BC regulatory framework, it is considered essential that a readily implementable screening risk assessment protocol be in place to facilitate less conservative, site-specific standards to be derived for sites, and that protocols be in place for technically defensible methods for soil vapour characterization.
- 2. For purpose of standard development, applicable media should be limited to groundwater and soil vapour, and should not include soil. However, the contaminated sites regulatory framework should incorporate a process by which site-specific remediation targets may be developed for soil to guide site remediation, where groundwater and/or soil vapour concentrations exceed relevant standards. Such site-specific remediation targets can be computed using partitioning relationships presented in SRA-2.

- 3. Groundwater standards are only applicable when contamination is limited to a dissolved plume in groundwater. If there is LNAPL at the water table or soil contamination above the water table, only vapour standards would apply. The implication is vapour characterization would be mandatory within and near to LNAPL zones.
- 4. Since petroleum hydrocarbon dissolved plumes are typically relatively short and since it is often difficult to distinguish between dissolved and residual NAPL zones, it is debatable whether groundwater standards would be of practical use at many petroleum hydrocarbon sites. Consideration could be given to only developing soil vapour standards for petroleum hydrocarbon compounds.
- 5. The regulation accompanying the vapour standards should include the preliminary screening step to identify whether vapour standards apply based on the 30 m rule. This, in concept, would be similar to the procedure followed to determine whether the aquatic life standards apply for groundwater flow to surface water.
- 6. The regulation accompanying the vapour standards should include a preliminary screening step to evaluate whether there are indications of significant health or safety risk (contamination in sumps or basements, chemical odours indicative of a subsurface vapour source) where immediate follow-up action including possible risk mitigation is required.
- 7. The protocol should recognize that the attenuation factors used for SRA and proposed for derivation of generic vapour standards may not be protective of all site conditions. The regulation accompanying the vapour standards should identify the site precluding factors which would require a detailed risk assessment to be conducted. These precluding factors could include sites with the following characteristics:
  - Very high gas permeability media such as vertically or near vertically fractured bedrock, karst, cobbles or other media with unusually high gas permeability;
  - Utility conduits that intersects a vapour contamination source is directly connected to the building, and;
  - Buildings with earthen basements.
- 8. A protocol for identifying chemicals of potential concern for vapour intrusion is required. It is recommended that this screening be based on the maximum predicted equilibrium vapour concentration and a conservative alpha factor of 0.02.

- 9. Since soil vapour measurements provide for a more direct indication of potential vapour intrusion risk, it is recommended that soil vapour standards take precedence over groundwater standards, when measurements for both media are available.
- 10. At this time, it is recommended that no biodegradation adjustment be incorporated in the calculation procedure for soil standard development purposes. Further research into hydrocarbon vapour biodegradation below buildings is recommended. If warranted, the protocol should be revised to incorporate biodegradation for applicable chemicals.
- 11. It is recommended that chemical-specific properties be used to calculate a chemical-specific alpha value used to derive groundwater and soil vapour standards.
- 12. Assuming an exposure term of 1.0 for non-threshold contaminants (i.e., CCME approach), regardless of the land use, is considered an overly conservative assumption. Instead the exposure terms proposed by Health Canada (with slight modification) is recommended. The following exposure terms are proposed and would apply to both threshold and non-threshold compounds:
  - Residential = ET<sub>1</sub> X ET<sub>2</sub> = 7 days/7days x 52 weeks/52weeks x 24 hrs/24hrs = 1.0
  - Commercial = ET<sub>1</sub> X ET<sub>2</sub> = 5 days/7days x 48 weeks/52weeks x 10 hrs/24hrs = 0.27
- 13. Further evaluation of exposure amortization may be warranted upon completion of the Health Canada study.
- 14. As part of the standard derivation process, it is recommended that the target riskbased indoor air concentration, if lower, be replaced with the median background air concentration based on a survey of literature values.
- 15. A mass flux adjustment should be considered if groundwater standards are included for petroleum hydrocarbon compounds. Alternately, if groundwater standards were not to be included for petroleum hydrocarbons (as suggested in Section 4.2.2), mass flux limitations and overly conservative groundwater standards would not be an issue.

# 5.0 HUMAN HEALTH PROTECTION: GROUNDWATER USED FOR DRINKING WATER

The existing CSST protocol derives a soil standard protective of groundwater used for drinking water.

### 5.1.1 Groundwater Model

The groundwater models are independent of the drinking water guideline used to backcalculate the soil standard. The proposed changes in the groundwater models described in Section 2.0 are equally applicable to this pathway.

## 5.1.2 Drinking Water Guideline Values

When available, the existing CSST protocol recommended using Health Canada drinking water quality guidelines as published in Guidelines for Canadian Drinking Water Quality (Health Canada 1993; revised 1996)<sup>8</sup>. In the absence of a Health Canada guideline, the Ministry approved drinking water criteria (BCMWLAP 1998) was selected. The CSR Schedule 6 water quality standards are compared to Canadian Federal water quality guidelines in Table 5.1.

<sup>&</sup>lt;sup>8</sup> The following web site should be checked for recent updates to the Health Canada drinking water quality guidelines http://www.hc-sc.gc.ca/hecs-sesc/water/dwgsup.htm.

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 Table 5.1

 Comparison CSR Schedule 6 and Canadian Federal Water Quality Guidelines

	CSR Schedule 6 (June 13, 2005)					<b>Canadian Environmental Quality Guidelines</b>				Canadian Drinking	
Chamical	Water: Aq	Water: Aquatic Life		Lifesteelr	Lifestock Drinking		juatic Life	Water: Agriculture		Water Quality	
Circinical	Freshwater	Marine	(ug/L)	LIIESTOCK	Water	Freshwater	Marine	Irrigation	Livestock	MAC	AO
	(µg/L)	$(\mu g/L)$	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)
	-		-		_			-	-		-
Arsenic	50	120	100	25	25	5	12.5	100	25	$25(5)^8$	-
Benzene	4000	1000	NS	NS	5	370	110	-	-	5	-
Benzo(a)pyrene	0.1	0.1	NS	NS	0.01	0.015	-	-	-	0.01	-
Cadmium	0.1 to 0.6	1	5	80	5	0.017	0.12	5.1	80	5	-
Chromium										50	-
Trivalent Chromium (Cr(III))	90	560	5	50	50	8.9	56	4.9	50	-	-
Hexavalent Chromium (Cr(VI))	10	150	8	50	50	1.0	1.5	8	50	-	-
Copper	20-90	20	200	300	1000	2-4 1,4	-	200-1000 6	500-5000 <sup>7</sup>	-	$\leq 1$
Ethylbenzene	2000	2500	NS	NS	2.4	90	25	-	2.4	-	≤2.4
Lead	40-160	20	200	100	10	1-7 1,5	-	2001	100	10	-
Pentachlorophenol	1-27.5	1-27.5	NS	30	30	$0.5^{-1}$	-	-	-	60	≤30
Polychlorinated Biphenyls (PCB)	NS	NS	NS	NS	NS	No EQG <sup>2</sup>	No EQG <sup>2</sup>	-	-	-	-
PCDD and PCDF	NS	NS	NS	NS	NS	No EQG <sup>2</sup>	No EQG <sup>2</sup>	-	-	-	-
Tetrachloroethylene (Perc)	1100	1100	NS	NS	30	111	-	-	-	30	-
Toluene	390	3300	NS	NS	24	2	215	-	24	-	≤24
trichloroethylene (TCE)	200	200	NS	50	50	21	-	-	50 <sup>1</sup>	$50(5)^8$	-
Total Xylene	NS	NS	NS	NS	300	-	-	-	-		≤300
Zinc	75-2400	100	1000-5000	2000	5000	30	-	1000-5000 1	50000 <sup>1</sup>		$\leq$ 5000 $^{3}$

1 No fact sheet created. For more information on this guideline, please refer to Canadian Water Quality Guidelines (CCREM 1987),

available electronically on the accompanying CEQG CD.

2 No EQG: No environmental quality guideline is recommended; see environmental quality guidelines for other media where appropriate.

3 The guideline is considered protective of human health against exposure to other microcystins (total microcystins) that may also be present.

4 Copper Freshwater Guideline =  $2\mu g/L$  at [CaCO<sub>3</sub>] = 0-120mg/L

5 Lead Freshwater Guideline =  $1\mu g/L$  at [CaCO<sub>3</sub>] = 0-60mg/L

 $= 4\mu g/L$  at [CaCO3] = 120-180mg/L

= 7µg/L at [CaCO3] > 180mg/L

6 Copper Irrigation Guideline =  $200\mu g/L$  for cereals,  $1000\mu g/L$  for tolerant crops

7 Copper Irrigation Guideline = 500µg/L for sheep, 1000µg/L for cattle, 5000µg/L for swine and poultry

8 Proposed Guidelines in brackets

# Recommendations

A review of the drinking water guidelines used to back calculate the soil standard should be conducted and if guidelines have changed or been revised, the standard should be updated.

### 6.0 HUMAN HEALTH PROTECTION: INTAKE OF CONTAMINATED SOIL

The review of the methods used for calculating soil standards for intake of contaminated soil (i.e., soil intake standard) is not intended to provide an exhaustive analysis of derivation methodologies from all jurisdictions; rather, the review focused on differences between the existing CSST protocol and CCME (2005). The CCME protocol was recently revised based on advances in the science and, where applicable, harmonization with recent Health Canada updates. Comparison to other jurisdictions, such as the USEPA, was incorporated in our review if an issue required further clarification.

Typically the derivation of soil quality standards via soil intake or direct exposure considers the following three exposure pathways: soil ingestion, dermal contact and dust inhalation. It is anticipated that for most contaminants, soil ingestion will be the dominant exposure pathway (USEPA 2002a; Health Canada 2004a). Particulate inhalation is not expected to contribute significantly to exposure for most substances; however inhalation may become more important for non-volatile substances with high inhalation toxicity (e.g., cadmium; CCME 2005).

### 6.1 Review of Selected Derivation Protocols

### 6.1.1 BCE 1996

The existing CSST protocol (BCE 1996) has been summarized below.

- **Basis of "Intake of Contaminated Soil" Standard** Although consideration of all three exposure pathways was allowed for in the existing CSST protocol (Exhibit 9A CSST protocol), only the direct soil ingestion route was used to derive the existing matrix standards (Exhibit 9B existing CSST protocol). The CSST indicated that there was insufficient data to derive standards based on the dermal contact and dust inhalation pathways. A standard developed using this approach was referred to as a preliminary human health soil quality standard (PSQS<sub>HH</sub>).
- Absorption Factor The relative absorption factor for soil ingestion was assumed to equal 100% unless verifiable scientific evidence indicated otherwise. The existing matrix standards were derived based on a relative absorption factor equal to 100% for all substances.
- Soil Allocation Factor (SAF) For the purpose of deriving soil intake standards, exposure to contaminated soil was apportioned to 20% of the TDI. The "soil allocation factor" (SAF) of 20% allows for 80% of remaining TDI to be reserved for other media.

- Background Adjustment Toxicologically derived soil standards for non-anthropogenic pollutants were compared to background soil concentrations for the Lower Mainland. Standards were capped at contaminant concentrations equivalent to the 90<sup>th</sup> percentile of the Lower Mainland background soil concentrations.
- Estimated Daily Intake Incorporation of the estimated daily intake (EDI) of a chemical due to normal background exposure (i.e., not including exposure from a contaminated site) was recognized by the CSST but the estimation of generic EDIs was considered both difficult and of questionable relevance for any specific site. For this reason, an EDI was not used in the soil standard derivation process. However, a methodology for incorporating background EDIs was provided in the protocol, which could be used when relevant information was available (see next bullet).
- Preliminary EDI Based Soil Standard (PSQS<sub>HH(EDI)</sub>) If published Health Canada data for both background EDI and national generic background soil concentrations are available, then these data can be incorporated into the equation used to derive preliminary human health EDI-based intake of contaminated soil standard (PSQS<sub>HH(EDI)</sub>; Exhibit 10 in CSST protocol) . No published Health Canada EDIs or background soil concentrations were available for matrix substances, at the time the soil standards were developed. The CSST protocol indicates that when a PSQS<sub>HH(EDI)</sub> can be calculated, it should be compared to the PSQS<sub>HH</sub> value calculated using CSST's preferred simplified formula (Exhibit 9B CSST protocol), and the "more reasonable" of the two preliminary values selected as the standard.

### 6.1.2 CCME (2005)

The CCME (2005) protocol is similar to the BCE (1996) protocol. Subtle differences between the two protocols are highlighted below.

• **Basis of Soil Intake Guideline** – The CCME soil intake guideline considers exposure from soil ingestion, dermal contact and dust inhalation. However, similar to BCE (1996), it appears that the majority of the existing CCME (1996) soil intake guidelines, were based on the ingestion pathway only. The only exception was volatile organic substances where ingestion was deemed to be an inappropriate exposure route as contaminants typically do not remain in surficial soil since they will volatilize over relatively short time frames. The recently revised CCME (2005) protocol allows for separate evaluation of each exposure pathway (i.e., soil ingestion, dermal contact, dust inhalation) in cases where the mechanism of toxicity may be different for the different exposure routes, and separate TDIs are available. This approach is reasonable since in many cases there are separate oral and inhalation TDIs and some chemicals are treated as a threshold chemical for some exposure routes and a non-threshold chemical for others. The lowest calculated value for any

of the separate exposure pathways is then selected as the preliminary soil quality guideline (PSQG<sub>HH</sub>). This applies to both threshold and non-threshold chemicals. The CCME also considers exposure from two indirect exposure pathways, referred to as check mechanisms, which can result in the lowering of the PSQG<sub>HH</sub>. Check mechanisms are described in more detail later in this section.

- Estimated Daily Intake The estimated daily intake (EDI) of a chemical due to normal background exposure (i.e., not including exposure from a contaminated site) is included in the derivation process. CCME (2005) indicates that risk posed by a contaminated site must be determined in addition to this background exposure. Therefore, for the purpose of back-calculating a soil standard, CCME (2005) calculated a residual tolerable daily intake (RTDI) which is the difference between the tolerable daily intake (TDI) and the EDI.
- Soil Allocation Factor A default value of 20% of the RTDI was apportioned to exposure to contaminated soil. However, if defensible contaminant-specific evidence exists demonstrating that the contaminant does not occur in a given medium, the SAF may be increased from 20% to a value given by:

SAF = 100% / (number of applicable exposure media)

- Absorption Factors When there is sufficient information to evaluate the absorption into the body from both the environmental exposure route being evaluated and the study exposure route, a relative absorption factor other than 1 can be used.
- **Background Adjustment** If the EDI is greater than the TDI, the CCME indicates that the provisional soil quality guideline should be set at the background soil concentration or analytical detection limit for that contaminant.
- **Check mechanisms** The CCME (2005) considers exposure from two indirect • exposure pathways that are referred to as check mechanisms. The two check mechanisms are consumption of produce, meat and milk and off-site migration of soil contaminants via wind and water erosion. Exposure from ingestion of food grown on contaminated soils applies to agricultural and residential sites and is treated as a required exposure pathway or primary exposure pathway for substances that biomagnify. The off-site migration via wind and water erosion to more sensitive neighboring properties only applies to commercial or industrial sites and applies to all non-volatile contaminants. Due to the imprecise nature of the models used to evaluate these mechanisms, the above check mechanisms are considered by CCME to be "Management Adjustment Factors" and may or may not be used to adjust a generic guideline value, based on professional judgment. The check mechanism can result in the lowering of the final soil quality guideline via the "Management Adjustment Factor".

### 6.2 Discussion of Differences

#### 6.2.1 Basis of Soil Intake Guideline

In theory, the existing CSST protocol for deriving the intake of contaminated soil standard took into account exposure from soil ingestion, dust inhalation and dermal contact by summing together exposure from each of these pathways. However, in practice, only the soil ingestion pathway was used to derive standards, as CSST was of the opinion that there was a lack of sufficient scientific data available to estimate exposures for the dermal contact and dust inhalation pathways. It is anticipated that for most contaminants, soil ingestion will be the dominant exposure pathway. However, for certain contaminants, other exposure pathways might be significant contributors to exposure (e.g., cadmium via dust inhalation). In these circumstances, it would be prudent to include these pathways in the derivation process.

If the mechanism of toxicity is the same for each exposure route and the same TRV is applied to all three exposure pathways, the equation for deriving the soil intake standard would be the same as was used in the existing CSST protocol. However, this is typically not the case. If the mechanism of toxicity is different for the different exposure routes and separate TRVs are available, exposure pathways can be evaluated separately. This is the approach that CCME (2005) recommends, with the lowest calculated value for any of the separate pathways selected as the soil standard. The equations for calculating the pathway specific soil intake standard for soil ingestion, dermal contact and dust inhalation are shown in Exhibit 6-1 for threshold substances and Exhibit 6-2 for non-thresholds substances.

Similar to the existing CSR Schedule 5 matrix soil standards, the soil standards calculated for each pathway would be shown in the Schedule 5 matrix template. Furthermore, as is the case today, we recommend that it be mandatory to calculate the soil ingestion standard for all Schedule 5 substances. When there is sufficient information to justify input parameters to calculate dermal contact and dust inhalation standards, these standards would also be calculated and shown in Schedule 5.

In the United States, different methods are used in different regions for developing soil intake guidelines. For example, US EPA Region III (US EPA Region III 2004) calculates risk based concentrations (RBCs) in soil for the soil ingestion pathway but not for the dust inhalation and dermal contact pathways. Region III guidance indicates that RBCs should only be applied when dermal contact and dust inhalation are not expected to be significant, otherwise a site specific risk assessment should be conducted. US EPA Region IX (US EPA Region IX 2004) calculates preliminary remediation goals (PRGs) in soil that include soil ingestion, dermal contact and dust inhalation pathways when sufficient information is available.
## Recommendations

If the mechanism of toxicity is different for the different exposure routes and separate TRVs are available as well as suitable absorption factors, exposure pathways can be evaluated separately. If the above information is not available or defensible for a specific pathway, a soil standard should not be calculated.

The pathway specific soil standards calculated for soil ingestion, dermal contact and dust inhalation would all be shown in the Schedule 5 matrix template. Furthermore, as is the case today, we recommend that it be mandatory to calculate the soil ingestion standard for all Schedule 5 substances. When there is sufficient information to justify input parameters to calculate dermal contact and dust inhalation standards, these standards would also be calculated and shown in Schedule 5.

## Soil/Dust Inhalation

It is anticipated that this exposure pathway will generally be insignificant relative to direct ingestion of soil and dermal absorption (Health Canada 2004a). US EPA (2002a) indicates that for semi-volatiles and metals, soil standards derived for the soil ingestion and dermal contact pathways are more conservative than the dust pathway. However, there are exceptions to the rule; for example, US EPA (2002a) reported that the carcinogenicity of hexavalent chromium via the inhalation route results in a soil screening level that is more stringent than the ingestion/dermal contact pathway. As a result, they recommend evaluating the fugitive dust pathway routinely for chromium.

Health Canada (2004a) recommends using an average airborne concentration of respirable particulate matter of  $0.76 \,\mu\text{g/m}^3$  (based on US EPA 1992) in the dust inhalation calculation. This is based on wind generated dust only. Where significant vehicle traffic is expected on unpaved surfaces, Health Canada (2004a) recommends using a value of 250  $\mu\text{g/m}^3$  for vehicle generated dust. In generating PRGs for the dust inhalation pathway, the US EPA Region IX use a generic particle emission factor (PEF; m<sup>3</sup>/kg) that corresponds to a receptor point concentration of approximately 0.76  $\mu\text{g/m}^3$ .

Exposures to dust could be calculated for selected constituents if potential risk from exposure from this pathway is significant. Both the CCME (2005) and the existing CSST protocol considered the dust inhalation pathway when developing soil standards/guidelines but have not identified default soil inhalation rates (DR; kg/day) or methods to calculate these rates. Based on guidance provided by Health Canada (2004a), the soil inhalation rate can be calculated as follows:

DR = PA x IR x ET<sub>2</sub> DR = soil inhalation rate (kg/d) PA = particulate concentration in air (kg/m<sup>3</sup>) IR = air inhalation rate (m<sup>3</sup>/d) ET<sub>2</sub> = hours per day/24 (unitless)

Exhibit 6-1 and 6-2 show the equation for the derivation of the soil standard for the dust inhalation pathway using the PA and IR.

The existing CSST protocol indicated that the default parameters used to estimate exposure for the dust inhalation pathway lacked sufficient scientific validation. Although Health Canada (2004a) recommends evaluating the dust inhalation pathway, there is inherent uncertainty that arises from calculating exposure from dust inhalation, as site specific factors play a large role in influencing dust generation (i.e., particle size, vegetation cover, wind, rain, etc).

#### **Exhibit 6-1 - Equations for Threshold Substances**

Soil ingestion only:

$$PSQS_{HH-SI} = \frac{SAF \times TRV \times BW}{(AF_G \times SIR) \times ET_1}$$

Dermal contact only:

$$PSQS_{HH-DC} = \frac{[SAF \times TRV] \times BW}{(AF_{S} \times SR) \times ET_{1}}$$

Particulate Inhalation only:

$$PSQS_{HH-PI} = \frac{\left[SAF \times TRV\right] \times BW}{\left(AF_{L} \times PA \times IR\right) \times ET_{1} \times ET_{2}}$$

where,

PSQS <sub>HH</sub>	= Preliminary human health TDI-based soil standard (mg/kg)
SIR	= soil ingestion rate (kg/day)
AFL	= absorption factor for lung (unitless)
PA	= particulate concentration in air $(kg/m^3)$
IR	= air inhalation rate $(m^3/d)$
AF <sub>S</sub>	= absorption factor for skin (unitless)
SR	= soil dermal contact rate (kg/day) see below
ET <sub>1</sub>	= exposure term 1 (unitless) – days per week/7 x weeks per yr/52
ET <sub>2</sub>	= exposure term 2 (unitless) – hours per day/24

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Soil Dermal Contact Rate (SR):				
$SR = (SA_H x DL_H) + (SA_O x DL_O) x EF$				
$\mathrm{SA}_\mathrm{H}$	= exposed surface area of hands $(m^2)$			
SA <sub>0</sub>	= area of exposed body surfaces other than hands $(m^2)$			
$DL_{H}$	= dermal loading of soil to hands $(kg/m^2)$			
DLo	= dermal loading of soil to other surfaces $(kg/m^2)$			
EF	= exposure frequency (events/d)			
The $PSQS_{HH}$ is then the lowest calculated value for any of the separate pathways.				

## Exhibit 6-2 - Equations for Non-Threshold Substances

Soil ingestion only:

$$PSQS_{HH-SI} = \frac{RSD \times BW}{(AF_G \times SIR) \times ET_1}$$

Dermal contact only:

$$PSQS_{HH-DC} = \frac{RSD \times BW}{(AF_s \times SR) \times ET_1}$$

Particulate Inhalation only:

$$PSQS_{HH-PI} = \frac{RSD \times BW}{(AF_L \times PA \times IR) \times ET_1 \times ET_2}$$

where,

PSQS <sub>HH</sub> RSD	<ul><li>Preliminary human health RSD-based soil standard (mg/kg)</li><li>risk specific dose (mg/kg day)</li></ul>
BW	= body weight (kg)
AF <sub>G</sub>	= relative absorption factor for gut (unitless)
SIR	= soil ingestion rate (kg/day)
$AF_L$	= relative absorption factor for lung (unitless)
PA	= particulate concentration in air $(kg/m^3)$
IR	= air inhalation rate $(m^3/d)$
AF <sub>s</sub>	= relative absorption factor for skin (unitless)
SR	= soil dermal contact rate (kg/day) see below
$ET_1$	= exposure term 1 (unitless) – days per week/7 x weeks per yr/52
ET <sub>2</sub>	= exposure term 2 (unitless) – hours per day/24

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Soil Dermal Contact Rate (SR):			
$SR = (SA^{H} x DL^{H}) + (SA^{O} x DL^{O}) x EF$			
$SA_{H}$	= exposed surface area of hands (m <sup>2</sup> )		
SA <sub>O</sub>	= area of exposed body surfaces other than hands $(m^2)$		
DL	= dermal loading of soil to hands $(kg/m^2)$		
DL <sub>O</sub>	= dermal loading of soil to other surfaces $(kg/m^2)$		
EF	= exposure frequency (events/d)		
The $PSQS_{HH}$ is then the lowest calculated value for any of the separate pathways.			

## Relative Contribution of Each Pathway

To evaluate the relative contribution of the soil ingestion, dermal contact and dust inhalation pathways to the final PSQS<sub>HH</sub>, sample calculations were performed for cadmium and hexavalent chromium (Table 6.1). Cadmium was selected as it is known to be sensitive via the inhalation pathway (i.e., treated as a carcinogen) and there is recent scientific information to support using a dermal absorption factor of 0.001 (US EPA 2004a). Hexavalent chromium was selected since it also is sensitive via the inhalation pathway. For chromium, the OME (1996) dermal adsorption factor of 0.09 was used. Calculations were conducted for the commercial land use scenario using the new receptor assumptions, exposure periods, and using Health Canada TRVs. The existing CSR commercial land use matrix soil standard (which is based only on the soil ingestion pathway) was shown for comparison purposes.

Substance Classification	Soil Ingestion	Dermal Contact	Dust Inhalation	Existing CSR CL Matrix Standard
Cadmium				
Carcinogenic	-	-	4,160	
Non-carcinogenic	50	58,140	-	100
Chromium (VI)				
Carcinogenic			539	
Non-carcinogenic	63	807		300

FABLE 6.1:	Pathway Specific Soil Standards for Cadmium and
Chromium	for the Commercial Land Use Scenario (mg/kg)

Notes:

1. For the dust inhalation pathway, the adult was the sensitive receptor and for the soil ingestion and dermal contact pathways, the sensitive receptors was a toddler. Receptor assumptions are based on the revised Health Canada values shown in Table 3-1.

2. Exposure terms used were:  $ET_1 = 0.66$  and  $ET_2 = 0.5$ .

3. For cadmium, the Health Canada TDI of 0.0008 mg/kg and inhalation slope factor of 42.9 (mg/kg-d)<sup>-1</sup> were used in calculations. For chromium, the Health Canada TDI of 0.001 mg/kg and inhalation slope factor of 331 (mg/kg-d)<sup>-1</sup>.

The results indicate that even though cadmium and chromium (VI) are considered non-threshold contaminants for humans via the inhalation pathway (Health Canada 2004b), they do not drive the risk for the soil intake pathway. Instead the soil ingestion pathway is the driver by one to three orders-of-magnitude. Using the dermal absorption factor recommended by the US EPA (2004) for cadmium resulted in a 1,000 fold higher standard for the dermal pathway compared to that for the ingestion pathway.

This exercise highlights the effect of removing the hours per day exposure term for the soil ingestion pathway and to a lesser degree for the dermal contact pathway (refer to Section 3.1.5 for a detailed explanation). The exposure term used in the existing CSST protocol was 0.33 (i.e., based on 12hr/24hr x 5d/7d x 48wk/52wk x 70yr/70yr). When the hours per day exposure is removed the exposure term becomes 0.66 and results in a two times more conservative or lower soil standard. This would have an impact on the final soil intake standard for the commercial land use scenario and threshold contaminants only (i.e., the residential and agricultural land use scenario have an exposure term of 1.0). The commercial standard for threshold contaminants is based on a toddler receptor, which is a conservative assumption, as discussed in Section 3.0. If the child is adopted as the sensitive receptor for the commercial land use scenario, then the soil ingestion standard would increase by a factor of eight from that shown above in Table 6.1.

#### Recommendations

For most contaminants, soil ingestion is the dominant exposure pathway. The above calculations for cadmium and chromium suggest that dermal contact and dust inhalation would not be significant contributors to potential risk, based on the assumptions made respecting exposure concentrations and absorption factors. There is uncertainty in exposure concentrations, absorption factors, TRVs and, in some cases, different mechanisms of toxicity for different exposure routes, which complicate the derivation of soil standards for dermal contact and dust inhalation pathways.

The minimum information that would typically be required to consider deriving a dust inhalation soil standard would be an inhalation TRV, especially when the mechanism of toxicity is different than the oral pathway. For the dermal pathway, in cases where only an oral TRV is available and a suitable relative absorption factor is not available for the dermal pathway, a soil standard should not be calculated for this pathway. Using the default relative absorption factor of 1 with an oral TRV would result in overly conservative dermal contact soil standards with high uncertainty.

While it appears that ingestion will be the dominant risk driver, including dermal contact and dust inhalation standards, when appropriate, will add to completeness and transparency of the derivation process. The pathway specific soil standards calculated for

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soil ingestion, dermal contact and dust inhalation would all be shown in the Schedule 5 matrix template. Furthermore, as is the case today, we recommend that it be mandatory to calculate the soil ingestion standard for all Schedule 5 substances. When there is sufficient information to justify input parameters to calculate dermal contact and dust inhalation standards, these standards would also be calculated and shown in Schedule 5.

## 6.2.2 Absorption Factors

The health risk posed by soil ingestion, dust inhalation or dermal contact depends on the absorbed dose of a contaminant. When the critical toxicological study has used a different medium than that under investigation, sometimes an absorption factor is applied to account for the difference in absorption of the contaminant by the body in the two different media, when this information is available. For the purpose of guideline development, it is usually assumed that the absorption factor will be 1 for the ingestion and inhalation pathways as most toxicity studies are based on ingested or inhaled doses of contaminants (i.e., assumes that absorption efficiency in the environmental exposure is equal to that of the toxicological study). However, if there is sufficient information to evaluate the relative absorption efficiencies between the media involved this should be considered.

Absorption factors are more likely to be applied for the dermal contact exposure route, since very few TRVs are based on dermal exposure. In the absence of dermal TRVs, oral TRVs are routinely applied to the dermal pathway. To account for the difference between the environmental exposure media and the toxicological study used to derive the oral TRV, a relative absorption factor should be applied. In cases where only an oral TRV is available and a suitable relative absorption factor is not available for the dermal pathway, a soil standard should not be calculated for this pathway. Using the default relative absorption factor of 1 with an oral TRV would result in overly conservative soil standards with high uncertainty.

Health Canada (2004a) has recommended the use of dermal relative absorption factors as outlined by OME (1996). The background supporting documents for the OME relative absorption factors are available from Health Canada (pers. comm. Mark Richardson, Health Canada). The US EPA also provides recommended dermal absorption factors in their recently revised Supplemental Guidance for Dermal Risk Assessment (US EPA 2004a). CCME (2005) currently allow for absorption factors other than 1.0 when there is sufficient information to evaluate the absorption into the body from both the environmental exposure route being evaluated and the study exposure route.

## Recommendation

Unless there is sufficient information to indicate otherwise, it is anticipated that the relative absorption factor will be assumed equal to 1 for ingestion and inhalation pathways. However, we recommend continuing to evaluate scientific defensibility of applying absorption factors other than the default value of 1 for the ingestion and inhalation pathways.

Absorption factors other than 1 are more likely to be applied for dermal contact exposure routes; since few TRVs are based on dermal exposure. Assuming that dermal TRVs are not routinely available and that the oral TRV would be adopted for the dermal pathway, a relative absorption factor other than the default value of 1 would be required to consider deriving a soil standard for the dermal pathway. Otherwise an overly conservative soil standard with high uncertainty would be generated for the dermal pathway.

## 6.2.3 Soil Allocation Factors

Both the existing CSST protocol and CCME (2005) apply a default "soil allocation factor" (SAF) of 20% for threshold substances. Assigning a default value of 20% for the soil intake pathway allows for 80% of the remaining TDI or RTDI to be reserved for other media (i.e., air, water, food, consumer products). If defensible contaminant-specific evidence exists demonstrating that the contaminant does not occur in a given medium, the CCME (2005) protocol allows for the SAF to be increased from 20% to a value given by:

SAF = 100% / (number of applicable exposure media)

Increasing the SAF would allow for a greater percentage of the allowable daily exposure for threshold substances to come from the contaminated soil medium versus other media. Further details on the SAF were provided in Section 3.1.2. An increase in the SAF would result in a corresponding increase in the soil standard.

#### Recommendations

Continue to use the default SAF of 20% but if defensible, allow for the SAF to be increased based on the equation provided by CCME (2005).

#### 6.2.4 Estimated Daily Intake

The estimated daily intake (EDI) is an estimate of the typical total background exposure from all known or suspected sources and exposure routes for the average Canadian. The EDI does not include exposure from a contaminated or remediated site. The rationale that CCME (2005) provides for including the EDI is that risk posed by a contaminated site must be determined in addition to this background exposure. Therefore, CCME (2005) soil guidelines are calculated by taking into consideration the background soil exposure as well as the SAF (20%) of the tolerable daily intake (TDI). The adjustment of the TDI to account for background exposure (i.e., EDI) is referred to as the residual tolerable daily intake (RTDI) by CCME (2005).

The CSST recognized the potential impact of normal background exposure; however, they also recognized that the estimation of generic EDIs was both difficult and of questionable relevance for any specific site. Furthermore, CSST noted that incorporation of an EDI often resulted in guidelines that typically approximated or on occasion were actually less than the background soil concentrations. Therefore, CSST recommended that the CCME methodology incorporating background EDIs not be followed. The CSST believed that apportioning 20% of the TDI (i.e., application of the SAF) to soil exposures would ensure an adequate level of protection.

The original CSST protocol did recommend that if published Health Canada data for both background EDI and national generic background soil concentrations were available, then these could be incorporated into the equation for calculation of a separate standard referred to as the preliminary human health EDI-based intake of contaminated soil standard (PSQS<sub>HH(EDI)</sub>). If a PSQS<sub>HH(EDI)</sub> could be calculated, it would be compared to the PSQS<sub>HH</sub> value calculated using CSST's preferred simplified formula and the "more reasonable" of the two preliminary values selected as the standard. However, no published Health Canada EDIs or background soil concentrations were available for matrix standard substances at the time the CSST protocol was developed and therefore, no PSQS<sub>HH(EDI)</sub> were derived.

EDIs are now available for several chemicals from CCME Ecological and Human Health Assessment documents (e.g., Canadian Soil Quality Guidelines for Pentachlorophenol: Environmental and Human Health [CCME 1997]). In addition, Health Canada has developed EDIs for a range of other substances (pers. comm. Mark Richardson, Health Canada). Furthermore, Health Canada indicated that in situations where the EDI is greater than the TDI, a 10% increase in the EDI could be considered for guideline/standard development purposes.

## Recommendation

No changes are recommended. The existing CSST protocol already recommends derivation of an EDI based soil guideline (i.e.,  $PSQS_{HH(EDI)}$ ) when information is available. The  $PSQS_{HH(EDI)}$  is then compared to the  $PSQS_{HH}$  and the "more reasonable" of the two preliminary values selected as the standard. Now that EDIs have been published for several substances, the  $PSQS_{HH(EDI)}$  could be calculated to determine the potential impacts of background exposure.

## 6.2.5 Check Mechanisms

The CCME (2005) considers exposure from two indirect exposure pathways that are referred to as check mechanisms; i) consumption of produce, meat and milk; and ii) off-site migration of soil contaminants via wind and water erosion. In the check mechanisms, exposure is evaluated through the use of simplified models that utilize conservative generic input values for site-specific characteristics. The CCME (2005) include the consumption of produce, meat and milk as a check mechanism for the agricultural and residential land use scenarios and the off-site migration of soil/dust check mechanism for the commercial or industrial land use scenarios. These two pathways are considered check mechanisms rather than actual soil quality guidelines as CCME (2005) acknowledges the imprecise nature of the models and the uncertainty in the underlying assumptions used for these pathways.

CSST did not consider either of these pathways in the existing protocol as they were of the opinion that models or default parameters lacked sufficient scientific validation. Given CSST's original opinion regarding the check mechanisms, our review did not focus on evaluating either of these check mechanisms. Rather our review focused on highlighting any changes to the methods used to calculate the check values.

Other than updating some of the assumptions, the calculation of the produce, metal and milk check value has not changed substantially from the original CCME (1996) protocol. The evaluation of the consumption of produce meat and milk pathway is required for agricultural land use if the substance biomagnifies. If it does not biomagnify, this pathway is recommended but not required to be evaluated. For residential land use, the evaluation of this pathway is recommended but not required regardless of the whether the substance biomagnifies. Given the inherent uncertainty involved in deriving values for this pathway due to the number of models and default assumptions, it may be more practical if substances that bioaccumulate or biomagnify be addressed on a site specific basis if they are present on an agricultural or residential site where produce, meat and milk are produced and consumed. ANZECC (NEPM 1999a,b) has developed a similar approach whereby numerical soil criteria are not derived for residential sites where vegetable gardens contribute greater than 10% of vegetable and fruit intake. For these scenarios a site specific assessment is required.

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The off-site migration of soil contaminants check mechanism was updated by CCME (2005) to include both environmental and human health soil quality at commercial and industrial sites. Previously, the model was only applied for human health at industrial sites. CCME (2005) indicated that the off-site migration check value calculated for nine metals was 12 times the value of the soil quality guideline for the more sensitive land use. CSST did not adopt this check mechanism in the existing protocol as they indicated that potential off-site pollution of neighboring properties can be better controlled through application of existing BC Environment legislative and regulatory controls.

Given that CSST was of the opinion that models or default parameters lacked sufficient scientific validation and considering the inherent uncertainty in these models, as recommended by CSST previously, the two indirect check pathways defined above should not be included in the protocol.

It is noted for cadmium, the CSR soil standard for intake of contaminated soil includes separate standards for an agricultural and residential scenario that does and does not include consumption of homegrown produce. If the ministry considers this warranted, the protocol should be revised to include consideration of homegrown produce or the alternative would be to address substances that bioaccumulate/biomagnify on a site specific basis if they are present on an agricultural or residential site where produce, meat and milk are produced and consumed.

#### Recommendations

The CSST did not consider either of the two indirect check pathways in the existing protocol as they were of the opinion that models or default parameters lacked sufficient scientific validation. A detailed review of the models and default assumptions used by CCME (2005) was not conducted at this time; however, the following is recommended:

Given the inherent uncertainty involved in deriving values for the consumption of produce, meat, and milk, due to the number of models and default assumptions, it may be more practical if substances that bioaccumulate or biomagnify be addressed on a site specific basis if they are present on an agricultural site where produce, meat and milk are produced and consumed or for a residential site where garden produce contributes more than 10% of the produce intake for a residence. However, the ministry's position on this is not clear as they have generated separate soil intake standards for cadmium for agricultural and residential sites that do and do not include consumption of homegrown produce.

Considering that the models and general assumptions used to evaluate the off-site migration of contaminated soil are similar to those used in the original CCME (1996) protocol, and given that CSST was of the opinion that that potential off-site pollution of

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neighboring properties can be better controlled through application of existing BC Environment legislative and regulatory controls this pathway is not recommended for inclusion in the protocol.

#### 6.3 Summary of Recommended Changes

A summary of the recommended changes to the existing CSST protocol have been summarized below in Table 6.2.

## **TABLE 6.2:** Summary of Recommended Changes to Existing CSST Protocol

Parameter	Rationale	Recommended Change	
Receptor Assumptions	Health Canada (2004a) recently updated human receptor characteristics that are representative of the Canadian population. CCME (2005) have adopted the human receptors characteristic recommended by Health Canada.	Adopt the values used by CCME and Health Canada.	Vari path
Exposure Period - Hours per day exposure	CCME and Health Canada do not include hours per day exposure for soil ingestion or dermal contact since soil ingestion and dermal contact are not expected to occur at a uniform rate throughout the day.	Do not include hours per day exposure for soil ingestion and dermal contact.	Expe incre more cont
-Child vs Toddler as Sensitive Receptor for Commercial Scenario (threshold contaminants only)	Toddlers are unlikely to be present at commercial sites for appreciable periods of time. For the commercial scenario and threshold contaminants, a more realistic sensitive receptor may be a child receptor. However, it is important that the commercial land use standard is defined to exclude any commercial scenarios where children or toddlers could be present for appreciable periods of time (e.g., daycare at commercial site, community centres, hospitals).	Consideration should be given to adopting a less conservative sensitive receptor (child versus toddler) for the commercial land use scenario for threshold contaminants. This change is contingent on an appropriate designation of the commercial land use scenario.	As a exposed of the scenario o
Separation of Equations	For most contaminants, soil ingestion is the dominant exposure pathway. However, for certain contaminants, dermal contact and dust inhalation might be significant contributors to exposure. In addition if the mechanism of toxicity is different for the different exposure routes and separate TRVs are available it would be prudent to consider these pathways in the derivation process when there is sufficient information available to support derivation (e.g., relative absorption factors, TRVs).	When necessary, derive separate guidelines for each soil intake pathway based on the equations shown in Exhibit 6-1 and 6-2.	All t Sche inge Sche justi inha and
Soil Allocation Factor (SAF)	Both the existing CSST protocol and CCME apply a default SAF of 20%. However, the CCME (2005) protocol allows for the SAF to be increased from 20% if defensible contaminant-specific evidence exists demonstrating that the contaminant does not occur in all given medium (e.g., soil, water, air food, consumer products). Increasing the SAF would allow for a greater percentage of the allowable daily exposure to come from the contaminated soil medium versus other media.	Continue to use the default SAF of 20% but if defensible, allow for the SAF to be increased as per CCME (2005).	An i in the cont
Absorption Factor (AF)	Unless there is sufficient information to indicate otherwise, it is anticipated that the AF will be assumed equal to 1.0 for ingestion and inhalation based pathways as most TRVs are based on ingested and inhaled doses. AFs are more likely to be applied for dermal contact exposure routes, since few TRVs are based on dermal exposure.	Continue to evaluate scientific defensibility of applying AFs other than the default value of 1.0, especially for the dermal contact pathway. The default value of 1.0 should be applied when there is insufficient scientific information to support otherwise.	App and

#### Impact

rious. Depends on the age category and the exposure hway.

bosure term for soil ingestion and dermal contact would rease from 0.33 to 0.66, which would result in a two times re conservative soil standard for the soil ingestion and dermal tact pathways.

indicated in the above row, removing the hours per day osure term for the soil ingestion pathway for the commercial nario would result in a 2 times decrease in the soil standard. he child receptor is used instead of a toddler, the soil intake ndard would increase by a factor of 5 for commercial sites ead of decreasing by a factor of 2.

three pathway specific soil standards would be shown in the redule 5 matrix template. However, at a minimum, the soil estion standard should be required to be derived for all redule 5 substances. When there is sufficient information to ify input parameters to calculate dermal contact and dust alation standards, these standards would also be calculated shown in Schedule 5.

increase in the SAF would result in a corresponding increase the soil standard. This is only applicable for threshold taminants.

plying an exposure factor less than 1.0 is less conservative would result in higher standards.

## 7.0 ENVIRONMENTAL PROTECTION: TOXICITY TO SOIL INVERTEBRATES AND PLANTS

#### 7.1 Review of Selected Derivation Protocols

#### 7.1.1 BCE (1996)

BCE (1996) describes the existing CSST derivation method as follows:

- Consider all appropriate invertebrate and plant toxicity data from CCME "Substance Assessment" documents<sup>9</sup>;
- Separate data into discrete lethal and non-lethal effects distributions;
- Calculate median effect concentrations for the lethal and non-lethal effects distributions. See below for additional information regarding calculation of median effects concentrations;
- Fit linear regression lines to the lethal and non-lethal effects distributions. Use the "Empirical Exception" rule<sup>10</sup> if the R-squared value of the linear regression is < 0.25.
- Determine the regression intercepts for  $EC_{50}$ -NL and/or  $LC_{20}$ , and apply the appropriate level of protection for different land uses (i.e., take the lower of the two values for agricultural, residential and parkland uses; take the greater of the two values for commercial and industrial uses).

Specific detailed guidance supporting the derivation method described in BCE (1996) is not available; however, the following clarification and additional information was obtained from a review of the working files (e.g., Excel spreadsheets) used to derive the CSST soil quality standards (BCE, undated):

Data compiled from the CCME "Substance Assessment" reports are assigned to the following standardized point-estimate statistics: acute (LC<sub>X</sub>) and sublethal (EC<sub>X</sub>-NL) "x" values of 0, 1, 10, 25, 50, 100. For example, a NOEC for a sub-lethal endpoint is considered an "EC<sub>0</sub>-NL", while a LOEC for a sub-lethal endpoint is considered an "EC<sub>1</sub>-NL". NOECs and LOECs for mortality endpoints are assigned as LC<sub>0</sub> and LC<sub>1</sub>, respectively. Other point estimate statistics (e.g., a LC<sub>23</sub>) are considered equivalent to the nearest standardized point estimate statistic (i.e., the LC<sub>23</sub> is classified as a LC<sub>25</sub>).

<sup>&</sup>lt;sup>9</sup> The CSST derivation method relies on the literature search conducted by CCME, although data used by CCME may be excluded from consideration by CSST.

<sup>&</sup>lt;sup>10</sup> Empirical exception rule: estimate  $EC_{50}$ -NL and/or  $LC_{20}$  via empirical extrapolation from the median effects distribution (BCE, 1996).

- A median value for each of the standardized point estimate statistics is calculated (i.e., the average of all available LC<sub>50</sub> data, etc). These median values are then plotted on a graph of contaminant of potential concern (COPC) concentration versus percent effect. In some instances, a standardized endpoint (for which a median value was calculated) may be excluded from the regression. A linear regression equation is then fit to the distribution of the median values. An R<sup>2</sup> value is calculated.
- The overall " $EC_{50}$ -NL" is defined as the intersection of the regression line of the distribution of the non-lethal median values with the 50% effect level. The " $LC_{20}$ " is defined as the intersection of the regression line of the distribution of the lethal median values with the 20% effect level. These values are rounded as necessary.
- If the  $R^2$  of the regression is less than 0.25, then the EC<sub>50</sub>-NL or LC<sub>20</sub> values used for setting the soil quality standard are visually estimated based on the distribution of the median effects concentrations.
- The lower of the " $LC_{20}$ " and " $EC_{50}$ -NL" values is used as the soil standard for agricultural, urban park and residential land uses, while the higher of the two values is used as the soil standard for commercial and industrial land uses.

## 7.1.2 CCME (2005)

In the case of CCME (2005), an initial literature search is used to obtain relevant toxicological data, followed by one of the following derivation methodologies (presented in order of their preference):

• Weight of Evidence (EC<sub>25</sub> Distribution) Approach: Assumes a minimum of 10 data points (from three different studies; including minimum of two soil invertebrate and two crop/plant species). EC<sub>20</sub> to EC<sub>30</sub> are acceptable substitutes. Geometric means are calculated for multiple data points for a single species. Data are assembled in a ranking distribution, and the 25<sup>th</sup> and 50<sup>th</sup> percentiles are calculated (i.e., ESSD<sub>25</sub> and ESSD<sub>50</sub> values). The threshold effect concentration (TEC) is equal to the 25<sup>th</sup> percentile of the distribution (ESSD<sub>25</sub>) divided by a safety factor<sup>11</sup> of between 1 and 5. The Effects Concentration Low (ECL) is equal to the 50<sup>th</sup> percentile of the distribution (ESSD<sub>50</sub>) without a safety factor.

<sup>&</sup>lt;sup>11</sup> Safety factor considerations: available amount of data relative to minimum requirements; greater than 50% of data less than 25<sup>th</sup> percentile; short-term toxicity data used; more than 50% of data based on toxicity data from "low bioavailability". A safety factor need not always be applied.

- Weight-of-Evidence (Effects/No Effect Distribution) Approach: Same as above, but using a combined distribution of LOEC and L(E)C<sub>50</sub> data (i.e., applied in instances where the available literature data do not include EC<sub>25</sub> values).
- Lowest Observed Effect Concentration Approach: For compounds with fewer than 10 data points (but still from three different studies, including a minimum of one soil invertebrate and one terrestrial plant species), a species sensitivity distribution is not used; only LOEC values are considered. The TEC is the lowest LOEC divided by a safety factor of between 1 and 5. The ECL is the geometric mean of LOEC values without a safety factor.
- Median Effects Method Approach: Same data requirements as LOEC approach. A species sensitivity distribution is not used; only  $L(E)C_{50}$  data are considered. TEC = Lowest  $L(E)C_{50}$  / safety factor of between 5 and 10. No ECL can be calculated for this method, since the resulting level of protection is considered inadequate.

The TEC is used as the soil quality guideline for residential/parkland and agricultural land uses, while the ECL is used as the soil quality guideline for commercial and industrial land uses. CCME (2005) derivation methods are the same as presented in CCME (2003), with the exception of the calculation of the ECL based on the effects/no effects distribution. CCME (2003) defined the ECL as the 25<sup>th</sup> percentile of the no-effects data only. CCME (2005) defines the ECL as the 50<sup>th</sup> percentile of the combined effects and no-effects data distribution.

#### 7.1.3 USEPA (2003a)

In the case of USEPA (2003a), an initial literature search was conducted and data were selected for consideration following a specific review process. This review involved a two-stage process:

- 1. Literature Exclusion: All papers identified from a literature search were checked against 22 literature exclusion criteria<sup>12</sup>.
- 2. **Study Acceptance:** Non-excluded literature were further checked against 11 study acceptance criteria<sup>13</sup>.

<sup>&</sup>lt;sup>12</sup> Examples of literature exclusion criteria (USEPA, 200a3): study conducted to test biological toxins, drugs, or sewage; study used *in vitro* (e.g., cell lines, tissue cultures) methods; testing involved a mixture of chemicals, or application of a petroleum product; data developed using QSAR or modeled results; data are not from a primary source; test duration not reported. USEPA (2003a) notes that for a total of 24 contaminants, the literature search identified 7,600 papers, which resulted in 5,200 acceptable papers.

Toxicity data were extracted from the resulting acceptable studies. Data values extracted were:  $EC_{20}$ , MATC (i.e. the geometric mean of NOEC and LOEC), or  $EC_{10}$  (presented in order of their preference).  $L(E)_{50}$  data values were not extracted. Extracted data were then scored against the following nine study evaluation criteria:

- 1. Testing was done under conditions of high bioavailability;
- 2. Experimental designs were documented and appropriate;
- 3. Concentration of test substances in soil were reported;
- 4. Control responses were acceptable;
- 5. Chronic or life-cycle tests were used;
- 6. Contaminant dosing procedure was reported and was appropriate;
- 7. A dose-response relationship was reported or can be established from available data;
- 8. Statistical tests used and level of significance were described; and,
- 9. Origin of test organisms was described.

Each of the nine study evaluation criteria received between zero and two points. Only studies that received a score of greater than 10 (of a possible 18) points were used in the derivation. The ECO-SSL value was calculated as the geometric mean of the available data at the highest bioavailability score. A minimum of three data values were required. Separate ECO-SSL values were calculated for plants and soil invertebrates.

#### 7.2 Scientific Issue: Compiling and Screening Literature Toxicity Data

7.2.1 Potential Influence of Scope of Literature Search

We recognize that a policy decision was made to base provincial soil quality standards for the protection of soil invertebrates and plants on existing CCME data compilations. However, this policy decision has implications in terms of the quantity and quality of data used in the derivation process. The existing CSST standards are based only on the

<sup>&</sup>lt;sup>13</sup> Examples of study acceptance criteria (USEPA, 2003a): chemical form and concentration are reported; test medium was a natural or artificial soil; pH reported and within range of 4 - 8.5; organic content reported and less than 10%; study includes at least one control treatment, at least two addition test treatments were included; study reports ecologically relevant endpoints [reproduction; population, growth or plant physiology endpoints]. USEPA (2003a) notes that only 7% of the 5,200 acceptable papers met all 11 study acceptance criteria.

data originally identified and deemed acceptable by CCME. Our experience in assembling toxicity data from the literature for the purpose of deriving environmental quality guideline values suggests that a considerable expenditure of resources is required to ensure a comprehensive literature search.

A comparison of the literature searches conducted to derive Canadian and US soil quality guideline values for lead was conducted to illustrate the potential influence of the scope of the literature search on the number of studies retrieved.

- The Canadian soil quality guideline for the protection of soil invertebrates and plants was based on a compilation completed in 1997 and updated in 1999 (CCME, 1999a). A total of 16 different studies<sup>14</sup> were included (and an additional 7 studies were consulted but not used in the derivation).
- Data used to derive the CSST matrix standard for the protection of soil invertebrates and plants (BCE, undated) was limited to three of the 16 studies compiled by CCME (1999a)<sup>15</sup>. We were unable to match six data values listed in the CSST working files to values listed in the CCME (1999a) compilation.

Conversely, the ECO-SSL value for lead (USEPA, 2003b) retrieved a total of 439 different papers for plants, and an additional 179 papers for soil invertebrates. The literature review process reduced this number substantially: 28 and 13 papers met all study acceptability criteria for plants and soil invertebrates, respectively. This number resulted in 30 and 18 data values (for plants and soil invertebrates, respectively) that had a study acceptability score of greater than 10. Four data values for each taxonomic group had bioavailability scores of 2 (and thus formed the basis of the ECO-SSL). None of the studies used to derive the ECO-SSL values for lead were included in CCME (1999a), despite the fact that they were published prior to the updated compilation reported by CCME (1999a)<sup>16</sup>.

#### 7.2.2 Status of ECO-SSL Literature Searches

ECO-SSL documents prepared by USEPA provide the most comprehensive review of soil toxicity data currently available in the literature, and therefore, are recommended for consideration by CSST in any revision of numerical standards for the protection of soil

<sup>&</sup>lt;sup>14</sup> Allinson and Dzialo (1981), Balba et al. (1991), Bengtsson et al. (1986), Dang et al. (1990), Davis and Barnes (1973), Dixon 1988, Hassett et al. (1976), Khan and Frankland (1983, 1984), Khan and Khan (1983), Ma (1982), Miller et al. (1977), Muramoto et al. (1990), Neuhauser et al. (1985), Spurgeon et al.

<sup>(1994),</sup> plus additional studies listed in Footnote 12.

<sup>&</sup>lt;sup>15</sup> Data used for CSST derivation were limited to the following studies listed in CCME (1999): Seiler and Paganelli (1987) using loblolly pine; Environment Canada (1995) using lettuce and radish, and Environment Canada (1995) using earthworms.

<sup>&</sup>lt;sup>16</sup> Data used for ECO-SSL lead values were Davis and Barnes (1973), Marques Des Santos et al. (1993), Singh and Jeng (1993) and Sandifer and Hopkins (1996; 1997).

invertebrates and plants. The status and scope of the ECO-SSL process is summarized in Table 7.1. Note that in most cases, data are summarized for ECO-SSL marked with insufficient data—the issue for these compounds is that there were insufficient data with an acceptable study evaluation score. Limited toxicity testing using aged natural soils may be required to supplement the existing data—additionally, we note that the costs associated with limited toxicity testing are likely less than the costs associated with reviewing and retrieving the amount of literature typically available. Conducting targeted toxicity testing also provides the greatest control over study design considerations such as those described elsewhere in this chapter.

Compound	Plants	Soil Invertebrates	
Aluminum	Screened as a COPC only	v if soil pH is less than 5.5	
Antimony	Insufficient data Available		
Arsenic	Available	Insufficient data	
Barium	Insufficient data	Available	
Beryllium	Insufficient data	Available	
Cadmium	Available	Available	
Chromium	Insufficient data	Insufficient data	
Cobalt	Available	Insufficient data	
Copper	Pen	ding	
Iron	Not toxic to plants if so	il pH is between 5 and 8	
Lead	Available Available		
Manganese	Pending		
Nickel	Pending		
Selenium	Pending		
Silver	Pen	ding	
Vanadium	Insufficient data	Insufficient data	
Zinc	Pending		
DDT and metabolites	Pending		
Dieldrin	Insufficient data	Insufficient data	
Pentachlorophenol	Available Available		
RDX	Pending		
TNT	Pending		
Total PAHs	Pen	ding	

# **TABLE 7.1:** Status of ECO-SSL Literature ReviewsFor Soil Invertebrates and Plants (June 2005)

#### Recommendations

- 1. Soil standards for the protection of soil invertebrates and plants should be based on the best available (i.e., comprehensive and recent) literature compilations. An assessment of the adequacy of the existing literature compilations used to derive CSST standards relative to: a) recent compilations published by other regulatory agencies; and/or, b) scientific literature published since the date of the original data compilation is recommended. Our experience suggests that additional toxicity data are available in the literature that has not been considered by CSST, although limited additional toxicity testing may still be necessary for some compounds.
- 2. A transparent mechanism for evaluating data quality should be established. The Ministry should review the data evaluation framework presented in USEPA (2003a)—the conservatism inherent in the USEPA (2003a) framework may be screening out studies that are in fact appropriate for use. As a guiding principle, studies that report nominal concentrations only should be rejected. The existing CSST derivation methodology requires clarification regarding the rationale used for excluding data that were otherwise included in CCME.

## 7.3 Scientific Issue: Selecting Appropriate Toxicological Endpoints

The three derivation protocols reviewed (BCE, 1996; CCME, 2005; USEPA, 2003a) differ in the toxicological endpoints included in their respective derivations.

- CCME (2005) notes that toxicity data used for the derivation of soil quality guidelines must be based on "recognized toxicological endpoints (e.g., mortality, reproduction, growth)", however, the preferred derivation methodology itself (as described in Section 7.1.2) is based only on sublethal data (e.g., the EC<sub>25</sub> not the LC<sub>25</sub>). Mortality data (if used) is subject to an extrapolation factor.
- USEPA (2003a) does not permit consideration of mortality in the first generation of test organisms (i.e., the mortality endpoint common in toxicity testing). The survivability of subsequent generations is considered acceptable (USEPA, 2003a). Other endpoints acceptable to USEPA (2003a), but not CCME (2005) include plant physiological endpoints such as CO<sub>2</sub> uptake rates, decrease in chlorophyll content, membrane damage, and detrimental changes in dormancy measures.
- The existing CSST derivation protocol (BCE, 1996) requires explicit consideration of mortality data (without the use of an extrapolation factor), which is inconsistent with CCME (2005).

#### Recommendation

We agree with BCE's (1996) decision to include mortality data in the derivation protocol, and recognize that this reflects a policy decision regarding the desired level of protection for different land uses.

## 7.4 Scientific Issue: Selecting Appropriate Toxicity Statistics

All three derivation protocols (BCE, 1996; CCME, 2005; USEPA, 2003a) have differing guidance regarding the selection of appropriate toxicity data for the derivation process. All three protocols support the use of point-estimate statistics (i.e.,  $EC_x$ ) over hypothesistesting statistics (i.e., NOEC/LOEC), but differ in terms of the mechanism involved in dealing with NOEC/LOEC data.

- CCME (2005) provides alternative derivation methodologies for those compounds where insufficient point-estimate data are available (but sufficient NOEC/LOEC data exist). A mathematical conversion of NOEC/LOEC to an equivalent point estimate statistic is not provided.
- The existing CSST derivation protocol (BCE, 1996) requires that NOEC data are converted to a L(E)<sub>0</sub>, while LOEC data are converted to a L(E)<sub>1</sub>.
- USEPA (2003a) requires that NOEC/LOEC data be converted to the maximum acceptable test concentration (MATC; the geometric mean of the NOEC and LOEC), and provides guidance in terms of which data are preferred for the distribution ( $EC_{20}$  is preferred over MATC is preferred over  $EC_{10}$ ).

The utility of point-estimate data  $(EC_x)$  versus hypothesis-based data (NOEC/LOEC) has been broadly debated in the literature—the general consensus is that the objective is to derive a threshold value that is considered adequately protective (i.e., "no adverse effects" or "an acceptable level of low effects", depending on the underlying regulatory objectives). Criticisms of the use of a NOEC (i.e., the highest test concentration not statistically different from the negative control) include (Hanson and Solomon, 2002):

- NOECs (and, by extension, LOECs) are limited to the concentrations used in the toxicity test, which are often selected for convenience (e.g., based on a log or serial dilution) rather than biological significance.
- NOECs tend to increase as the precision of the study decreases (e.g., a NOEC from a rangefinder study tends to be larger than a NOEC from a definitive study).

The reliance of statistically significant differences on the selection of NOEC and LOEC values means that a NOEC can, depending on the dose response, represent a substantial effect. Isnard et al. (2001) evaluated an aquatic data set<sup>17</sup>, and found that the average effect level at the calculated NOEC and LOEC was 5 and 37%, respectively. Radix et al. (2000) evaluated an aquatic data set<sup>18</sup> and found that NOECs typically fell within the 95% confidence interval of the EC<sub>10</sub> value. However, Fairchild et al. (1997) found that NOECs for pesticide toxicity testing using algal reproduction and growth tests were frequently within the 95% confidence interval of the EC<sub>50</sub> value. In terms of testing with effluents (instead of single chemical compounds), Chapman et al. (1996) found NOEC values obtained by two testing facilities conducting independent oyster, mussel and echinoderm toxicity testing on the same effluent were considerably influenced by relatively minor differences in test concentration selection, as well as the statistical package used in the analyses. In short, a no observed effect concentration is not equivalent to a no effect concentration (van der Hoeven, 1997; Chapman et al., 1996), which is the assumption inherent in converting the NOEC values to an L(E)<sub>0</sub> value.

Although the majority of studies investigating the relationship between hypothesis-based and point-estimate measures utilize aquatic toxicity data, the following terrestrial papers were identified that calculated both  $EC_x$  and NOEC data points:

- Lock et al. (2002) found that 13 of 17 experiments on the effects of lindane on soil invertebrates<sup>19</sup> resulted in NOEC values that were higher than the EC<sub>10</sub> value, but less than the EC<sub>50</sub> value.
- Arrate et al. (2002) found that NOECs for earthworm reproduction<sup>20</sup> were at least twice the  $EC_{10}$  value, and concluded that the  $EC_{10}$  values were a more reliable measurement for risk assessment purposes.

#### Recommendation

The current CSST practice of converting NOEC and LOEC statistics to  $L(E)_0$  and  $L(E)_1$  statistics for derivation purposes should be discontinued. Instead, the underlying dose-

<sup>&</sup>lt;sup>17</sup> Data consisted of: 7 studies from a 72-h algal (*Raphidocelis subcapitata* or *Scenedesmus subspicatus*) growth test; 8 studies from a 21-d cladoceran (*Daphnia magna*) reproduction test; 5 studies from a 7-d cladoceran (*Ceriodaphnia dubia*) reproduction test, and 7 studies from a fish early life stage (*Danio rerio*) development test.

<sup>&</sup>lt;sup>18</sup> Data consisted of: 16 chemicals tested with 72-h algal (*Psuedokirchneriella subcapitata*) growth test; 21d cladoceran (*Daphnia magna*) reproduction test; 48-h rotifer (*Brachionus calyciflorus*) reproduction test, and Microtox.

<sup>&</sup>lt;sup>19</sup> Data consisted of: 3 experiments using a 28-d springtail (*Folsomia candida*) reproduction test; 2 experiments using a 42-d potworm (*Enchytraeus albidus*) reproduction test, and a 21-d earthworm (*Eisenia foetida*) reproduction test

<sup>&</sup>lt;sup>20</sup> Data consisted of 21-d potworm (*Enchrytraeus coronatus*) reproduction toxicity tests using a pesticide degradation product (carbendazim) and potassium dichromate.

response in the original paper should be reviewed in order to determine the appropriate  $L(E)C_x$ . This may require recalculation based on original (measured concentration) data to determine the values for the standardized point-estimate statistics (e.g.,  $EC_{25}$  and  $EC_{50}$ ) and/or determination of the effect size at the NOEC/LOEC test concentrations (e.g., a 33% reduction at the NOEC is equivalent to an  $EC_{33}$ ).

## 7.5 Scientific Issue: Incorporating Bioavailability in the Derivation Protocol

## 7.5.1 Introduction to the Issue

Consideration of contaminant bioavailability is increasingly common in risk assessment and remediation planning, although wide-spread use remains limited by a lack of standardized guidance regarding the level of information that must be included in a bioavailability assessment as well as the scientific validity of different assessment tools and models (Ehlers and Luthy, 2003). Preparation of regulatory guidance is underway, however, as demonstrated by recent publications by the US National Research Council (NRC, 2002), as well as a draft USEPA framework for assessing risks associated with metals which emphasizes consideration of bioavailability (USEPA, 2004). However, the lack of a consistent definition of what constitutes the "bioavailable fraction" creates problems in terms of preparing the necessary regulatory frameworks. The following operational definitions are proposed, based on Semple et al. (2004):

- *Bioavailable fraction*: the fraction of the total contaminant concentrations that is <u>immediately</u> available for uptake by organisms.
- *Bioaccessible fraction*: the fraction of the total contaminant that <u>may</u> be available to an organism. This fraction includes the portion of the total that is currently bioavailable, plus the portions that may become bioavailable over time.

The difference between bioavailable and bioaccessible is illustrated in Figure 7.1; the importance of differentiating bioaccessible versus bioavailable fractions with respect to developing numerical soil standards is that it facilitates an appropriate consideration of what is being measured by the various assessment tools. For example:

- Equilibrium partitioning approaches (see Section 7.5.3) are focused on the bioavailable fraction, but may not adequately address the potential variations in the bioavailable fraction as changes in soil conditions mobilize the bioaccessible fraction.
- Different chemical extractions (see Section 7.5.4 and 7.5.5) may measure different proportions of the bioaccessible fraction, depending on the solvents used.

• Toxicity testing (see Section 7.5.6) using artificial soil samples spiked with contaminants may be measuring the effects associated with the bioavailable fraction, while toxicity testing with natural soil with aged contaminants may be measuring the effects associated with the bioaccessible fraction.

The degree to which contaminant bioavailability is considered has substantial implications on the calculation of numerical soil standards.

#### Recommendation

Semple et al. (2004)'s operational definitions of bioavailable and bioaccessible fractions should be incorporated into future revisions of the CSST derivation protocol.

FIGURE 7.1: Conceptual Model of Bioavailability Versus Bioaccessibilty in Soil (from Semple et al. 2004)



(Used with permission of K. Semple)

#### 7.5.2 Surrogate Methods for Measuring Bioavailability/ Bioaccessibility

The development of surrogate methods to estimate COPC bioavailability in soil has been the subject of considerable research, in part, due to a desire to develop reliable and predictive analytical techniques (i.e., chemical methods) as a substitute for studies using biological test organisms. These surrogate methods can be broadly categorized as: 1) equilibrium partitioning, 2) chemical extraction, and 3) solid-phase extraction. A brief summary of each method as well as recommendations regarding their potential use for deriving provincial soil standards for the protection of soil invertebrates and plants is provided below.

#### 7.5.3 Equilibrium partitioning

Considerable research into the equilibrium partitioning of COPCs between solid and liquid phases of the soil matrix has been conducted (e.g., Sauve et al., 2000; Janssen et al., 1997a). Equilibrium partitioning assumes that the dissolved fraction of the COPC in the interstitial porewater represents the bioavailable fraction that could potentially be taken up by plant roots or soil invertebrates (and thus, cause toxicity). The remaining balance of the COPC concentrations is assumed to be tightly retained by soil solids, and therefore, unavailable for biological uptake<sup>21</sup> (Sauve et al., 2000).

Equilibrium partitioning models rely on  $K_d$  (i.e., the solid-water partition coefficient), which varies according to soil characteristics such as pH, cation exchange capacity, organic carbon content (Janssen et al., 1997a), and in the case of organic compounds, the octanol-water partition coefficient ( $K_{ow}$ ). Numerous models for predicting  $K_d$  exist, ranging from univariate linear regression models (i.e.,  $K_d$  varies according to soil pH) to estimates of the free ion concentration (e.g., similar to biotic ligand models for aquatic toxicology; e.g., Lofts et al., 2004).

These equilibrium partitioning based models have been used to describe:

- Relationships between dissolved porewater concentrations and COPC accumulation for metals in soil invertebrates (e.g., Janssen et al., 1997b) as well as organic compounds in plants (e.g., Dowdy and McKane, 1997; Burken and Schnoor, 1998).
- Relationships between dissolved porewater concentrations and toxicity of metals to soil invertebrates (e.g., van Gestel and Mol, 2003; Smit and van Gestel, 1998), metals to plants (e.g., Weng et al., 2004), and organics to soil invertebrates (e.g., Lock et al., 2002).

<sup>&</sup>lt;sup>21</sup> "Unavailable for biological uptake" as defined by Sauve et al. (2000) consists of both the bioaccessible and non-bioaccessible fractions. Sauve et al. (2000)'s use of equilibrium partitioning means only the bioavailable fraction is being estimated.

Although the conceptual approach of equilibrium partitioning is attractive (and is useful for groundwater modeling purposes), its utility for predicting chronic soil toxicity is limited. Peijnenburg and Jager (2003) noted that equilibrium partitioning as a model for predicting soil toxicity suffered from its inability to account for other relevant exposure pathways—although uptake of many COPCs in soft-bodied organisms is largely influenced by direct contact with the dissolved fraction (e.g., Scott-Fordsmand et al., 2004), the contribution of the dietary fraction is not negligible (e.g., Vijver et al., 2003). Additionally, equilibrium partitioning has not been validated for hard-bodied soil invertebrates, which represent a significant portion of the soil invertebrate community.

Most equilibrium partitioning models focus on a single contaminant or invertebrate/plant species; they consider a relatively small number of factors that control  $K_d$ ; and, in many cases, they are not able to accurately predict the dissolved porewater concentration in field collected soils. Additionally, the assumption that the dissolved porewater concentration is the primary factor governing soil toxicity has not been proven true for all contaminants. Fairbrother (2005) examined the utility of equilibrium partitioning for predicting the toxicity of PAH mixtures in soil and concluded that equilibrium partitioning was inappropriate, except as a means to identify conservative screening levels below which there would likely not be appreciable ecological risk<sup>22</sup>: The following limitations were noted (Fairbrother, 2005):

- Equilibrium assumptions are violated in nearly all soils. Most soils are not saturated, and therefore, equilibrium between soil and interstitial water is rarely (if ever) attained. Equilibrium partitioning in sediments assume an organic content greater than 0.2%. Low organic carbon contents in soil are more frequent than in sediment.
- Weathering and aging occur faster in soil than in sediment. This topic is discussed in greater detail in Section 7.5.9, however, the net effect of aging and weathering on soil COPC bioavailability means that the assumption that COPC bioavailability is governed solely by the sorption of COPCs to particle surfaces (inherent in equilibrium partitioning) is overly simplistic. Microbial degradation also confounds the assumption that equilibrium is achievable.

These limitations do not invalidate the conceptual approach, nor do they suggest that further research into equilibrium partitioning should be discontinued—they simply indicate that the sophistication of the available models is not suitable for predicting contaminant toxicity under field conditions at this time.

<sup>&</sup>lt;sup>22</sup> In other words, equilibrium partitioning only provides an alternate method for generating highly conservative (and therefore less ecologically-relevant) guideline values.

#### Recommendation

Equilibrium partitioning is not recommended as an approach for deriving soil quality standards for the protection of soil invertebrates and plants.

#### 7.5.4 Chemical Extractions

Chemical extractions have been proposed as an alternate measurement of the "bioavailable" fraction—they represent an intermediate measurement between the total concentration in the soil sample as a whole, and soil porewater concentrations described above in the equilibrium partitioning approach (Peijnenburg and Jager, 2003). Numerous extraction techniques have been proposed in the literature<sup>23</sup>; however, they generally fall into one of three categories:

- Non-exhaustive: Chemical solvents are relatively mild, and intended to measure the bioavailable fraction.
- Exhaustive: Chemical solvents are increasingly "stronger" and intended to measure varying degrees of the bioaccessible fraction.
- Sequential: Different solvents applied in sequence (i.e., non-exhaustive to exhaustive) to measure the proportion of a COPC associated with different organic and inorganic ligands in the soil.

COPC concentrations in the extracted soil leachate are used to explore relationships between the supposed "bioavailable" fraction and bioaccumulation/toxicity in soil invertebrates and plants. Different extraction techniques have demonstrated relatively high degrees of concordance with bioaccumulation/toxicity in soil samples, including the following examples from the recent scientific literature:

- Barriuso et al. (2004): extracts using a combination of CaCl<sub>2</sub> and methanol were correlated to the amount of atrazine mineralized by soil bacteria.
- Conder and Lanno (2000), Conder et al. (2001): extracts using 0.1 M Ca(NO<sub>3</sub>)<sub>2</sub> were correlated to acute toxicity to earthworms associated with Cd, Pb and Zn.
- Lock and Janssen (2003a): extracts using 0.1 M Ca(NO<sub>3</sub>)<sub>2</sub> were correlated to toxicity to potworms, red clover and springtails associated with Cu.

<sup>&</sup>lt;sup>23</sup> Nineteen different chemical extractions for assessing the bioavailable fraction of metals in soil were listed in Peijnenburg and Jager (2003). Numerous other chemical extractions were also identified in the literature consulted for this project.

- Dai et al. (2004): extracts using diethylenetriaminepentaacetic acid (DTPA) were correlated to the Zn, Cd, Pb and Cu concentrations in earthworm tissues.
- Dean and Scott (2004): cyclodextrin extracts were correlated to the bioavailability of persistant organic pollutants.
- Liste and Alexander (2002): extracts using n-butanol extraction as a surrogate for PAH bioaccumulation in earthworms. Tang et al. (2002) also found strong correlations for PAH bioaccumulation and two other extraction techniques (ethanol or tetrahydrofuran).

However, there is no consensus regarding the selection of an appropriate subset of extraction techniques for regulatory purposes, nor have the chemical extraction techniques currently described in the literature been adequately validated for a broad range of soil contaminants or species normally considered representative of the larger soil invertebrate/plant communities.

#### Recommendation

Chemical extraction methods are not recommended as an approach for deriving soil quality standards for the protection of soil invertebrates and plants.

#### 7.5.5 Solid-Phase Extraction

Solid phase extraction techniques have been developed as a substitute for using test organisms in bioaccumulation testing—they involve the insertion of fibers or membranes coated with a substance that absorbs the contaminant from the porewater phase. Examples of solid-phase extraction include:

- Conder et al. (2001): ion-exchange membranes coated with DTPA were used as a surrogate for earthworm accumulation of Zn and Pb.
- Van der Wal et al. (2004): fibers coated with polydimethylsiloxane (PDMS) were used as a surrogate for earthworm accumulation of organic compounds.
- Tang et al. (2002): C<sub>18</sub> membrane disks were used as a surrogate for earthworm accumulation of PAHs.

Results from the solid phase extraction techniques described above were mixed, and thus cannot be considered reliable. Tang et al. (2002) found a correlation of 0.77 or higher for four different PAHs, while van der Wal et al. (2004) found that the measured

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concentrations of organic compounds in earthworms were "close to estimated concentrations" in the solid-phase extracts. Conversely, Condor et al. (2001) found that uptake of metals by the solid-phase extraction technique was highly variable, and not well correlated to earthworm toxicity.

#### Recommendation

Solid-phase extraction techniques are not recommended as an approach for deriving soil quality standards for the protection of soil invertebrates and plants.

7.5.6 Differential Bioavailability/Bioaccessibility between Laboratory and Field-Based Toxicity Testing

Reliance on laboratory-based toxicity test data as the basis for developing soil quality guidelines has been criticized in the literature (e.g., Cook and Hendershot, 1996), despite its advantages over chemistry-based estimates of bioavailability, whose failing are described above. These criticisms generally relate to the known differences in contaminant bioavailability/bioaccessibility between laboratory-based toxicity testing and actual adverse effects under field conditions<sup>24</sup>. Differences between laboratory-based and field-based toxicity are divided into the following major topics:

#### Artificial Soil

Artificial soils for acute toxicity testing were introduced as a replacement for toxicity testing using filter paper impregnated with the compound of interest based on criticism that filter paper-based toxicity tests had minimal relevance in terms of the toxicity of a compound in soil (Neuhauser et al, 1986; van Gestel and van Dis, 1988; Fitzpatrick et al., 1996). The use of artificial soil facilitated comparison of the relative toxicity between different compounds (e.g., pesticides and chemical formulations) for regulatory purposes.

Chronic toxicity testing protocols were based on guidance from acute toxicity testing (Van Gestel et al., 1992). Although arguments against the use of artificial soil toxicity testing for risk assessment purposes have been presented in the literature (e.g., Gibbs et al., 1996), artificial soil continues to be used for pesticide testing (e.g., USEPA, 1996); it is advantageous for situations where information regarding the relative toxicity of compounds under standardized test conditions is desired. Artificial soil toxicity testing is also advantageous for developing mathematical relationships between individual soil parameters (e.g., pH, calcium content, organic carbon content) and toxicity—the

<sup>&</sup>lt;sup>24</sup> Acclimation and adaptation of populations to elevated COPC concentrations under field conditions is also a potential factor when extrapolating laboratory toxicity data as indicative of adverse effects under field conditions.

simplicity of the geochemical interactions facilitates model development. However, Lock and Janssen (2001) found that a mathematical model<sup>25</sup> was able to predict chronic zinc toxicity in an artificial soil, but not in contaminated field soils. Amorim et al. (2002) found that the bioavailability and toxicokinetics of lindane in artificial soil and natural soils<sup>26</sup> over the course of a 10-month experiment were substantially different.

Artificial soil does not reflect the natural capacity of soil to reduce contaminant bioavailability (i.e., render a portion of the bioavailable fraction non-bioaccessible). The bioavailability of contaminants in natural soil is a function of both the total contaminant concentration as well as the effects of numerous geochemical processes that cannot be readily simulated using an artificial soil. Consequently, the toxicity of a given concentration in artificial soil is not the same as under field conditions—for example, Fountain and Hopkin (2004) found that zinc toxicity to *F. candida* was greater in artificial soil than in field-collected soils. In general, artificial soil testing tends to demonstrate greater toxicity than natural soils.

We recognize that artificial soil provides a standardized matrix that facilitates comparisons between different contaminants, however, if this level of standardization is desired, we suggest that the Ministry establish specific locations from which appropriate natural soil should be collected. However, we believe that this level of standardization is unnecessary for the purposes of developing soil quality guidelines since it would greatly limit the amount of acceptable toxicity data and would reduce the applicability of the resulting soil guidelines to an unnecessary narrow subset of soil types.

#### Recommendation

Toxicity test data from studies using natural soils are preferred for the purposes of setting soil standards for the protection of soil invertebrates and plants over those using artificial soils.

## Spiked Soil Testing

Artificial soils are often used in conjunction with spiked-soil toxicity testing<sup>27</sup> involving the addition of a single contaminant type via solution. COPCs under field conditions, however, exist as the sum of numerous organic and inorganic ligands, each with varying degrees of bioavailability/bioaccessibility. Davies et al. (2003) conducted earthworm (*Eisenia foetida*) toxicity testing in natural soil samples spiked with various forms of lead

<sup>&</sup>lt;sup>25</sup> The mathematical model was based on pH, cation exchange capacity, and total zinc concentrations.

Toxicity testing was conducted using a 28-d springtail (Folsomia candida) survival and reproduction test.

<sup>&</sup>lt;sup>26</sup> Toxicity testing was conducted using a 28-d springtail (*Folsomia candida*) survival and reproduction test.

<sup>&</sup>lt;sup>27</sup> Examples include a metal salt dissolved in water, or an organic compound dissolved in a solvent.

salts<sup>28</sup>, and found that the toxicity of the lead increased with the solubility of the form of the lead salt used. Interpretation of the toxicity data in the literature (typically reported in terms of total metal concentrations) needs to consider the form of the metal used in the investigation. Similar challenges exist with the assessment of organic compounds in that spiked soil toxicity testing may not adequately evaluate the toxicity of the original compound plus its byproducts.

#### Recommendation

Toxicity data from spiked soil studies are acceptable for derivation purposes, however, the uncertainty associated with using data from a single "type" of contaminant (e.g., metal species) as representative of the toxicity of the compound as a whole should be acknowledged. Side-by-side toxicity testing with soils spiked with different metal species should be encouraged. *Note: The use of aged natural soils for toxicity testing (see below) partially addresses this uncertainty.* 

#### Soil Aging

Toxicity testing conducted with freshly-spiked soil samples does not adequately represent the bioavailability of a soil that has been subjected to weathering and aging processes; newly-added contaminants are more bioavailable than an identical concentration in a aged soil. During aging, molecules of a COPC slowly move into locations within the soil matrix that cannot be accessed by organisms (Alexander, 2000); sorption to organic carbon is also a significant aging mechanism. In effect, aging renders a portion of the bioavailable COPC fraction less bioaccessible. Decreased bioavailability (and thus, toxicity) associated with soil aging has been well-documented in the literature, including the following recent examples:

- Morrison et al. (2000) found the bioavailability of dieldron to the earthworm *Eisenia foetida* were reduced by up to 72% in soils aged for 49 years. The bioavailability of DDT to earthworms was also markedly reduced in soils aged for only 190 days.
- Smit and van Gestel (1998) found that the toxicity of spiked zinc to the collembolan *Folsomia candida* was 5-8 times greater in a natural soil that was freshly spiked versus the same soil that was spiked and then allowed to age for 1.5 years.
- Ahmad et al. (2004) found that the bioavailability of a weakly-sorbed pesticide (1-naphthyl methylcarbamate) to microbes was reduced by 50% in natural soils that had been aged for 12 years.

<sup>&</sup>lt;sup>28</sup> Forms of lead included: Pb(NO<sub>3</sub>)<sub>2</sub>, PbCO<sub>3</sub> and PbS.

However, it is not possible to develop a single "aging factor" that can predict toxicity as a function of time. The magnitude of the aging effect is likely soil- and contaminant-specific. For example, Lock and Janssen (2003b) found that the effect of aging on zinc toxicity increased with soil pH. Sverdrup et al. (2002) found that aging did not significantly reduce the toxicity of pyrene and phenanthrene to the collembolan *Folsomia fimetaria* over 120 days, however, this was thought be the result of a relatively low organic carbon content (1.6%) that reduced the aging effect.

A standardized protocol for appropriate soil aging is not available (USEPA, 2003a). Several studies investigated the effects of aging using a side-by-side comparison of historically contaminated soil and clean soil that was freshly spiked to a similar COPC concentration (Lock and Janssen, 2001), or by repeated testing of soil over time (Amorin et al., 2002; Ahmad et al., 2004). Examples of the aging used for soil toxicity testing from the literature include:

- Kuperman et al. (2004): Freshly-spiked soil was stored in open plastic bags in a greenhouse for three weeks. The soil was rehydrated back to its original mass by the addition of water twice per week.
- Morrison et al. (2000): Freshly-spiked soil was stored in sealed glass jars in the dark at 22°C for 90 days. Samples were rehydrated prior to use.
- Pedersen et al. (2000): Freshly-spiked soil was stored in closed plastic pots at 20°C for up to 12 weeks.
- Alexander (2000): A summary of aging times used in seven different studies ranged from 68 to 365 days.
- Smit and van Gestel (1998): Freshly-spiked soil was placed in uncovered outdoor plots and left undistributed for 1.5 years except for the removal of weeds.

#### Recommendation

Toxicity test data from studies using aged soils should be preferred over those using non-aged soils. We recommend that soil aging for toxicity testing should involve storage in containers that allow air circulation (outdoor storage where aerial deposition of other contaminants can occur is not recommended). Aging should be conducted at ambient room temperatures (either at a constant temperature if stored under controlled conditions or naturally variable if stored in a non-controlled room). Samples should be rehydrated to their original moisture content at least weekly. Large soil volumes (e.g., 4-L or more) should be rehomogenized weekly. Samples should be aged for a minimum of 3 months prior to testing.

#### 7.5.7 How is Bioavailability/Bioaccessibility Addressed in Existing Protocols?

The available derivation protocols differ significantly in terms of the methods used to address the potential uncertainty associated with differential bioavailability/ bioaccessibility between laboratory-based toxicity tests and field conditions.

**CCME (2005):** CCME (2005) allows consideration of bioavailability through use of professional judgment. CCME (2005) states that, ideally, soil contact guidelines should be developed based on data reflective of typical Canadian soils; however, they acknowledge that data are frequently reflective of a limited range of conditions, and often biased towards conditions of relatively high bioavailability. CCME (2005) suggests that data be reviewed in terms of identifying data points based on low bioavailability conditions. Specific "low bioavailability" conditions (CCME, 2005) include: soil organic carbon contents of 6% or greater, or a soil pH outside a range of 5.5 - 7. If more than 50% of the data used for the guideline derivation are considered indicative of "low" bioavailability, the safety factor should be increased to compensate (CCME, 2005).

BCE (1996): Bioavailability is not addressed.

**USEPA (2003a):** USEPA (2003a) provides the following two-stage method for incorporating bioavailability considerations:

- Qualitative bioavailability ratings (e.g., high, medium, low) are assigned to each study based on soil and contaminant properties. Examples of the framework used to assign the bioavailability ratings are provided in Table 7.2.
- Bioavailability scores (e.g., 0, 1, 2) are assigned to each study based on the qualitative bioavailability ratings.<sup>29</sup>

<sup>&</sup>lt;sup>29</sup> A bioavailability score of "2" is assigned if the study was based on natural soil with a qualitative rating of "high" or "very high". A bioavailability score of "1" is assigned if the study was based on natural soil with a qualitative rating of "medium" or a standard artificial soil. A bioavailability score of "0" is assigned if the study was based on natural soil with a qualitative rating of "medium" or a standard artificial soil. A bioavailability score of "0" is assigned if the study was based on natural soil with a qualitative rating of "low" or "very low".

Qualitative Bioavailability of Metal Cations in Natural Soil to Plants	<2% organic matter	2 to <6% organic matter	6 to 10% organic matter	
$4 \le $ Soil pH $\le 5.5$	Very High	High	Medium	
5.5 < Soil pH < 7	High	Medium	Low	
7 ≤ Soil pH ≤ 8.5	Medium	Low	Very Low	

<b>TABLE 7.2:</b>	Examples of Qualitative Bioavailability Ratings Based
	on Soil Properties (From USEPA, 2003A)

Qualitative Bioavailability of Non Ionizing Organic Compounds in Natural Soil		<2% organic matter	2 to <6% organic matter	6 to 10% organic matter
$4 \le $ Soil pH $\le 5.5$	$Log K_{OW} >$ 3.5	High	Medium	Low
	Log K <sub>OW</sub> < 3.5	Very High	High	Medium
5.5 < Soil pH < 7	$Log K_{OW} > 3.5$	Medium	Low	Low
	Log K <sub>OW</sub> < 3.5	High	Medium	Low
$7 \le \text{Soil pH} \le 8.5$	$\frac{\text{Log } K_{\text{OW}} >}{3.5}$	Low	Low	Low
	Log K <sub>OW</sub> < 3.5	Medium	Low	Low

Bioavailability scores are used to sort the data for guideline derivation. ECO-SSLs are calculated using only the minimum amount of data with the highest available bioavailability score<sup>30</sup>. This approach encourages the generation of toxicity data under conditions of natural bioavailability, since all toxicity data with artificial soil would be excluded from consideration if a minimum of three acceptable data values conducted using natural, aged soils were available (as was the case for manganese<sup>31</sup>).

<sup>&</sup>lt;sup>30</sup> For example, if four data values had a bioavailability score of 2, then the ECO-SSL would be calculated on only those data (i.e.,  $\geq$  3 values). If there were only two data values with a bioavailability score of 2, but an additional five data values with a bioavailability score of 1, then the ECO-SSL would be calculated on all seven data values (i.e.,  $\geq$  3 values with a combined bioavailability score of 1 or 2).

<sup>&</sup>lt;sup>31</sup> Kuperman et al. (2004) spiked a natural sandy loam (pH 5.0; organic content 1.5%) with a manganese salt (MnSO<sub>4</sub> x H<sub>2</sub>O), and aged the soil for three weeks using an alternating sequence of wetting and drying cycles.  $EC_{20}$  values were determined for earthworm (*Eisenia foetida*), potworm (*Enchytraeus crypticus*). and collembolan (*Folsomia candida*) reproduction. These were the only data used for the derivation of a manganese ECO-SSL value for the protection of soil invertebrates.

## Recommendation

Numerical soil standards for the protection of soil invertebrates and plants should be based on toxicity data from natural, aged soils, even to the extent of excluding data from artificial soil toxicity testing from the derivation process (provided that sufficient natural soil toxicity data are available). The minimum data threshold (3 studies) set by USEPA (2003a) should, ideally, be exceeded, as its adequacy is uncertain.

## 7.6 Scientific Issue: Use of Species Sensitivity Distributions versus Lowest Toxicity Value Divided by an Uncertainty Factor

7.6.1 Introduction to the Issue

Derivation methods for establishing numerical environmental quality guidelines based on laboratory-based toxicity tests tend to utilize one of the following general approaches:

- Single Toxicity Data Value (and Uncertainty Factor) The use of laboratorybased toxicity data to set protective environmental quality guideline values often involves the selection of a single data value, followed by the application of an uncertainty factor. The lowest available data value is typically selected (i.e., the lowest NOEC, NOEC, or L(E)C<sub>50</sub>), and one or more of the following uncertainty factors are applied: intra-to-interspecies, acute-to-chronic, NOEC-to-LOEC, laboratory-to-field. A default value of 10 is typically applied for each area of uncertainty, resulting in an overall safety factor ranging from 10 to 10,000. Safety factors are frequently misapplied—their original purpose was to compensate for sparse data sets, not to facilitate an extreme application of the Precautionary Principle that requires the use of an infinitely large (and thus overprotective) safety factor (Chapman et al., 1998).
- Species Sensitivity Distributions (SSDs) SSDs provide a method for developing environmental quality guidelines that emphasize protection at the community level rather than traditional methods that emphasize protection of individual species (Posthuma et al., 2002). The basic premise of a SSD is that a "safe" concentration for the community at large can be extrapolated based on the distribution of toxicity data for the individual species that make up the community. In this respect, SSDs are fundamentally different from the common practice of dividing the lowest toxicity data point by a safety factor—the SSD relies on the entire data distribution, not just the lowest data value. The common practice and terminology refers to the "safe" concentration as the HC<sub>5</sub>, defined as the concentration that protects 95% of the species (Posthuma et al., 2002). Other HC<sub>x</sub> values can be calculated that reflect varying degrees of protection. SSDs are increasingly used to derive environmental quality guidelines for aquatic compounds, either at a national level (e.g., USEPA and EU water quality guidelines), or for ecological risk assessment purposes (e.g., tributyltin in Cheasapeake Bay: Hall et al., 2000).

#### 7.6.2 Derivation Methods Currently in Use

There are substantial differences in the preferred derivation methods for each of the protocols reviewed:

- CCME (2005) derives soil quality guideline values for different land uses based on the 25<sup>th</sup> and 50<sup>th</sup> percentile from a single distribution (consisting of sublethal EC<sub>25</sub> data)<sup>32</sup>. Mortality data are not included in the distribution.
- USEPA (2003a) derives a single ECO-SSL value for all land uses based on a geometric mean of a subset (based on bioavailability) of the available  $EC_{20}$ , MATC, and  $EC_{10}$  data. Mortality data are not included in the distribution.
- The existing CSST protocol (BCE, 1996) derives soil standards for different land uses using a distribution of median values (based on a set of standardized endpoints). A regression line is used to identify the 20<sup>th</sup> percentile of the mortality data distribution, and the 50<sup>th</sup> percentile of the sublethal data distribution.

**CCME (2005)** — Two of the four CCME derivation methodologies reflect an SSD approach. For example, the weight-of-evidence (effects/no effect distribution) approach (described in Section 7.1.2) was the preferred method in previous versions of the CCME derivation methodology (CCME, 1996) and is still available in the current protocol (CCME, 2005). This method relies on a ranking of the available toxicity (LOEC and  $L(E)_{50}$ ) data, followed by interpolation (or extrapolation) of the 25<sup>th</sup> percentile (i.e., an HC<sub>25</sub>) and application of a safety factor. This approach differs from a classic SSD methodology in two respects: a) multiple types of data values are combined into a single distribution, and b) a safety factor is applied to the "HC<sub>25</sub>".

The recent update to the Canadian derivation protocol (CCME, 2005) provides another methodology that utilizes a SSD approach. The weight-of-evidence (EC<sub>25</sub> distribution) approach (described in Section 7.1.2) requires compilation of a single type of data (i.e., EC<sub>25</sub>), and interpolation of the 25<sup>th</sup> and 50<sup>th</sup> percentiles (i.e., HC<sub>25</sub> and HC<sub>50</sub>). This approach differs from a typical SSD procedure only in the respect that CCME (2005) still requires consideration of a safety factor to derive a soil quality guideline value<sup>33</sup>, rather than incorporating statistical considerations of the uncertainty in the data set (e.g., use the lower 95% confidence interval of the "HC<sub>25</sub>" rather than apply a safety factor).

<sup>&</sup>lt;sup>32</sup> Weight-of-evidence (EC<sub>25</sub> distribution) approach.

<sup>&</sup>lt;sup>33</sup> Note that CCME (2005) states that: a) an uncertainty factor of between 1 and 5 <u>can</u> be applied to the ESSD<sub>25</sub> (i.e., the HC<sub>25</sub>) based on examination of the data used in the distribution; and b) "an uncertainty factor need not always be applied". Uncertainty factors are not normally applied to the ESSD<sub>50</sub> (i.e., the HC<sub>50</sub>).

Widespread use of SSDs is limited by the availability of sufficient toxicity data to meet the minimum data requirements. CCME (2005) uses a linear regression model (the most commonly-applied model), and requires a minimum data set consisting of ten data points from three different studies. Recommendations regarding the minimum number of data points needed to generate a relatively stable SSD (for aquatic contaminants) vary widely (e.g., from 10 to 15 by Wheeler et al., 2002; from 15 to 55 by Newman et al., 2000). No papers were identified that examined the minimum data points needed to generate a stable SSD for soil contaminants.

Additionally, consensus on appropriate mathematical models (e.g., linear regression versus other types of statistical models) has not yet been achieved in the literature, and likely, will require consideration on a compound-by-compound basis.

**USEPA (2003a)** — The ECO-SSL approach does not utilize an SSD approach; instead, it adopts a modified "selected toxicity data" approach where the application of uncertainty factors is replaced by calculating a geometric mean of the selected toxicity data. Emphasis is placed on the selection of high-quality data with relatively protective toxicological endpoints. The laboratory-to-field extrapolation is partially addressed through the consideration of bioavailability under field conditions.

**Existing CSST Derivation Method (BCE, 1996)** — The existing CSST practice (BCE, 1996) contains several elements that are inconsistent with an SSD approach:

- Calculating a median value for each standardized point estimate statistic based on multiple species. SSDs are typically based on the distribution of the same point estimate statistic for multiple species. Calculating a geometric mean for a single species (or genus) is commonly used so that multiple studies using the same test organism do not overly bias the species distribution; however, calculation of a single median value based on a combination of plant and invertebrate data is not appropriate.
- Calculating a soil standard based on a distribution of the median values for multiple standardized point estimate statistics on the same graph. This approach results in a form of pseudo-replication in that the EC<sub>10</sub>, EC<sub>25</sub>, and EC<sub>50</sub> values from a single study are counted towards three distinct data points for the distribution of median values.

In effect, the existing CSST approach eliminates the underlying rationale of the species sensitivity distribution in that the distributions no longer represent the response of multiple species to a given contaminant. The potential bias that this approach introduces cannot be determined (i.e., are the standards over or under-protective), since the calculation of a median value eliminates consideration distribution of species- and contaminant-specific sensitivities that would normally be expected in a natural ecosystem.
We agree, however, with the CSST decision to develop separate distributions for lethal and non-lethal data. The use of two separate distributions for lethal and non-lethal data provides a broader range of potential protection goals than CCME (2005), which is based on a single distribution of only  $EC_{25}$  data. This methodology (i.e., weight-of-evidence:  $EC_{25}$  distribution) cannot generate a similar range of differing levels of protection, and as a result, CCME (2005) is limited to the following narrative explanation of its protection goals:

- 1. Agricultural, residential and parklands are allowed to have 25% of their species demonstrate a 25% reduction in the performance of sublethal endpoints (or less, if a safety factor is applied).
- 2. Commercial and industrial lands are allowed to have 50% of their species demonstrate a 25% reduction in the performance of sublethal endpoints.

The existing CSST protocol allows a broader range of available protection goals by virtue of consideration of mortality data using a separate distribution. The selection of specific protection goals to reflect differing land uses is a policy-based decision and, therefore, is not considered within this scientific review.

# Recommendation

CSST soil standards for the protection of soil invertebrates and plants should be based on a species sensitivity distribution approach wherever possible. Alternate methods for guideline derivation are available if data are insufficient. <u>Separate</u> distributions for mortality (e.g.,  $LC_{50}$  or  $LC_{25}$ ) and sublethal ( $EC_{50}$  or  $EC_{25}$ ) data should be derived, instead of a single distribution consisting of only  $EC_{25}$  data. This approach reflects the existing differences between existing Ministry and CCME policy.

# 7.6.3 Using Separate or Combined Distributions for Plants and Invertebrates

CCME (2005) and the existing CSST derivation methods often (but not always) result in the derivation of a single guideline/standard to protect both soil invertebrates and plants<sup>34</sup>. USEPA (2003a) requires separate screening values for soil invertebrates and plants.

<sup>&</sup>lt;sup>34</sup> CCME (2005) indicates that separate distributions should be used if the data are sufficient.

# Recommendation

Separate numerical standards for soil invertebrates and plants should be derived for those contaminants that have sufficient and appropriate toxicity data. Combination of soil invertebrate and plant data on a single sensitivity distribution is acceptable.

# 7.7 Summary of Proposed Derivation Methodology

# Recommendations

- 1. The following derivation methodology is proposed, based on the scientific review described above and ensuing recommendations:
- 2. Assemble a toxicity data set where each toxicity data value has been screened, and assigned an appropriate bioavailability rating. The data review and bioavailability protocols established by USEPA (2003a) are recommended for consideration by BCWLAP. A policy decision regarding minimum data review scores is required (i.e., the requirement specified in USEPA 2003a may be overly conservative).
- 3. Data sets recently prepared and/or updated by USEPA, CCME, or other jurisdictions should be reviewed to determine if the data sets can be adopted for use by CSST. Supplemental literature searches should be conducted for those compounds not already recently reviewed by other jurisdictions. Regardless, additional toxicity testing may be required.
- 4. Select the appropriate test statistic for use in a species sensitivity distribution, based on the desired level of protection. We agree with the current BCWLAP approach of compiling both  $LC_{20}$  and  $EC_{50}$  test statistics, but recommend that a range of acceptable test statistics be established for each SSD in order to maximize the amount of data available. For example, the  $EC_x$  SSD may include test statistics ranging from  $EC_{25}$  to  $EC_{50}$ , while the  $LC_x$  SSD may include test statistics ranging from  $LC_{10}$  to  $LC_{25}$ .
- 5. Determine if sufficient toxicity data exist to allow calculation of a SSD based on testing with natural, aged soils. Determine if sufficient data exist to allow separate SSDs for plants and soil invertebrates. We agree with CCME (2005) that a minimum of 10 data values are desired for the SSD approach: under the proposed derivation method, this will translate into a minimum of 10 EC<sub>x</sub> values and 10 LC<sub>x</sub> values required per analyte.

- 6. Toxicity data from testing with artificial soil should only be included if data from natural aged soils are insufficient to meet the minimum data requirements above. Data from soil invertebrates and plants should be combined on the same distribution only if there are insufficient data to allow separate distributions.
- 7. Select the appropriate " $HC_x$ " value to be derived for each SSD, based on the desired level of protection. Based on existing policy, this would consist of an  $HC_{20}$  from the mortality ( $LC_x$ ) data distribution, and an  $HC_{50}$  from the sublethal ( $EC_x$ ) data distribution. Differing levels of protection to reflect the increased range of proposed land uses may be appropriate.
- 8. Determine if application of a safety factor is necessary, and if so, what is reasonable (i.e., don't simply use a default value of 10). Safety factors are likely unnecessary except under exceptional circumstances.
- 9. If data are insufficient to support a SSD approach, other derivation methods as described by CCME are appropriate for developing interim soil quality standards. These interim standards should be reviewed every five years to determine if sufficient data are available for the SSD approach.
- The preferred order of these alternate CCME-based methods are the same as described in CCME: Weight-of-Evidence (Effects/No Effect Distribution) Approach, Lowest Observed Effect Concentration Approach, and Median Effects Method Approach.
- 11. These alternate CCME methods should be modified as follows: a) separate analyses of lethal and non-lethal data should be conducted, b) data from natural, aged soil should be preferred over non-aged or artificial soil, and c) unnecessary safety factors should not be incorporated. The data evaluation used for this alternate CCME-based methods should be the same as for the proposed SSD approach as described above.

# 8.0 ENVIRONMENTAL PROTECTION: TOXICITY TO SMALL MAMMALS AND BIRDS

Soil standards for the protection of small mammals and birds are desirable for assessing contaminated sites, despite the fact that equivalent approaches are not currently incorporated into the federal guidance (CCME, 2005). We disagree with the following CCME (2005) assumptions that:

- The level of protection offered to soil-dependent organisms from direct contact exposures is adequate to protect wildlife from dermal and ingestion exposures. We are not aware of any data to support this assumption.
- Information on the effects of wildlife exposure to soil contaminants is severely lacking. In fact, a considerable body of literature exists regarding this potential exposure pathway.

Developing soil standards for the protection of small mammals and birds would accomplish the following objectives:

- They would provide a basis for screening potential risks to a broader selection of terrestrial receptors than currently available. At present, the decision to conduct an ERA at a contaminated site is largely driven by potential toxicity to soil invertebrates and plants. Potential adverse effects on small mammals and birds associated with ingestion of dietary items and soil are not considered<sup>35</sup>.
- Soil standards for the protection of small mammals and birds would increase the consistency in terms of screening sites for potential risks to wildlife.

However, the context for the application of soil standards for the protection of small mammals and birds needs to be fully considered. We envision that soil standards for the protection of small mammals and birds would act only as a conservative screening tool applied to only land uses that have the physical habitat necessary to support small mammal and bird populations<sup>36</sup>. The intended purpose of the standards is to identify those sites where risks to small mammals and birds are clearly negligible, and therefore, would not require further assessment.

<sup>&</sup>lt;sup>35</sup> Incidental soil ingestion rates for small mammals and birds vary considerably depending on feeding behaviour; however, Beyer et al. (1994) estimated that near 0 to 30% of an organism's diet consisted of soil (depending on the species).

<sup>&</sup>lt;sup>36</sup> Soil standards for the protection of small mammals and birds are only envisioned for the Wildlands and Agricultural land use (and potentially, the Urban Park land use). The remaining land uses are unlikely to contain sufficient habitat to support populations, and therefore, the soil standard would have minimal ecological relevance (Tannenbaum, 2005).

The proposed methodology is not intended to generate quantitative risk estimates for those sites where the potential for adverse effects cannot be excluded; numerical soil standards are not intended as a replacement for a properly designed ecological risk assessment<sup>37</sup>.

### Recommendation

CSST should develop soil standards for the protection of small mammals and birds for selected land uses. The Ministry should decide which land uses will have a small mammal and bird exposure pathway—we envision that these soil standards would only apply to Wildlands and Agricultural land uses (and potentially, Urban Park and Residential). Standards for the protection of small mammals and birds should not be applied to Commercial, High Density Urban Residential or Industrial land uses.

# 8.1 Review of Selected Derivation Protocol (USEPA, 2003a)

At present, soil standards and/or guideline values for the protection of small mammals and birds are not available at the provincial (BCE, 1996) or federal (CCME, 2005) level. USEPA (2003a) provides a framework for calculating soil standards for the protection of small mammals and birds. ECO-SSLs are derived for the following receptor groups (representative species in brackets):

- Mammalian herbivore (meadow vole);
- Mammalian ground insectivore (short-tailed shrew);
- Mammalian carnivore (long-tailed weasel);
- Avian granivore (mourning dove);
- Avian insectivore (American woodcock); and,
- Avian carnivore (red-tailed hawk).

For each receptor, an appropriate toxicity reference value (in terms of mg contaminant per kg body weight per day; mg/kg/day) is derived from the available scientific literature. The literature review consists of initial study retrieval, followed by a literature exclusion and study acceptance review<sup>38</sup>. Each data value that passes the literature exclusion and

<sup>&</sup>lt;sup>37</sup> Further discussion of the intended role of numerical soil standards for the protection of small mammals and birds relative to the ecological risk assessment process is provided in Section 8.7.

<sup>&</sup>lt;sup>38</sup> Literature exclusion and study acceptance reviews were similar to the process described for ECO-SSL soil invertebrate and plant screening levels (Section 7.1.3).

study acceptance reviews is scored (on a scale of 0 to 10) for each of the following ten study evaluation criteria:

- 1. Data source: Data from non-primary sources were excluded.
- 2. **Dose route:** Dietary exposures were scored higher than gavage or capsule exposures. Non-oral studies (e.g., injection) were excluded.
- 3. Test substance concentrations: Measured concentrations were scored higher than nominal concentrations.
- 4. **Contaminant form:** Contaminant forms similar to those encountered in soil were scored higher than those with dissimilar contaminant forms.
- 5. **Dose quantification:** Exposures reported in terms of dose (e.g., mg/day) were scored higher than those reported in terms of concentration (e.g., mg/kg).
- 6. **Endpoints:** Reproductive endpoints were scored higher than lethality or growth, while other endpoints (e.g., biochemical, behavioural) were scored lower.
- 7. **Dose range:** Studies with both NOEAL and LOEAL values were scored higher than studies reporting only one value.
- 8. Statistical power: The power associated with the NOEAL was scored.
- 9. **Exposure duration:** Multiple generation and critical life stages were scored higher than chronic, subchronic or acute studies.
- 10. **Test conditions:** Studies reporting standard exposure conditions were scored higher than studies that report non-standard exposure conditions (or that did not report exposure conditions).

Data values that receive a total score of 65 or less are excluded from TRV derivation. The remaining data values are sorted according to toxicological endpoint—the selected TRV is based on the available reproduction and growth NOAEL values. Avian and mammalian toxicity data are plotted separately. The distribution of the NOAEL-based data for the remaining toxicological endpoints (e.g., behavioural, biochemical), as well as the LOAEL-based data for all endpoints is used to select the specific method used to calculated the TRV. This procedure is illustrated in the flowchart provided in Figure 7.2.

A food chain model is then used for each receptor in order to predict the ingested dose from the following exposure pathways:

#### **Golder Associates**

- Incidental soil ingestion (e.g., through grooming, foraging, etc).
- Consumption of dietary items (e.g., tissue concentrations predicted from soil concentrations using bioaccumulation factors or regression models from the literature).

The soil concentration that would result in a daily ingested dose equal to the wildlife TRV (i.e., resulting in a hazard quotient of 1) is backcalculated and used as the ECO-SSL value for the receptor group. USEPA (2003a) includes the following guidance regarding the appropriate application of the ECO-SSL values which would be equally applicable to any CSST soil standards derived using a similar methodology:

"It is emphasized that the Eco-SSLs are soil screening numbers, and as such are not appropriate for use as cleanup levels. Screening ecotoxicity values are derived to avoid underestimating risk. Requiring a cleanup based solely on Eco-SSL values would not be technically defensible."





### 8.2 Scientific Issue: Compiling and Selecting Appropriate Toxicity Data

The USEPA (2003a) derivation method relies on a data set compiled through a comprehensive search of the available scientific literature, as well as a rigorous evaluation process. Although the USEPA (2003a) approach represents a considerable investment of resources, the magnitude of the literature search, combined with the transparency of the data review process, provides confidence in the resulting TRV. The utility of the TRV is also enhanced by the fact that all available data (with a data evaluation score greater than 65) are used in the derivation process. Growth and reproduction data are used as the basis of the TRV, while data from other endpoints are used to select the specific means of calculating the TRV, as well as to provide necessary context. The current scope of the ECO-SSL process includes 17 metals and 5 organic compounds<sup>39</sup>, including a substantial number of contaminants that currently have matrix-based soil standards in British Columbia.

One potential limitation with respect to the available mammalian and avian toxicity data is the reliance on NOAEL and LOEAL-based reporting (see Section 7.4 for general discussion on the limitations of this approach). However, emphasizing point-estimate based TRVs (e.g.,  $EC_{20}$ ) for avian and mammalian toxicity data is unlikely to be practical. The majority of studies are limited in terms of the number of test concentrations and replicates available (i.e., chronic, long-term mammalian studies are costly to run), and therefore, data are typically insufficient to accurately estimate point-estimate values for the desired lower percentiles.

<sup>&</sup>lt;sup>39</sup> Metals (the term "metals" used to include metalloids such as As and Se) include: Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Fe, Mn, Pb, Ni, Se, Ag, V, and Zn. Organics include: DDT and metabolites, dieldrin, pentachlorophenol, RDX, TNT and total PAHs.

# Recommendation

Soil standards for the protection of small mammals and birds should be based on literature searches with a level of effort and data evaluation process consistent with that described in USEPA (2003a). Data sets for many contaminants that may require matrix standards for protection of small mammals and birds are already being prepared by the USEPA.

Point-estimate test statistics (e.g.,  $EC_{20}$ ) are preferred over NOAEL and LOAELs; however, they are not generally available in the mammalian and avian toxicological literature. Instead, the no-observed adverse effect level (NOAEL) is the appropriate test statistic for calculating highly conservative soil standards for the protection of individual small mammals and birds. The lowest-observed adverse effect level (LOAEL) is the appropriate test statistic to protect populations of small mammals and birds. A Ministry decision regarding the desired level of protection is required.

The decision flowchart regarding the specific method for calculating the wildlife TRVs (see Figure 7.2) is recommended for use with either NOAEL or LOAEL data (suitably modified).

# 8.3 Scientific Issue: Selecting Appropriate Receptors of Concern

The selection of receptor groups (and representative surrogate species) by USEPA (2003a) incorporated the following considerations:

- Generalist species (e.g., species with variable diets such as raccoons, crows) were excluded from consideration. Aerial insectivores and piscivores were excluded because their dietary composition lacked a direct connection to terrestrial habitats.
- Surrogate species were generally smaller in size than other species in the receptor group in order to maximize food consumption rates (i.e., smaller organisms have higher metabolic rates and therefore consume more food on a body weight basis). These surrogate species were assumed to be protective of larger species within the same receptor group.

The guiding principles listed above are reasonable and appropriate for deriving soil standards for the protection of small mammals and birds in British Columbia; however, the following additional principles are also recommended:

• Surrogate species should be native to British Columbia, and preferably, resident on a year-round basis. The surrogate species for mammalian ground insectivores (short-

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tailed shrew), mammalian ground herbivore (meadow vole), and avian granivore (mourning dove) are appropriate in this respect. However, the range of the avian insectivore surrogate species (American woodcock) is limited to the eastern United States and Canada (Alsop, 2001) and, therefore, a different surrogate species should be selected.

• Receptor groups should be limited to those groups that consume food items with a direct exposure pathway to soil (e.g., soil invertebrates and plants). Inclusion of higher trophic level receptor groups (e.g., carnivores) is not recommended since the calculations requires an additional level of assumptions (and thus uncertainty) regarding COPC bioaccumulation. Additionally, draft provincial screening-level ERA guidance requires a detailed ERA and/or site remediation if biomagnifying compounds are present (SAB, 2004), and therefore, soil standards would be inappropriate for those compounds.

# Recommendations

The following receptor groups (and surrogate species) from the existing USEPA (2003a) guidance may be applicable to British Columbia: mammalian ground insectivores (short-tailed shrew); mammalian ground herbivore (meadow vole); and avian granivore (mourning dove). A different surrogate species for the avian insectivore receptor group is required. Potential candidates include black-billed magpie (*Pica hudsonia*) or ruffed grouse (*Bonasa umbellus*) based on dietary preferences (i.e., soil invertebrates) and habitat range that includes British Columbia. We recommend that the Ministry provide guidance on specific receptors to be included in the soil guideline backcalculation based on the guiding principles described above. Further discussion regarding the selection of specific receptors is required. Soil standards for the protection of small mammals and birds are not recommended for biomagnifying compounds<sup>40</sup> or higher trophic levels (e.g., carnivores).

# 8.4 Scientific Issue: Receptor Parameterization

Selection of receptor parameters by USEPA (2003a) incorporated the following conservative assumptions:

• Surrogate species were assumed to reside and forage exclusively at the contaminated site, and therefore, habitat range was not incorporated.

<sup>&</sup>lt;sup>40</sup> This proposed exclusion includes biomagnifying compounds under consideration for ECO-SSL values, including DDT and organo-Se. The proposed risk assessment guidance (SAB, 2004) explicitly requires assessment of biomagnifying compounds through an ecological risk assessment process.

- The bioavailability of the contaminant in soil and dietary items was assumed to be comparable to the bioavailability of the compound in the laboratory studies used to set the TRV<sup>41</sup>.
- The diet of the surrogate species was simplified to a single food type (e.g., the avian insectivore was assumed to have a diet of 100% soil invertebrates).
- Estimates for other receptor parameters (e.g., body weight, food ingestion rates, soil ingestion rate) were based on conservative estimates (e.g., 90<sup>th</sup> percentile).

### Recommendation

The USEPA (2003a) assumptions for selecting receptor parameters are appropriate for use in deriving CSST soil standards for the protection of small mammals and birds, however, the Ministry should review receptor parameters with respect to the desired level of conservatism and level of protection. For example, the use of 90<sup>th</sup> percentile parameters is considered to be highly conservative, while the use of median parameters is considered to be moderately conservative.

# 8.5 Scientific Issue: Allometric Scaling

Allometric scaling refers to the process of estimating a value for a physiological parameter for a given species, based on the mathematical relationship between that parameter and a measure of body size determined for similar species. In wildlife toxicology, allometric scaling is used to estimate the following types of physiological parameters based on body weight:

- Food ingestion rates; and,
- Toxicity reference values.

Allometric scaling relies on an underlying relationship between body weight and metabolic rate: smaller organisms have higher metabolic rates as a function of body weight. Toxicokinetic variables linked to metabolic rate (e.g., blood flow, renal clearance, respiration rate; metabolic half-life) also share an allometric relationship (Bachmann et al., 1996; Kirman et al., 2003; Savage et al., 2004). The relationship between field metabolic rate and body weight has been well-documented, and is consistently found to approximate a value of <sup>3</sup>/<sub>4</sub> (Nagy et al., 1999; Savage et al., 2004).

<sup>&</sup>lt;sup>41</sup> Bioavailability of a compound in the laboratory studies used to set the TRV is maximized, since the dose under laboratory conditions is typically delivered via drinking water (e.g., metal salts dissolved in water), or food (e.g., an organic compound mixed with moist food using a carrier solvent).

Other authors have argued that the scaling factor is closer to  $\frac{2}{3}$  (e.g., Dodds et al., 2001), however, these relationships were based on basal metabolic rates and earlier assumptions that metabolism was a function of surface area instead of body weight (Savage et al., 2004).

### 8.5.1 Food Ingestion Rates

Allometric scaling is used to predict wildlife food ingestion rates based on a species' body weight. Standardized formulae for food ingestion rates (FIR) are available for different taxonomic groups (USEPA, 1993), including:

- All mammals: FIR  $(g/day) = 0.235 \text{ BW}^{0.822}(g);$
- Rodents: FIR (g/day) = 0.621 BW <sup>0.564</sup> (g);
- All birds: FIR (g/day) = 0.648 BW <sup>0.651</sup> (g); and,
- Passerine birds: FIR  $(g/day) = 0.398 \text{ BW}^{0.850}(g)$ .

These food ingestion rates are calculated from the allometric relationship between body weight (BW) and field metabolic rates, and estimates of the metabolizable energy of various dietary items (e.g., in calories per gram of food) (from Nagy, 1987) needed to maintain field metabolic rates. The use of the allometric scaling models described above provides a "very rough estimate of food ingestion rates for any given species" (USEPA, 1993). USEPA (2003a) converted the models presented by Nagy (1987; updated with data provided by Nagy et al., 1999) to a form suitable for Monte Carlo probabilistic modeling, and generated a distribution of FIR values for each receptor species based on the distribution of species-specific body weight data from the literature. The 90<sup>th</sup> percentile of the range of estimated FIR values was then used in the ECO-SSL calculation.

# Recommendation

Allometric scaling based on a probabilistic distribution of a receptor's body weight is an appropriate method for generating conservative estimates of food ingestion rates for wildlife receptors. A Ministry decision regarding the desired level of protection in this soil standards is required to decide between 90<sup>th</sup> percentile (highly conservative) and median (moderately conservative) body weight values.

A detailed literature review for species-specific information on food ingestion rates should also be conducted for each receptor as a backcheck to the allometric scaling approach.

# 8.5.2 Toxicity Reference Values

Allometric scaling is used to extrapolate a "safe" dose ( $R_fD$ ) for humans based on toxicological investigations involving non-human mammalian species (e.g., rats, mice, rabbits, dogs); allometric scaling for wildlife toxicity reference values (TRVs) between non-human mammalian species follows an identical approach.

The <sup>3</sup>/<sub>4</sub> scaling factor has been previously shown to adequately explains the variation in acute mammalian toxicity data sets (i.e., an empirical test of the utility of the allometric scaling approach) (e.g., Goddard and Krewski, 1992; Travis and White, 1988) and has since been adopted by USEPA (1999) for human health assessment, as well as wildlife toxicology (Sample et al., 1996). Sample et al. (1996) converted toxicity reference values (TRVs; expressed in terms of mg COPC/kg body weight/day) using the formula below and a scaling factor (i.e., "b") of <sup>3</sup>/<sub>4</sub> :

$$LOAEL_{W} = LOAEL_{T} \left(\frac{bw_{T}}{bw_{W}}\right)^{1-b}$$

There are limited and contradictory data regarding the selection of an appropriate scaling factor for avian species. Nagy et al. (1999) calculated a scaling factor of 0.681 based on an analysis of field metabolic rates for 95 bird species, suggesting that an allometric scaling factor for avian toxicity data would in fact be appropriate. However, a single scaling factor for all birds may not be appropriate, given the likely differences in energy requirements for various avian species (e.g., passerine versus non-passerine). Additionally, an empirical examination of acute avian toxicity data (pesticides) failed to support the use of the <sup>3</sup>/<sub>4</sub> or <sup>2</sup>/<sub>3</sub> scaling factors used for mammalian toxicity data; in fact, a scaling factors were used for avian TRVs (Sample et al., 1996). Different approaches to allometric scaling of TRVs in guidance documents have been adopted:

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- USEPA (2003a) does not use any scaling factors in deriving ECO-SSL values for the protection of small mammals and birds. A detailed rationale is not provided.
- USEPA Region 9/US Navy TRVs for screening-level wildlife ERA suggest that allometric scaling occur only if the difference in the body weight between the laboratory and wildlife species is greater than 2 orders of magnitude (DTSC, 2000).
- Sample et al. (1996) used a scaling factor of <sup>3</sup>/<sub>4</sub> for mammals, and 1 for birds in screening-level ERA wildlife TRVs. These TRVs have been used to backcalculate preliminary soil remediation goals for Superfund sites (Efroymson et al., 1997).

Reexamination of the ability of default scaling factors (e.g., 1, 0.75 and 0.66) to explain variations in acute toxicity data (Sample and Arenal, 1999) suggests that default scaling factors may not be appropriate in all instances. Sample and Arenal (1999) calculated a mean scaling factor of  $0.94 \pm 0.03$  (range: -0.15 to 1.69) for mammalian species based on a broader variety of compounds than previously examined. A mean scaling factor of 1.19  $\pm$  0.05 (range: 1.16 to 3.09) was determined for avian species, which was consistent with the 1.2 scaling factor proposed by Mineau et al. (1996). However, the majority of compound-specific scaling factors were not statistically different than any of the existing default scaling factors (0.66, 0.75 or 1). Sample and Arenal (1999) concluded that the default scaling factors were appropriate for drug compounds (e.g., the data originally used to evaluate rodent-to-human scaling factors), but might not be applicable for all classes of compounds. Conversely, Kirman et al. (2003) used physiologically-based pharmacokinetic (PBPK) modeling, and demonstrated that the <sup>3</sup>/<sub>4</sub> scaling factor was applicable over a broad range of compounds other than drugs<sup>42</sup>.

# Recommendation

Allometric scaling should not be used to extrapolate wildlife TRVs for the purposes of backcalculating conservative screening soil standards for the protection of small mammals and birds, due to the uncertainty in selecting an appropriate default scaling factor. However, allometric scaling may still be appropriate for detailed ERAs (where the uncertainty with respect to the resulting risk estimate can be discussed in detail).

<sup>&</sup>lt;sup>42</sup> Compounds tested by PBPK modeling by Kirnan et al. (2003) included benzene, carbon tetrachloride, chloroform, ethanol, ethylene oxide, methylene chloride, methylmercury, tetrachloroethene and vinyl chloride.

# 8.6 Scientific Issue: Incorporating Bioavailability in the Derivation Protocol

Differential bioavailability between laboratory and field exposures represents a source of uncertainty in the development of soil standards for the protection of small mammals and birds. Current practice assumes that the bioavailability of a COPC under all field conditions is equal to that of the COPC under the laboratory test conditions; however, this assumption is rarely true. After feeding Japanese quail different diets (one containing lead acetate, the other containing oysters grown in lead-containing seawater), Stone et al. (1981) concluded that biologically-incorporated lead was substantially less bioavailable than lead acetate. Multiple authors have also demonstrated that the bioavailability of soilbound COPCs in the digestive tract is lower than 100% (Ruby et al., 1996; Casteel et al., 1997).

The bioavailability of a COPC under laboratory testing methods is also influenced by the dosing methods used to administer the COPC to the test organism. Dosing methods used in mammalian and avian toxicology include administration via diet, drinking water, or gavage<sup>43</sup>. Spann et al. (1986) evaluated the effects of methylmercury on northern bobwhite (*Colinus virginianus*) using four different carrier solutions<sup>44</sup> to incorporate equal concentrations of methylmercury chloride into a moist diet fed to the birds, and found that the differences in bioavailability (and thus, toxicity) in different carrier compounds were substantially different, despite an ingested dose (mg/kg Hg in food) that was consistent across all four dosing methods.

Several approaches to reduce the uncertainty associated with differential bioavailability of COPCs in the dietary exposure pathways (especially, differences in the bioavailability of ingested soil) are available, as described below.

# 8.6.1 In Vivo Laboratory Experiments

Direct measurement of the bioavailability of soil-bound contaminants by administering contaminated soil to laboratory test organisms (e.g., rats, juvenile pigs) has been used successfully (e.g., Casteel et al., 1997). However, this level of investigation requires considerable investment of project resources and specialized testing facilities.

# 8.6.2 In Vitro Digestion Models for Soil

In lieu of in vivo laboratory experiments, multiple in vitro digestion models have been developed to simulate bioavailability in the digestive system. After ingestion, soil-bound

<sup>&</sup>lt;sup>43</sup> Gavage refers to force-feeding the COPC (typically in a carrier solution such as corn oil) via syringe.

<sup>&</sup>lt;sup>44</sup> Carriers included: powdered methylmercury chloride (MeHgCl) mixed directly into the diet; MeHgCl dissolved in corn oil; MeHgCl dissolved in acetone and then into propylene glycol; or MeHgCl dissolved in acetone only. All four carrier methods are common in mammalian and avian toxicology.

contaminants are partially released into digestive juices (and are thus available for absorption across the intestinal wall). Measurement of the COPC concentration in the digestive juices provides a more realistic estimate of the bioavailable fraction than measurement of the total COPC concentration in the soil. In vitro models simulate the physical and chemical activity of the multistage digestion process to varying degrees of complexity, including:

- Variations in pH in different digestive compartments<sup>45</sup>;
- Temperature of different digestive compartments;
- Addition of gastric secretions (e.g., bile);
- Volume of digestive fluids;
- Physical mixing of compartment contents (e.g., stirring, rotation, or peristaltic action); and,
- Incubation time.

Numerous digestion models are available, including models proposed in the literature (e.g., Ruby et al., 1996; Oomen et al., 2003), as well as models designed by regulatory agencies<sup>46</sup>. These models have been validated through comparison of *in vitro* results to those obtained by *in vivo* approaches (i.e., dosing of juvenile swine with soil from the area under investigation), although this level of validation is typically limited to metals such as arsenic, cadmium and lead (Schroder et al., 2004; Ellickson et al., 2001; Ruby et al., 1996).

Researchers have also applied *in vitro* digestive models (without *in vivo* validation) to examine the bioavailability of other contaminants in soil, including Pu et al., 2004 (phenanthrene); Ruby et al., 2002 (dioxins and furans); Holman et al., 2002 (petroleum hydrocarbons); Oomen et al., 2000 (lindane, PCBs); and Hack and Selenka, 1996 (PAHs and PCBs).

# 8.6.3 Measurement of Relative Bioavailability Using In Vitro Models

Although the *in vitro* digestion models described above were designed primarily to assess bioavailability of soil for human health risk assessments, the general principles are also

<sup>&</sup>lt;sup>45</sup> Digestive compartments include: oral cavity, stomach and intestine (some models further subdivide the intestinal compartment).

<sup>&</sup>lt;sup>46</sup> A summary of five different models used in the UK, Germany, Netherlands (two models) and Belgium is provided in Oomen et al. (2002).

being applied for wildlife risk assessments. Golder Associates (Mississauga, ON) is currently using an *in vitro* digestion model to determine the <u>relative</u> bioavailability between:

- a) COPC dosing methods used in the original laboratory mammalian toxicity study that forms the basis of a given wildlife TRV, and,
- b) COPC concentrations in soil from a contaminated site.

This approach has advantages compared to the traditional application of *in vitro* digestion models in that validation with *in vivo* studies is not required. It also addresses the differential bioavailability between laboratory and field-based exposures, in that the bioavailability of a COPC under the dosing conditions used in the original laboratory investigation is compared to the bioavailability of the COPC in soil using an identical *in vitro* model. This approach has been accepted by regulatory agencies in Ontario for metals and PAHs; work continues for other COPCs including PCBs and dioxins (M. Dutton, Golder Associates Ltd., pers. comm). Extension of this approach to examine the relative bioavailability of COPCs in dietary items (e.g., soil invertebrates and plants) is also possible.

# 8.6.4 Application of In Vitro Digestion Models to Soil Standard Development

Data from *in vitro* digestion models could be used to increase the relevance of standards involving ingestion of soil, provided that a conservative, standardized value for the relative bioavailability of each COPC in soil could be determined. However, bioavailability of a COPC appears to be highly site specific, and influenced by the *in vitro* digestion model selected. Oomen et al., (2002) found that the bioavailability of COPCs in a round-robin experiment involving five different *in vitro* digestion models was highly variable:

- Arsenic bioavailability ranged from 6-95%, 1-19%, and 10-59% for three different contaminated soils, respectively.
- Cadmium bioavailability ranged from 7-92%, 5-92%, and 6-99% for three different contaminated soils, respectively.
- Lead bioavailability ranged from 4-91%, 1-56%, and 3-90% for three different contaminated soils, respectively.

Although the selection of a standardized *in vitro* digestion model would reduce the variability in the estimated soil bioavailability, the differences in bioavailability between samples from different areas would still remain. Determination of a single conservative

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soil bioavailability fraction for standard derivation purposes is unlikely<sup>47</sup>. Modifications to existing in vitro digestion models to more closely simulate small mammal and bird digestive processes (rather than humans) would also need to be considered (e.g., simulated gizzards for birds; Levengood and Skowron, 2001).

### Recommendation

Conservative soil standards for protection of small mammals and birds should continue to assume 100% bioavailability given the absence of a transparent, reproducible and defensible method to account for differential bioavailability.

# 8.7 Linkages Between Proposed Soil Standards and Ecological Risk Assessment

Development of soil standards for the protection of small mammals and birds is not intended as a replacement for a properly-conducted ecological risk assessment, although the food chain model used to back-calculate a protective soil standard shares many similarities with food chain models used in a detailed ERA. These food chain models have a <u>subtle yet highly significant difference</u> in their intended application, as follows:

- The food chain model for back-calculating a soil standard is intended only to identify those sites where risks to small mammals and birds are clearly negligible, and therefore, do not require a detailed assessment. It does not provide a quantitative risk estimate, and by design, is highly conservative.
- The food chain model used in an ERA is intended to quantify the magnitude of potential risks to small mammals and birds. By design, food chain models for this application should maximize their ecological relevance to reduce the likelihood of generating unrealistically high estimates.

The appropriate balance between conservatism and ecological relevance is a source of considerable debate in the literature when food chain models are used in risk assessments at contaminated sites. Food chain models used for ERA purposes typically contain numerous default conservative assumptions (each intended to compensate for areas of uncertainty) that contribute to unrealistic risk estimates (McDonald and Wilcockson, 2003). These food chain models tend to predict adverse biological effects (i.e., generate hazard quotient values) that prove to be unrealistically large or toxicologically impossible

<sup>&</sup>lt;sup>47</sup> As an example, consider the differences in bioavailability at sites impacted by lead from different potential sources such as sandblasting grit, ore extraction, application of lead-based paint, leaded gasoline, and lead shot. All five sites would share the same COPC, but likely have very different gastrointestinal bioavailability.

(Tannenbaum et al., 2003). Predicted effects from a food chain model are rarely confirmed with field-based measurements (Tannenbaum, 2003). Sites with high hazard quotients are described as having a healthy and thriving ecology; the role that habitat plays in determining species assemblages at a site is ignored (Tannenbaum, 2005).

Despite the differences in the intended application, the challenges associated with balancing conservatism and ecological realism must be considered with respect to using a food chain model to backcalculate protective soil standards. The use of <u>appropriately</u> conservative assumptions and parameters is paramount, and will likely require policy decisions regarding the desired level of conservatism. Also, the context of the soil standards needs to be clearly communicated. Exceeding a soil standard for protection of small mammals and birds at any given site does not indicate that adverse biological effects are in fact occurring; it simply indicates that the potential for risks cannot be excluded based on the available data. Therefore, further assessment using a properly conducted risk assessment (where food chain modelling is not the only line of evidence) is required.

### Recommendation

Regulatory decisions regarding the desired level of protection for small mammals and birds are required in order to set an appropriate level of conservatism in the food chain model. If the decision is that the standard should protect populations of organisms, then it is appropriate to use less conservative assumptions such as LOAEL-based TRVs; median BAFs; median body weight; and median ingestion rates. If the decision is to protect individual organisms, then more conservative assumptions should be used, such as NOAEL-based TRVs and upper estimates of BAFs, body weight and ingestion rates.

### 8.8 Summary of Proposed Derivation Methodology

### Recommendations

The following derivation methodology is proposed, based on the scientific review described above and ensuing recommendations:

Identify appropriate toxicity reference values for birds and mammals based on a comprehensive literature review and screening process. Data from existing compilations may be appropriate for use. Allometric scaling to adjust this TRV is not recommended.

Determine relevant surrogate species for the desired receptor groups. Prepare conservative estimates of food and soil ingestion rates for the selected surrogate species. Food and soil ingestion rates may be derived using allometric scaling (preferably, within a probabilistic approach).

Backcalculate protective soil standards using a mechanistic food chain model, assuming that there are no differences in bioavailability between soil versus food or laboratory versus field exposures.

Additional safety factors in this backcalculation are not recommended given the conservatism already present in the model (i.e., 100% bioavailability).

# 9.0 ENVIROMENTAL PROTECTION: GROUNDWATER FLOW TO SURFACE WATER USED BY AQUATIC LIFE

Consideration of potential changes as a result of this review to the numerical soil standards for the protection of groundwater flow to surface water used by aquatic life can be divided into the following two conceptual categories:

- Potential changes to the groundwater models, which are used to backcalculate a protective soil standard from an appropriate ambient water quality guideline (WQG).
- Potential changes to the ambient WQG derivation protocols that would influence the backcalculation of the numerical soil standard.

# 9.1 Groundwater Models

The groundwater models are independent of the WQG selected as the basis of the backcalculation.

# 9.2 Ambient Water Quality Guideline Values

Our review included consideration of the potential implications of proposed changes in the existing CCME WQG derivation process. At present, the preferred method for deriving a CCME WQG involves selection of the lowest available and appropriate lowest observed effect concentration (LOEC) divided by a safety factor of 10 (i.e., similar to the single toxicity data value (and uncertainty factor) approach described in Section 7.6.1. A new methodology for deriving WQGs is currently under development by Environment Canada. This methodology will likely involve the use of species sensitivity distributions<sup>48</sup> (see Section 7.6.1) however; several technical issues have not yet been resolved, including:

- The definition of the WQG (e.g., the  $HC_5$  or the lower 95<sup>th</sup> percentile of the  $HC_5$ ).
- The appropriate mathematical models to be applied to the data distribution.
- The minimum data requirements (e.g., how many individual taxa and/or taxonomic groups are required).
- The number of distributions required (e.g., separate acute and chronic distributions; separate distributions for different taxonomic groups).

<sup>&</sup>lt;sup>48</sup> A species sensitivity approach was used by industry representatives to propose a draft Canadian WQG for alcohol ethoxylates (Belanger and Dorn, 2004). The regulatory status of the alcohol ethoxylate WQG was not known at the time this report was prepared.

- The preferred toxicological endpoint used in the distribution (e.g., NOEC; LOEC; EC<sub>20</sub>).
- The integration of toxicity modifying factors (e.g., hardness, pH) within the species sensitivity distribution approach. A biotic ligand model (for selected metals) is one potential approach being considered as a method for normalizing toxicity data.

The absence of a revised CCME derivation methodology at this time prevents a detailed review of its potential implications on the backcalculation of numerical soil standards for the protection of groundwater flow to surface water used by aquatic life. We cannot predict whether a SSD approach for WQG derivation would tend to result in lower or higher WQGs than the existing CCME approach. Regardless, our understanding is that an immediate recalculation of all existing CCME WQGs in the event that a SSD approach is approved is not contemplated. Existing CCME WQG based on the lowest LOEC divided by a safety factor would remain in effect until each WQG is reviewed in the normal course of events.

# 10.0 LIVESTOCK INGESTING SOIL AND FODDER

### **10.1** Review of Selected Derivation Protocols

Both CCME (2005) and BCE (1996) share a similar approach in that they backcalculate a protective soil standard for livestock<sup>49</sup> ingesting soil and fodder using a simplified food chain model approach that accounts for the daily dose ingested via soil, plus the daily dose ingested from fodder (estimated from soil concentrations using a bioaccumulation factor). There are subtle differences, however, in how the models are constructed and applied.

### **10.2** Scientific Issue: Parameterization of Food Chain Model

CCME (2005) and BCE (1996) have subtle differences in terms of the parameterization of their respective simplified food chain models.

### 10.2.1 Apportionment

CCME (2005) allocates a percentage of the allowable dose to different exposure pathways through the use of apportionment factors. CCME (2005) assumes that:

- Water consumption contributes 20% of an animal's daily intake (based on the assumption used in human health risk assessment).
- Dermal absorption and inhalation is thought to be a relatively minor exposure pathway, and therefore, was assumed to contribute 5% of an animal's daily intake.
- Soil and food ingestion contributes the remaining 75% of an animal's daily intake.

As a result, CCME (2005) backcalculates the soil concentration that results in an ingested daily dose equal to 75% of the applicable TRV. Conversely, BCE (1996) does not include apportionment in its derivation approach, and backcalculates the soil concentration that results in an ingested daily dose equal to 100% of the applicable TRV. BCE (1996) notes that this modified approach was adopted because the CCME procedure was considered too complex and too dependent on default assumptions of questionable scientific veracity.

<sup>&</sup>lt;sup>49</sup> Herbivore checks for the CSST protocol described in this chapter also includes livestock species other than cattle, such as chicken, lamb, pigs, and duck.

We agree that the assumptions regarding dose apportionment in CCME (2005) are not well supported by relevant scientific data<sup>50</sup>; however, the underlying need for apportionment factors remains relevant dependent on the method used to calculate protective standards for livestock drinking water.

CCME (2005) calculates soil quality guidelines for protection of livestock watering using a groundwater transport model, and WQG for the protection of agricultural water uses (CCME, 1999b). These WQG are based on the total tolerable daily intake (TDI), plus safety factors and the underlying assumption that water consumption consists of 20% of the daily intake. Apportionment is necessary for CCME (2005) since otherwise, livestock would have the potential to ingest more than the allowable daily intake (i.e., livestock could receive their TDI from soil and fodder ingestion, <u>and</u> receive an additional TDI from water consumption). We note that CCME (1999b) includes a safety factor, which may be overly conservative when combined with the apportionment approach.

The specific method used to calculate soil standards for the protection of livestock watering is not provided in BCE (1996), and therefore, it is not possible to examine in detail the use of apportionment in the BCE (1996) methodology. Additional guidance with respect to the CSST methodology is available from internal memorandum (BCMELP 1995, 2000a,b).

Further examination of the BCE (1996) approach to calculating soil standards for the protection of livestock watering and, standards for the protection of ingestion of soil and fodder, may be justified, depending on the implications of proposed changes to the groundwater model, as well as policy decisions regarding the desired level of protection for livestock in general (rather than on a pathway-by-pathway basis).

### Recommendation

Incorporation of an apportionment factor in the calculation of soil standards for protection of livestock ingesting soil and fodder may be appropriate, depending on the level of desired protection for livestock and existing safety factors incorporated into the BCE (1996) approach. Further examination of the existing BCE (1996) approach was not possible based on the available documentation.

<sup>&</sup>lt;sup>50</sup> The water apportionment factor in CCME (2005) is based on humans, not livestock; the inhalation/ dermal absorption apportionment factor does not appear to be based on any measured data.

### 10.2.2 Receptor Parameters

Differences in the specific parameters used in the simplified food chain models by CCME (2005) and BCE (1996) were also observed. These differences are summarized in Table 10.1 and discussed below:

- **Body weight:** CCME (2005) recommends a standardized cattle body weight of 550 kg, based on the approach adopted in the Canada-wide Standards for Petroleum Hydrocarbons (CCME, 2000). BCE (1996) uses a standardized cattle body weight of 600 kg, which is cited as a default value without a specific reference. Both body weights fall within the range for dairy cattle (540-862 kg) provided in CCME (1999b).
- **Food ingestion rate:** We were unable to verify that the formula provided in BCE (1996) resulted in a food ingestion rate of 13.5 kg/day based on a body weight of 600 kg; however, the stated food ingestion rate of 13.5 kg is similar to that calculated by the formula provided in CCME (2005).
- Soil ingestion rate: Methods used to calculate the soil ingestion rate are identical between CCME (2005) and BCE (1996).

	CCME (2005)	BCE (1996)
Body weight (kg)	550	600
Food ingestion rate (kg/day)	0.0687 x BW <sup>0.822</sup> ; results in estimate of 12.3 kg/day	0.687 x BW <sup>0.651</sup> ; but formula does not result in 13.5 kg/day as stated in BCE, 1996
Soil ingestion rate (kg/day)	0.083 x total dry matter intake rate	0.083 x total dry matter intake rate

<b>TABLE 10.1:</b>	Differences in	Parameterization	for Cattle
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### Recommendation

Future updates to the CSST protocol should use the same default body weight and food ingestion rates as CCME (2005).

# 10.3 Scientific Issue: Soil-to-Plant Bioaccumulation Factors

CCME (2005) suggests that bioaccumulation factors (BAFs) for soil-to-plant should be developed based on the geometric mean of the available and appropriate literature data. BAFs should preferably be based on field data instead of laboratory-based data, although it is permissible to estimate BAFs based on chemical properties (e.g.,  $K_{ow}$ ) in the absence of measured values.

BCE (1996) uses BAFs from a single literature source (ORNL, 1984). ORNL (1984) generated two different BAFs in order to model the movement of radionuclides from soil to leafy vegetation ( $B_V$ ), and from soil to reproductive vegetation ( $B_R$ ) (e.g., grains) throughout the continental United States. These country-wide estimates of  $B_V$  and  $B_R$  include an inherent weighting of the available literature data according to the relative importance of the crop to US agricultural output. Consequently, although ORNL (1984) provides a systematic summary of BAFs for all metals and metalloids, it is unclear as to the extent to which its intended application may have influenced its derivation method.

Regardless of the potential limitations of ORNL (1984), an update of the soil-to-plant BAFs used in the CSST derivation process is justified, given the availability of reputable compilations of soil-to-plant BAFs, including other publications from the Oak Ridge National Laboratory (Efroymson et al., 2001), and the ECO-SSL guidance document (USEPA, 2003a).

### Recommendation

Soil-to-plant BAFs should be reviewed and updated as necessary.

# **10.4** Scientific Issue: Updates in Available Toxicity Data

The livestock TRVs used in the existing CSST derivation method (BCE, 1996) was based on Puls (1994). We were unable to identify other compilations of relevant livestock toxicity data published subsequent to Puls (1994); additionally, our literature search indicates that the Puls compilation (with various printing dates of the 2<sup>nd</sup> edition) continues to be widely cited as a source of TRVs. However, our understanding is that a new publication entitled "Minerals and Toxic Substances in Diets and Water for Animals" is currently being prepared by the US National Academy of Sciences (NAS, 2005). The scope of this report is described as: "The report will address recent research on tolerance and toxicity of minerals in animal diets including the following areas: general considerations; mineral sources, discrepancies and difficulties in methods of analyses and evaluation of biological status; metabolic mineral interactions; assessments of form and species interactions; supplementation considerations; bioavailability of different mineral forms and sources; maximal tolerable levels; effects of diet composition, stressors, and animal physiological status on mineral utilization; and environmental exposure considerations. The report will include all species for which adequate information is available--updating the previous report, greatly expanding the topics covered, and increasing the usefulness of the report. Recommendations will be provided on maximum tolerable and toxic dietary levels of minerals in animal diets. Potential for toxic exposure, toxicosis, factors affecting toxicity, and essentiality of dietary minerals in various animal species will be discussed." (NAS, 2005).

NAS (2005) should be reviewed to determine if livestock TRVs reported by Puls (1994) require modification. The anticipated publication date for NAS (2005) is July 2005 (A. Lewis, NAS, pers. comm.).

### Recommendation

Livestock TRVs should be reviewed and updated as necessary.

# 11.0 MATRIX PATHWAYS NOT REVIEWED

The following matrix pathways were not included within the scope of this scientific review due to the requirement to allocate limited project resources to address high-priority issues (as described in Section 1.1). A brief summary of each pathway excluded from the detailed scientific review is provided below:

- **Major microbial function:** BCE (1996) recommends inclusion of a soil standard for the protection of major microbial function for agricultural land uses only. This soil standard is adopted directly from CCME without modification, and therefore, it was not necessary to review differences in protocol derivation.
- **Groundwater used for irrigation watering:** BCE (1996) does not provide a detailed description of derivation methods used to develop soil standards for the protection of groundwater used for irrigation watering, and therefore, it was not possible to review specific differences in protocol derivation. CCME (2005) backcalculates a protective soil standard from a water quality guideline to prevent phytotoxicity, and therefore we anticipate that any modification to the groundwater models will be equally applicable to this pathway.
- **Groundwater used for livestock watering:** BCE (1996) does not provide a detailed description of derivation methods used to develop soil standards for the protection of groundwater used for livestock watering, and therefore, it was not possible to review specific differences in protocol derivation. The potential interaction of this exposure pathway with the methods used to derive soil standards for the protection of livestock ingesting soil and fodder was described in Section 10.2.1. Additionally, CCME (2005) backcalculates a protective soil standard from a water quality guideline for livestock watering and, therefore, we anticipate that any modification to the groundwater models will be equally applicable to this pathway.

# 12.0 HIGH DENSITY URBAN RESIDENTIAL LAND USE

### 12.1 Land Use Scenario

Conceptually, a High-Density Urban Residential (HDUR) site is assumed to consist primarily of a multi-storey building with underground parking (i.e., apartments, condominiums<sup>51</sup>) located in areas without natural vegetation or exposed soil. Surrounding areas are assumed to be primarily paved and vegetation, if present at the site, is assumed to be actively managed (e.g., ornamental plants and/or landscaping) and growing on imported topsoil. Examples of areas that would fall into this category are Pacific Place and east False Creek area.

Consultation with CCME indicated that a HDUR land use scenario was not being considered for future guideline development (J. Vigano, pers. Comm., January 2005). Based on a further review of jurisdictions outside of Canada, ANZECC (Australia and New Zealand Environment and Conservation Council) was identified as the only jurisdiction that had adopted an HDUR-like land use for developing soil guidelines. ANZECC (NEPM 1999a,b) refer to this land use as "Residential D" and define it as follows: residential setting with minimal opportunity for soil access, including dwellings with fully and permanently paved yard space such as high-rise apartments and flats.

The definition of a HDUR scenario is important as it links back to the potentially operable pathways for that scenario. For example, if a HDUR site is assumed to consist of multi-family dwellings with little to no soil access due to paving or ground cover, some of the human and ecological exposure pathways could be excluded (e.g., human health soil intake pathway and ecological protection of soil invertebrates and plants). Further, if the HDUR scenario includes at least one level of underground parking, it is considered appropriate to apply residential exposure assumptions but indoor vapour concentrations representative of a commercial scenario, since there would be significant ventilation of vapours migrating into the building for this scenario. We note that when there is at least one level of parking or separation between soil and residential dwellings, conceptually the HDUR scenario is similar to the live-work scenario, where there is commercial use of the first floor, and where currently, the CSR commercial land use soil standards would apply (both the exposure assumptions and the indoor vapour concentrations are based on the commercial scenario).

Ministry input will be required to define the HDUR scenario. However, the following sections will outline some of the options and their implications for development of soil standards for human and ecological receptors in a HDUR setting.

<sup>&</sup>lt;sup>51</sup> We assume that townhomes or other multifamily dwellings with yard space are considered residential, not high-density urban residential.

### 12.2 Application to Human Health Matrix Standards

### 12.2.1 ANZECC Approach

The high density residential scenario defined by ANZECC (NEPM 1999a,b) only considers protection of human health and not protection of ecological receptors. Default exposure ratios were derived by NEPM (1999b) to account for differences in exposure between the typical residential scenario and the high density residential scenario. The default exposure ratios were developed by assigning a multiplication factor to each land use to take into account expected differences in levels of exposure ratios were assigned based on professional judgment about what is likely to be protective of human health. In the case of the high density residential scenario, it was assumed that ingestion of contaminated soil or dust from on-site sources would be reduced by a factor of at least four; giving rise to a default exposure ratio of 0.25 for the high density residential scenario would result in a lead guideline of 1,200 mg/kg for the high density scenario. Given that this default exposure ratio was unsubstantiated, and not scientifically based, we do not consider it an appropriate approach for CSST to pursue.

### 12.2.2 Develop Quantitative Exposure Factors Approach

Another approach considered was to develop a unique exposure scenario for HDUR sites. For example, the amount of time a child spends outside playing at a high rise complex may be considerably less than the time that would be spent playing in their own backyard. The US EPA (2002b) Child Specific Exposure Factors Handbook was consulted to determine whether there was information related to the amount of time a child would spend playing outdoors in one's own backyard versus a common green space associated with a high rise complex. Information of this nature was not available through the US EPA, Canada Mortgage and Housing Corporation, or other sources consulted (Richardson 1997, AIHC 1994). Statistics Canada was also consulted but a response was not received prior to finalization of this report. Without scientific justification to support a reduced or different exposure time for children that live in a HDUR setting, developing numerical soil guidelines for the soil intake pathway that differ from the residential scenario would not be justifiable and therefore, is not recommended at this time.

One potential source of information that could be investigated further is the Pest Management Regulatory Agency (PMRA). The PMRA is jointly conducting a risk assessment with the US EPA on chromated copper arsenate (CCA) treated wood used on playgrounds and decks (Zartarian et. al., 2003). A preliminary risk assessment document was released in November 2003 (http://www.epa.gov/scipoly/sap/2003/index.htm) and a finalized risk assessment is expected to be completed in 2006. The study uses data

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compiled by the US EPA from various American surveys compiled into CHAD (Consolidated Human Activity Database). The primary population of interest for the assessment was children in the United States who frequent public playsets (e.g., at a playground, a school, a daycare centre) and residential playsets. The results from both groups of children (those who contact public playsets only and those who contact public and residential playsets) are presented in the report.

### 12.2.3 Qualitative Exposure Pathway Approach

A potential alternative to developing unique numerical soil standards for the human health exposure pathways for the HDUR scenario would be to define the HDUR scenario such that the existing land use scenarios under the CSR would apply.

The typical HDUR scenario that is encountered involves multi-storey buildings (i.e., condominiums) with underground parking located in areas without natural vegetation or exposed soil. Surrounding areas are assumed to be paved (i.e., "hard surfaces") and vegetation, if present at the site, is assumed to be actively managed (e.g., ornamental plants and/or landscaping) and growing on imported topsoil.

Based on the above, the exposure would be considered similar to the commercial scenario. For the indoor inhalation of volatiles, a hybrid residential/commercial soil standard unique to the HDUR land use scenario would need to be developed. The hybrid inhalation soil standard would be based on the receptor characteristics and exposure time for a residential scenario but the indoor air concentration assumed for a commercial building. Table 12.1 shows the pathways and the proposed land use standards that would apply under a HDUR scenario using this approach.

### **12.3** Application to Environmental Matrix Standards

We envision that the HDUR land use scenario will be similar to the existing commercial land use with respect to the existing environmental matrix standards (Schedule 5 of CSR). For example, both Commercial and HDUR sites are largely covered by impervious surfaces (e.g., parking lots, building structures), and will tend to be located near urbanized areas. Therefore, we recommend applying the commercial land use standards to the HDUR scenario for the protection of ecological receptors. The SRA-1 guidance in terms of screening commercial sites is also applicable to this land use.

We anticipate that toxicity to soil invertebrates and plants, and toxicity to small mammals and birds pathways would tend to screen out HDUR properties during the SRA-1 ecological exposure questionnaire based on the consideration of undeveloped land on the site (see SAB, 2004). Matrix standards unique to the agricultural land  $use^{52}$  are not considered relevant for this land use.

# 12.4 Proposed Land Use Standards

The HDUR scenario identified as the preferred option considering the information available is defined as follows:

- 1. Multi-storey building with minimum one-level underground parking below building (i.e., condominium, apartment).
- 2. Surrounding areas are either paved (i.e., hard) surfaces or small landscaped areas without natural vegetation.
- 3. Landscaped areas are actively managed (e.g., ornamental plants) and covered with imported topsoil.
- 4. There are no grass playing fields or play grounds.

Based on the above definition, the commercial standards are considered applicable. The only exception is the proposed new indoor inhalation soil standards which would be derived based on a hybrid of the residential/commercial land use assumptions (residential exposure assumptions for indoor vapour concentrations based on commercial vapour intrusion assumptions). If further refinement of the HDUR scenario is required, further efforts should be focused on obtaining realistic estimates of the exposure time for children playing outdoors in a playground/greenspace in a HDUR setting where there is exposed soil. Adopting the commercial land use standards for the HDUR scenario scenario would result in a significant change (i.e. increase) in the applicable standards as previously the residential land use standards would have been applicable. Table 12.1 shows the proposed land use standards selected for human health and ecological exposure pathways for the HDUR scenario.

<sup>&</sup>lt;sup>52</sup> Protection of microbial function; livestock ingesting soil and fodder; groundwater used for irrigation; groundwater used for livestock watering.

Exposure Pathway	Proposed Land Use Standard
Definition	Multi-storey building, minimum one-level underground parking below building, paved surfaces or small landscaped areas.
HH Intake of Soil	Commercial
HH Indoor Inhalation	Hybrid Residential/ Commercial
ECO Plants, Inverts	Commercial

#### **TABLE 12.1:** Summary of Land Use Standards Proposed for the HDUR Scenario

1. The soil standards protective of groundwater used for drinking water and protection of aquatic life are the same regardless of land use, and are therefore not included in the table.

#### Recommendations

Consideration should be given to incorporating a HDUR scenario in the protocol since there are substantial and definable differences in this exposure scenario compared to conventional residential land use. The HDUR scenario identified as the preferred option is defined as consisting of a multi-storey building with minimum one level of underground parking below the building, and either paved surfaces or small landscaped areas, covered with imported topsoil, beside building. Based on the above definition, the commercial standard would apply to the different human health and ecological exposure pathways with the exception of the inhalation pathway (see Table 12.1).

Adopting the commercial land use standards for the HDUR scenario would result in a significant change (i.e. increase) in the applicable standards as previously the residential land use standards would have been applicable. If further refinement of this scenario is required, further efforts should be focused on obtaining realistic estimates of the exposure time for children playing outdoors in a playground/greenspace in a HDUR setting where there is exposed soil.

Consideration should be given to development of a hybrid HDUR standard for soil vapour intrusion that assumes a residential receptor, and indoor air concentration predicted for a commercial scenario.

### 13.0 WILDLANDS LAND USE

### 13.1 Land Use Scenario

Conceptually, the Wildlands land use is envisioned to be similar to the existing Urban Park land use although, potentially, with a different level of protection to reflect that urbanized park areas do not support the same level of ecological function as wild areas by virtue of their proximity to anthropogenic influences. We envision that the Wildlands land use would apply to all areas not already covered by one of the other land use categories. A partial list of defined Wildlands land uses is included in the existing urban park land use definition, as follows:

"the use of urban land for the primary purpose of outdoor recreation, including... but does not mean <u>wildlands such as ecological reserves</u>, national or provincial parks, protected wetlands or woodlands, native forests, tundra or alpine meadows<sup>53</sup>."

Examples of additional biological factors that may be relevant for defining the Wildlands land use include:

- Ability of the area to support populations of small mammals and birds. The SRA-1 terrestrial habitat screening process includes several relevant factors such as distance to sensitive habitats; connectivity to other undeveloped areas; size of the area in question; and shape of the area in question (SAB, 2004). We envision that designation of the Wildlands land use could be based on these considerations, which would effectively limit Wildlands areas to those areas that do not contain significant anthropogenic influences in close proximity.
- The degree to which vegetation on the site is actively managed. We envision that wildlands would have negligible vegetation management, whereas urban parks are actively managed (e.g., playing field upkeep, ornamental planting, tree trimming, brush removal, path maintenance, etc). The existing CCME (2005) residential/parkland land use specifies that both ornamental and native vegetation should be maintained—the new Wildlands land use would address only native (and natural) vegetation, while the existing Urban Park land use would address ornamental (or managed) vegetation. Specification that the Wildlands land use is only applicable to native vegetation would assist in excluding managed areas that are more appropriately designated as Urban Park.

<sup>&</sup>lt;sup>53</sup> There are virtually no toxicity data available for representative soil invertebrate and plant species from tundra or alpine meadow environments. Extrapolation of existing toxicity data to these environments is uncertain due to unknown influences of different soil types and seasonal effects, as well as evolutionary changes in native species that may have resulted.

• The degree to which the site has been subjected to historical or wide-area impacts. How should one classify reclaimed mining areas (or other reclaimed industrial lands) that are surrounded by wild areas and support substantial wildlife populations? We envision that areas that have been subject to broad historical impacts but are no longer active industrial sites would be classified as wildlands. Specific areas surrounding the former industrial site (e.g., abandoned structures; waste rock dumps; former fuel storage locations; former roads and railways) would be classified as Industrial under this scenario; however, this classification may also require consideration of the length of time involved, as well as the desired future land use.

A summary of matrix standards considered applicable to the proposed Wildlands land use is provided in Figure 13.1. We anticipate that this definition and selection of applicable matrix standards will require policy decisions in order to reconcile the Wildlands land use with other existing land uses. The following questions were identified for consideration by policy makers based on our review of which matrix standards would be applicable to the proposed Wildlands land use:

- How should one classify park areas that are in proximity to urbanized areas, are intended to protect a natural ecosystem, but have not formally been designated as ecological reserves?
- How should one classify natural forested areas surrounding a residential dwelling or commercial structure (e.g., a small building on an otherwise undeveloped 5 acre lot)?
- How should one classify natural forested areas that are managed for timber harvesting?
- Are there instances where groundwater wells located on Wildlands are used to draw water from crop irrigation and livestock watering? We assume that the use of any area for livestock or crops means that it would be classified as Agricultural.

# 13.2 Application to Human Health Matrix Standards

The Wildlands land use primary function would be to protect wildlife. However, considering that Wildlands includes areas such as provincial parks and forestry camp sites where the general public may hike or camp, human receptors also need to be considered, but are not likely to be the risk drivers.

We envision that under a Wildlands type scenario, human receptor use would include overnight camping, ranging from 2 weeks up to 2 months, but not year round occupancy. The residential/urban park soil standards were not considered suitable as the assumptions were overly conservative for human receptor use in a Wildlands scenario (i.e., toddler

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spending 100% of their time in the area). The commercial land use soil standards also tend to over estimate exposure for human receptors in a Wildlands type scenario (i.e., 5 days/week, 48 weeks/year), but are more realistic than the residential/urban standards, especially if the child receptor is adopted as the sensitive receptor for the commercial scenario (see Section 3.0). Deriving a new land use scenario for human receptors in a Wildlands scenario is not considered warranted given that risks to ecological receptors will be the risk drivers. Based on the above, we recommend adopting the commercial land use standard for the Wildlands scenario. The applicable pathways for human receptors under the Wildlands scenario are listed below:

- Intake of contaminated soil (soil ingestion, dermal contact and dust inhalation); and,
- Groundwater used for drinking water.

The inhalation of volatiles in indoor air was not considered applicable to this land use as human exposure is primarily anticipated to be via outdoor exposure.

# 13.3 Application to Environmental Matrix Standards

The Wildlands land use supports the broadest range of potential ecological receptors and, therefore, also has the greatest number of relevant matrix standards, including:

- Toxicity to soil invertebrates and plants;
- Toxicity to small mammals and birds; and,
- Groundwater flow to surface water used by aquatic life.

Existing policy restricts protection of microbial function to agricultural land uses only and, therefore, it was not included in the list of relevant matrix standards for the proposed Wildlands land use. Our opinion is that the existing level of protection afforded to Urban Park locations is likely adequate for the Wildlands land use (e.g., an EC<sub>20</sub>-based approach for soil invertebrates and plants; a LOAEL-based approach to protect populations of small mammals and birds), however, we caution that formal research into the field-based validation of these theoretical levels of protection has not been conducted.
Exposure Pathway	Proposed Approach			
Human Health				
Intake of contaminated soil	Pathway is applicable. No additional changes (beyond those recommended for other land uses) for application to Wildlands			
Groundwater used for drinking water	Pathway is applicable. No additional changes (beyond those recommended for other land uses) for application to Wildlands			
Vapour inhalation	Pathway is not applicable.			
Ecological				
Toxicity to soil invertebrates and plants	Pathway is applicable. Recommended modifications are described in Section 7.			
Groundwater flow to surface water used by aquatic life	Pathway is applicable. Recommended modifications are described in Section 9.			
Toxicity to small mammals and birds	Pathway is applicable. Recommended derivation methodology is described in Section 8.			
Livestock ingesting soil and fodder	Pathway is potentially applicable. No modifications to existing derivation methodology is contemplated.			
Major microbial function	Pathway is not applicable.			
Groundwater used for livestock watering	Pathway is potentially applicable. No modifications to existing derivation methodology is contemplated.			
Groundwater used for irrigation watering	Pathway is potentially applicable. No modifications to existing derivation methodology is contemplated.			

# FIGURE 13.1: Summary of Matrix Standards Applicable to Wildlands

#### 14.0 CLOSURE

We have appreciated the opportunity to complete this review of the CSST protocol on behalf of the Science Advisory Board for Contaminated Sites in British Columbia. Should there be questions on this report or further work required, please do not hesitate the contact Dr. Hers (604-298-6623) or Dr. Chapman (604-986-4331).

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04-1412-228

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# **APPENDIX I**

# REVIEW OF METALS PARTITIONING FOR GENERIC SOIL STANDARD DEVELOPMENT

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# 1.0 INTRODUCTION

The purpose of this Appendix is to provide an overview of the current approach used by the Province of British Columbia for evaluating metal partitioning in the vadose zone. Soil-water metal partitioning is considered in the context of contaminant fate and transport for the purpose of soil matrix standard calculation. In the vadose zone, the primary means of metal attenuation is adsorption from pore-water to the solid phase. In the Province of British Columbia, soil matrix standards are calculated according the Contaminated Sites Soil Task Group (CSST) protocol (CSST, 1996).

The objectives of this appendix are:

- 1. To summarize regulatory approaches to development of the soil-water partition coefficient for the purpose of soil screening level generation;
- 2. To identify limitations of the current method of determination of soil-water partitioning coefficients; and,
- 3. To identify transparent, conservative methods more appropriate to the development of conservative soil-water metal partitioning coefficients for the use of calculation of soil matrix standards.

# 2.0 FATE AND TRANSPORT OF METALS

The CSST protocol utilizes the results of geochemical models for the purpose of deriving soil matrix standards in the context of metals fate and transport. An understanding of fate and transport principles is important when evaluating the results of geochemical models. Therefore, mechanisms controlling the interaction of metals between the aqueous and solid phases are reviewed below.

Consideration of metal fate and transport encompasses physical and chemical processes along a groundwater migration pathway in both the unsaturated and saturated zones. Fate processes describe contaminant persistence, whereas transport processes address contaminant mobility. Transport in the subsurface is a function of several processes, including advection, dispersion, molecular diffusion and retardation. Advection and dispersion are mechanical processes that are independent of solute character, and the effect of diffusion is generally negligible. The key processes that define the mobility of metals in the subsurface are sorption and precipitation, which result in retardation of metal species during groundwater transport relative to chemicals that do not interact with aquifer materials.

Migration of metals from soil to groundwater is dictated by the mechanism of release of the contaminant from soil and transport of the contaminant in groundwater to a receptor (USEPA, 1996). According to Langmuir et al. (2004), while metals can undergo a

variety of inter-media transfers in the groundwater environment, they are "indefinitely persistent and conservative" in the environment.

### 2.1 Metal mobility

The complex environmental chemistry of trace metals makes it difficult to predict mobility in the groundwater environment. Adsorption and precipitation are the key processes that retard trace metal transport in groundwater (Freeze and Cherry, 1979). Chemical characteristics affecting the subsurface behavior of metals include:

- Metal complex formation;
- Reduction / oxidation (redox) state of the system;
- Metal solubility controls; and,
- Solid-water metal partitioning (adsorption).

These processes are described in detail in the following sections.

The pH generally is the dominant factor governing metal sorption, but other factors control sorption as well. Several variables may influence metal sorption at the soil-water interface (Table 1).

**Table 1:** Factors mediating metal sorption from pore water to soils,sorted with respect to characteristics impacting soil solids, soil solution and solutes(adapted from Langmuir et al., 2004).

Soil Solids	Soil Solution	Solutes
Soil mineral composition	pН	Character of chemical solute
Specific surface areas of metal sorbing sites	Eh	Complexation chemistry
Surface site density or cation exchange capacity of metal sorbing solids	Dissolved oxygen	Solubility
Aeration status	Solute composition and concentrations (activities)	Precipitation chemistry
Microbial type, activity, and population	Ionic strength	Redox chemistry
Organic matter content and character	Temperature	Vapor pressure
Temperature		

1)

# 2.1.1 Metal complex formation

Laboratory analyses of metals in solution are generally reported as "total metal" concentrations. However, in natural waters, metals form hydrolyzed and complexed species by combining with inorganic anions such as  $HCO_3^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$ , and less commonly Cl<sup>-</sup> and F<sup>-</sup> (Freeze and Cherry, 1979), as well as organic chelates. This "total analytical" concentration of an unfiltered sample is therefore equal to the sum of the free ions and metal complexes formed by that ion in solution (Equation 1).

$$[\Sigma M] = [M^+] + [MI_{i,j,\dots n}] + [MO_{i,j,\dots n}] + [M(suspended solids)]$$
(Equation

## Where:

 $[M^+]$ : Concentration of free metal ions  $I_{i,j,\dots n}$ : Inorganic ligands  $O_{i,j,\dots n}$ : Organic ligands

Metal speciation, as introduced in Equation 1, can be calculated using geochemical equilibrium modeling programs such as MINTEQA2 (Allison et al, 1991) or PHREEQC (Parkhurst and Appelo, 1999) (see Section 4.3).

Metal complexes are an indirect control on metal fate in the environment as they influence metal sorption and metal solubility, as discussed in Sections 2.1.3 and 2.1.4, respectively.

# 2.1.2 Reduction / oxidation condition

The reduction / oxidation (redox) state of the system influences the behavior of dissolved metals in the unsaturated and saturated groundwater zones (Freeze and Cherry, 1979). Some examples of impacts of redox conditions on metal fate and transport are presented below:

- Change in metal oxidation state can influence its capability to form complexes in solution, which holds solubility implications;
- Solid phases may dissolve, or precipitation of dissolved metals may occur, as a result of changing redox conditions; and,
- Metals may encounter solubility constraints based on redox state. For example, sulfide phases have very low solubility in anaerobic groundwater, and coprecipitation of metals with sulfide phases lowers the dissolved metal concentrations (Freeze and Cherry, 1979).

# 2.1.3 Metal adsorption

Sorption is the process of formation of a layer of metals on mineral particles and organic matter due to chemical interactions between dissolved metals and charged functional groups at the solid surface. (Langmuir, 1997). A discussion of metal adsorption in the context of solid-water metal partitioning is provided in Section 4.

Metal adsorption is impacted by a number of independent system variables, including the character of sorbate phases in soil, surface charge on the solid sorbate phase, the concentration of metal in solution, metal complexation, and pH and redox state of the system. Organic matter, Fe- and Mn-oxyhydroxides and clay minerals are important sorbent phases, as outlined in Table 2 (Langmuir et al., 2004).

Table 2:	Geochemical	behavior	of sorbent	phases	in natural	environments.
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Sorbent phase	Geochemical behavior in natural environments
Organic matter	Surface charge controlled by system pH, where surface charge is positive in law pH conditions, and possible pH conditions:
Fe- and Mn- oxyhydroxides	in low pri conditions, and negative in high pri conditions,
Clays	Surface charge controlled by defects in mineral structure.

Examples of sorption edges, defined as plots of percent metal sorbed versus pH, illustrate the pH dependence of metal sorption for cationic and anionic species (Figure 1). Figure 1 shows that sorption of cationic species generally becomes more effective with increasing pH, whereas the opposite behavior is observed for anionic species.



**Figure 1:** Adsorption of metal cations and oxyanions by ferrihydrite as a function of pH. (Metal concentrations =  $5 \times 10^{-7}$ M,  $\Sigma$ Fe[III] =  $10^{-3}$ M, ionic strength = 0.1 mol/kg, 2.4  $\times 10^{-4}$  M ferrihydrite reactive sites). From Stumm and Morgan, 1996.

2.1.4 Metal solubility controls

Mineral precipitation and dissolution can exert a significant control on dissolved metals concentrations. In general, mineral solubility increases with increasing ionic strength due to formation of aqueous complexes. Mineral solubility also depends on temperature, with most minerals becoming more soluble as temperature increases. Kinetic impediments may hinder the dissolution or formation of minerals. In addition, biological mediation may affect mineral solubility. Therefore, metal concentrations in natural waters may deviate from those expected based on equilibrium solubility considerations.

# 2.2 Summary

It is important to recognize that, while relatively simple models are used for the purpose of soil standard development, the behavior of metals in the soil-water system is highly complex and dependent on site specific conditions. Relatively slight variations in geochemical conditions can result in large variations in metals sorption behavior. Since geochemical conditions tend to vary along a groundwater migration pathway, the mobility of metals will vary spatially as well. Therefore, a thorough understanding of geochemical processes affecting metals transport is vital.

# 3.0 CSST PROTOCOL FOR DETERMINATION OF SOIL MATRIX STANDARDS

The Contaminated Sites Soil Task Group (CSST) protocol for determining soil matrix standards for inorganic and organic contaminants was developed in 1996 (CSST, 1996). Matrix soil standards for the protection of groundwater receptors were derived using a model developed by BC Environment and approved by the CSST (henceforth referred to as the "CSST groundwater model"). The model simulates the movement of contaminants from soil to groundwater, and groundwater to receptor in four components:

- 1. Contaminant partitioning between soil, soil pore air and soil pore water;
- 2. Contaminant leachate movement and attenuation through the unsaturated soil zone;
- 3. Contaminant leachate mixing with groundwater; and,
- 4. Contaminant movement and attenuation through the saturated zone to a receptor (CSST, 1996).

The four-component model assumes one-dimensional groundwater flow, and considers major groundwater and attenuation processes that affect contaminant movement (CSST, 1996). The framework used to develop the CSST groundwater model was the draft "Soil Screening Guidance, 1994" (CSST, 1996; USEPA, 1994).

In the 1996 CSST model, metal attenuation is addressed through the following processes:

- Partitioning between sorbed and pore-water phases in the unsaturated zone ("leaching");
- Dilution through mixing between leachate and groundwater; and,
- Dispersion.

(Equation 2)

Dilution and dispersion are physical properties that are independent of the chemical characteristics of the contaminant. Adsorption is a function of the character of the contaminant (solute), and the soil (sorbent). The CSST considered the extent of soil-water partitioning in terms of the soil-water partition coefficient ( $K_d$ ). The CSST provides partition coefficients for six parameters: arsenic, cadmium, chromium (VI), copper (II), lead and Zn (II) (Table 3, Figure 1). There is limited documentation in the CSST literature referring to the derivation of the isotherms presented in Table 3. According to CSST (1996),  $K_d$  values were determined by considering the pH of the system, and an idealized soil with assigned physical and chemical parameters.

The  $K_d$  values for arsenic and chromium (VI) appear to be the same as values presented in USEPA (1996b), where values were determined using an empirical relationship between  $K_d$  and solution pH. There is no detailed reference describing the development of the CSST  $K_d$  values for cadmium, copper, lead or zinc. The values of  $K_d$  for cadmium and zinc in Table 3 are higher than those recommended by the USEPA (1996b). A comparison of USEPA isotherms and CSST isotherms is provided in Section 6.

Soil matrix standards were calculated by CSST considering partitioning between solids and groundwater. According to the 1996 CSST guidelines, soil concentrations at the source are calculated using Equation 2:

 $C_{s} = \frac{C_{L} \{K_{d} + (n_{u} + H' n_{a})\}}{\rho_{b}}$ Where:  $C_{s}: \text{ Soil concentration at source (mg/kg)}$   $C_{L}: \text{ Leachate concentrations at source (mg/L)}$   $K_{d}: \text{ Partition coefficient for a chemical (cm<sup>3</sup>/g)}$   $n_{u}: \text{ Water-filled porosity}$  H': Henry's law constant (where H' = H\*42.3)  $n_{a}: \text{ Air-filled porosity}$   $\rho_{b}: \text{ Dry bulk density of soil (g/cm<sup>3</sup>)}$ 

Equation 2 is based on the soil screening level partitioning equation for migration to groundwater presented in EPA (1996a). The Henry's Law constant (H') is typically not included in the calculation of inorganic soil matrix concentrations, as most inorganics (with the exception of mercury) do not readily volatilize. Default input values for Equation 2 are listed in Table 4.

**Table 4:** Default input values used in the calculation of CSST soil quality standards for<br/>the protection of groundwater (USEPA 1996a).

Par	Parameter		Default
Cs	Soil concentration at source	mg/kg	Calculated
$C_{\rm L}$	Leachate concentration at source	mg/L	
K <sub>d</sub>	Soil-water partition coefficient	L/kg	Chemical specific, as listed in Table 1
n <sub>u</sub>	Water-filled soil porosity	Lwater/Lsoil	0.1
n <sub>a</sub>	Air-filled soil porosity	Lair/Lsoil	n-n <sub>u</sub> ; 0.2
$\rho_{b}$	Dry soil bulk density	kg/L	1.75; based on "Fraser River sand" characteristics
Η'	Dimensionless Henry's law constant		Chemical-specific, 0 for all elements except mercury

# 4.0 METHODS FOR PREDICTING METALS PARTITIONING

The current CSST protocol relies on the use of soil-water metal partition coefficients for the calculation of site-specific soil screening levels. Therefore, a thorough understanding of the theory supporting metal partitioning is necessary. Empirical, parametric and mechanistic methods used to develop metal partitioning isotherms are summarized. This section also considers the use of the chemical reaction code MINTEQA2 to generate metal  $K_d$  values.

## 4.1 Empirical models

Empirical models of predicting metal partitioning include the constant partition coefficient model ( $K_d$ ), the Langmuir isotherm model and the Freundlich isotherm model. Empirical models are based on use of experimental data to develop sorption isotherms (USEPA, 1999). The empirical isotherm is specific to the conditions under which the experiment is performed (e.g., pH and chemical concentration), and does not take into consideration sorbent properties and metal speciation. Since empirical partition coefficients are sensitive to changes in the above properties, they are approximate, and may under- or over-estimate actual partitioning in natural soils.

## 4.1.1 Theoretical background

Constant partition coefficient model (K<sub>d</sub>)

The thermodynamic basis of the measurement of the constant partition coefficient ( $K_d$ ) is based on equilibrium sorption of a contaminant onto a solid phase, as outlined in Table 5 (USEPA, 1999). Sorption is defined as the ratio of the quantity of aqueous contaminant adsorbed per unit mass of solid phase adsorbent to the total concentration of the contaminant phase in solution at equilibrium. The resultant parameter is the  $K_d$ , with units of mL/g.

Model	Assumptions	Formula	Limitations
Constant partition coefficient	<ol> <li>Reaction is at equilibrium;</li> <li>{A<sub>i</sub>} is in excess with respect to {C<sub>i</sub>};</li> <li>{A} is equal to 1; and,</li> <li>The reaction is reversible, and independent of the aqueous concentration of the contaminant in groundwater.</li> </ol>	A + C <sub>i</sub> $\Leftrightarrow$ A <sub>i</sub> $K_d = \frac{\{A_i\}}{\{C_i\}}$ Where: A: Unoccupied sorption sites on solid material C <sub>i</sub> : Total dissolved contaminant in solution at equilibrium A <sub>i</sub> : Concentration of contaminant adsorbed to surface sites on solid material	Model assumes linear evolution of K <sub>d</sub> .
		K <sub>d</sub> : Partition coefficient	

Table 5:	Summary of the	constant partition	coefficient model.
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The thermodynamic constant partition coefficient model assumes that sorption sites are unlimited. According to this model, with increasing contaminant concentration in solution, the concentration of contaminant sorbed on the solid will increase linearly. This behavior rarely occurs in natural systems: natural soils have limited sorption sites, and more than one sorbent phase competes for the available sorption sites. As the sorption sites reach saturation, a linear model of adsorption cannot be maintained (USEPA, 1999).

## Isotherm adsorption models

More complex methods of empirical isotherm determination include the Langmuir or Freundlich models. These models utilize the results of a suite of experiments to evaluate the effect of contaminant concentration on adsorption, where some reaction components are held constant. Isotherm models account for deviation from linear sorption in natural soils (USEPA, 1999). A summary of the Langmuir and Freundlich models, and their potential limitations is provided in Table 6. It is important to note that these isotherm models also do not consider several soil and solution parameters that can influence adsorption, such as bulk solution chemistry, redox conditions, temperature, or heterogeneity of sorbent surfaces (USEPA, 1999).

Model	Assumptions	Formula	Limitations
Langmuir	<ol> <li>Constant energy of adsorption; and,</li> <li>Finite number of binding sites.</li> </ol>	$Ai = \frac{K_L A_m C_i}{1 + K_L C_i}$ <b>Where:</b> $A_i: \text{ Concentration of contaminant}$ adsorbed per unit mass solid $K_L: \text{ Langmuir adsorption constant}$ $A_m: \text{ Maximum sorption sites on}$ per unit mass solid $C_i: \text{ Equilibrium concentration of}$ contaminant in solution	Model was derived to describe adsorption of gas molecules onto homogenous, crystalline material with one type of adsorption site. <i>These</i> <i>conditions are rarely</i> <i>maintained in natural soils.</i>
Freundlich	1. Low contaminant concentration.	$A_i = K_F C_i^N$ <b>Where:</b> $A_i: \text{ Concentration of contaminant}$ adsorbed per unit mass solid $K_F: \text{ Freundlich adsorption constant}$ $C_i: \text{ Equilibrium concentration of}$ contaminant in solution $N: \text{ Empirical constant}$	Does not account for finite adsorption capacity at high contaminant concentrations.

Table 6: Summary of the Langmuir and Freundlich isotherm model	ls.
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## $4.1.2 \quad Measurement \ of \ K_d \ values$

The partition coefficient can be determined experimentally by a number of methods, including batch methods, flow-through methods, and modeling of field data. Only batch and flow-through methods are considered below.

## Batch methods

Batch tests are the most common method of deriving a contaminant partition coefficient from a bulk soil sample (USEPA, 1999). A known volume of a well-characterized soil is reacted with a known volume (and concentration) of contaminant solution in a sealed beaker. The soil-solution mixture is allowed to equilibrate until sorption is assumed to be complete. Methodology, advantages and disadvantages of simple batch tests are listed in Table 7.

## Flow-through column methods

Flow-through column tests are a less common method of  $K_d$  determination (USEPA, 1999). Flow-through column methods are not as straightforward as batch tests. A solution of known contaminant concentration is introduced to a column of packed soil of known bulk density and porosity. A conservative chemical tracer is added to the solution to measure the pore-water velocity. The concentration of the effluent solution is measured as a function of time, and the results are plotted as a breakthrough curve (Figure 1). The breakthrough curve is used to determine contaminant velocity versus solution velocity. Based on the breakthrough curve, a retardation factor ( $R_f$ ) is established as the ratio of the pore water velocity to the contaminant velocity (Equation 3). Equations describing the derivation of the partition coefficient using the retardation factor are provided in Table 7.



Figure 2: A typical setup for flow-through column experiments (from USEPA 1999).

$$R_f = \frac{v_p}{v_c}$$
(Equation 3)

# Where:

- R<sub>f</sub>: Retardation factor
- v<sub>p</sub>: Pore-water velocity
- v<sub>c</sub>: Contaminant velocity

A key advantage of  $K_d$  values calculated from flow-through columns versus batch experiments is that use of a flow-through  $K_d$  in transport models requires fewer assumptions.
### 4.2 Parametric models of Kd prediction

Parametric models generate K<sub>d</sub> values based on empirically-determined relationships between aqueous and solid phase independent parameters including pH, solution chemistry, soil texture, and redox state. A wide range of independent input parameters are varied simultaneously to generate multiple K<sub>d</sub> values. From these results, "predictor equations" are generated using statistical methods. Parametric models are capable of determining K<sub>d</sub> values for multiple sets of environmental conditions, and are therefore more robust than strictly empirical models (USEPA, 1999). The product of a parametric model is a parametric K<sub>d</sub> equation, which is limited for use to the range of independent variables (pH, solution chemistry) used to generate the equation. A key restriction is that this statistical relationship provides no means of defining the mechanism of contaminant removal from solution, whether by adsorption, absorption or precipitation, whereas detailed geochemical characterization of solids following adsorption experiments can be used to elucidate the actual removal mechanisms. The parametric K<sub>d</sub> adds complexity to transport models, as the selected model code must be updated to track independent and dependent variables in the system. Thus, the parametric approach has not been widely used to determine partitioning in natural systems (USEPA, 1999).

### 4.3 Mechanistic models of Kd prediction

Mechanistic models account for the dependency of  $K_d$  values on contaminant concentration, competing ion concentration, variation in surface charge on the sorbent phase, and solute speciation. These models are based on the thermodynamic concepts of mass action and mass balance. Mechanistic models are more complicated than the empirical models, but they contribute to the understanding of chemistry at the solid / solution interface. Input requirements include adjustable system parameters, which compromises the universal application of  $K_d$  values. Because of the heterogeneity of microcrystalline structures, amorphous coatings, and natural organic matter comprising natural soils, definition of average conditions is difficult at best. Rigorous data collection is more costly than empirical models. Therefore, mechanistic models are rarely applied to natural soils.

# 4.4 Metal partitioning coefficient definition using the chemical reaction model MINTEQA2

A chemical reaction model consists of a combination of mathematical expressions describing theoretical concepts and thermodynamic relationships for aqueous speciation, oxidation/reduction, precipitation/dissolution and adsorption/desorption of metals in a soil-water system.

MINTEQA2 is a well-documented, technically defensible tool for the interpretation of the geochemical behavior of metals in well-defined soil-water systems (USEPA, 1999). A brief description of the capabilities of MINTEQA2 with respect to modeling of adsorption in geochemical systems is provided below (from USEPA, 1999).

The MINTEQA2 code utilizes a mechanistic approach, where chemical equilibria among aqueous species, gases and solids in a well-defined system are calculated in conjunction with a thermodynamic database. MINTEQA2 employs four sub-models: aqueous speciation; solubility; precipitation / dissolution; and adsorption.

The sub-models are capable of calculating aqueous speciation and complexation, redox state, gas phase equilibrium, solubility and saturation state of aqueous phases, precipitation and dissolution of solids, and adsorption of aqueous phase components to solid phases. Mass action and mass balance expressions are also incorporated as part of the MINTEQ2A code (USEPA, 1999).

An understanding of the speciation, solubility and precipitation components is key to the adsorption sub-model:

- Speciation sub-model: Calculates activities of aqueous species and complexes;
- Solubility sub-model: Reports the saturation state of mineral species. Knowledge of the solubility of a contaminant-bearing solid phase allows for interpretation of the effect of precipitation on contaminant retardation; and,
- Precipitation sub-model: The predicted mass of solid that may dissolve or precipitate is calculated. If solubility limits are reached during the experiment, the K<sub>d</sub> value reflects both attenuation and precipitation effects, and is an overestimation of contaminant attenuation due to sorption.

Surface adsorption reactions are included as part of the equilibrium speciation calculations performed by MINTEQA2 (USEPA 1996c). Metal adsorption occurs at surface reactive sites; several metal-complexing solution ligands may be in competition for surface sorption sites. At a given metal concentration in solution, equilibrium partitioning between sorbed and solvent phases depends on the affinity between the surface sorption sites and the metal in solution. MINTEQA2 contains extensive options for modeling adsorption of dissolved constituents onto the surfaces of solid phases chosen by the code user. The seven model options are listed in Table 8.

Non-electrostatic adsorption	Electrostatic adsorption
Activity partition coefficient $(K_d^{act})$ model	Constant capacitance model
Activity Langmuir model	Diffuse layer model
Activity Freundlich model	Triple layer model
Ion exchange model	

**Table 8:** Adsorption models utilized in MINTEQA2 reaction code (USEPA, 1999).

A detailed description of MINTEQA2 adsorption modeling capabilities is provided in Allison et al. (1991).  $K_d^{act}$ , Langmuir, and Freundlich adsorption models are the simplest approaches to determining metal sorption in solution. These non-electrostatic models are formulated with respect to species activity, rather than the total concentration. The total concentration of a contaminant phase is equal to the sum of all dissolved species of that phase in solution. If a total concentration approach is utilized, then it is assumed that all species of that phase adsorb with the same strength. However, experimental evidence proves this is not the case in natural systems. Therefore, MINTEQA2 is programmed to allow adsorption of specific aqueous species of each metal (USEPA, 1999).

Reaction models such as MINTEQA2 do not predict  $K_d$  values as part of the data output, but rather  $K_d$  is calculated from MINTEQA2 output as the ratio of equilibrium concentration of the metal sorbed to the solid phase to the dissolved metal in solution (USEPA, 1996c). MINTEQA2 calculates the mass of the contaminant phase that dissolves / adsorbs in user-defined reaction conditions (pH, redox state, temperature).

The user provides surface reactions and equilibrium components expected to be utilized in the experimental system as part of the input data set. MINTEQA2 requires the consideration of sorption onto one specific mineral phase, such as ferrihydrite  $[Fe(OH)_3]$ , rather than a heterogeneous soil mixture. Therefore, the user must also define a solid phase for sorption based on the average characteristics of the system.

Since geochemical conditions, reactions and sorbents must all be defined, the determination of  $K_d$  values via MINTEQA2 relies heavily on user input and interpretation. A key limitation in calculating  $K_d$  values using MINTEQA2 is that sorption is defined for one aqueous contaminant phase to one solid mineral phase. This approach is conservative with respect to the fact that natural soils are mineralogically complex, and rarely consist of a single sorbent phase (USEPA, 1999). Therefore, the user is responsible for supporting the application of these results to heterogeneous soils.

## 5.0 APPROACHES AND PROTOCOLS FOLLOWED BY OTHER REGULATORY JURISDICTIONS

### 5.1 USEPA

### 5.1.1 Soil Screening Guidance

The USEPA soil screening guidance is outlined in "Soil Screening Guidance: Technical Background Document" (USEPA, 1996b). A preliminary version of this guidance was published in 1994 (USEPA, 1994). According to CSST (1996), this draft guide was the "framework" for the CSST matrix soil standards for the protection of groundwater.

As part of USEPA (1994 and 1996b), Soil Screening Levels (SSLs) were developed to assess the ingestion of contaminated groundwater caused by migration of contaminants through soil to an underlying potable aquifer. Soil screening levels were developed for a select number of priority pollutants at waste disposal sites. The 1994 draft considered five metals (arsenic, cadmium, chromium (VI), mercury and nickel). As discussed below, the 1996 Technical Document considers 15 metals.

USEPA considers soil to groundwater migration as a two-stage fate and transport process, where:

- 1. The contaminant is released to the soil leachate; and,
- 2. The contaminant is transported through the underlying soil and aquifer to a receptor well.

Contaminant release in leachate is estimated using a linear equation for equilibrium partitioning between sorbed and aqueous phases, which is considered in detail in this section. The attenuation between the soil leachate concentration, and groundwater concentration at a receptor well is characterized by considering dilution of leachate in an aquifer, using a water-balance equation, and attenuation in groundwater as contaminants are transported away from the contamination source zone. A "dilution factor", or "dilution attenuation factor (DAF)" is often used to quantify the ratio of the soil leachate concentration to the groundwater concentration at the receptor.

Calculation of USEPA Soil Screening Levels

The SSL is back-calculated from an acceptable groundwater concentration, which may be a maximum contaminant level (MCL) or site-specific target concentration. A DAF of 20 was selected as the default value to estimate the target soil leachate concentration. For metals, the SSL is calculated using a chemical-specific  $K_d$  (Equation 4). Default values for input into Equation 4 are presented in Table 9.

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(Equation 4)

SSL =  $C_w[K_d + \frac{(\theta_w + \theta_a H')}{\rho_b}]$ Where: SSL: Soil Screening Level (mg/kg)  $C_w$ : Target soil leachate concentration (L/kg)  $K_d$ : Partition coefficient for a chemical (cm<sup>3</sup>/g)  $\theta_w$ : Water filled soil porosity ( $L_{water}/L_{soil}$ )  $\theta_a$ : Air filled soil porosity ( $L_{air}/L_{soil}$ ) H': Henry's law constant (where H' = H\*42.3)  $\rho_b$ : soil particle density (kg/L)

**Table 9:** Default input values used in the calculation of USEPA soil screening levels(USEPA 1996a).

Par	ameter	Units	Default
$C_{w}$	Target soil leachate concentration	mg/L	Chemical specific based on acceptable groundwater concentration and DAF
K <sub>d</sub>	Soil-water partition coefficient	L/kg	Chemical specific
$\theta_{\rm w}$	Water-filled soil porosity	Lwater/Lsoil	0.3
$\theta_a$	Air-filled soil porosity	Lair/Lsoil	$n-\theta_w$
$\rho_b$	Dry soil bulk density	kg/L	1.5
n	Soil porosity	L <sub>pore</sub> /L <sub>soil</sub>	$1-(\rho_b/\rho_s)$
$\rho_s$	Soil particle density	kg/L	2.65
Η'	Dimensionless Henry's law constant		Chemical-specific, 0 for all elements except mercury

The use of Equation 4 to calculate soil screening levels requires the assumption of an infinite source of the contaminant (USEPA 1996a). This assumption is required for the calculation of  $K_d$ , as discussed below.

USEPA Soil-water partitioning coefficients

USEPA initially considered the use of single-value soil-water partitioning coefficients calculated with the Freundlich Equation (Equation 5).

 $K_d = C_s (C_w^n)^{-1}$ 

### Where:

K<sub>d</sub>: Freundlich soil/water partition coefficient (L/kg)

C<sub>s</sub>: Concentration sorbed on soil (mg/kg)

 $C_w$ : Solution concentration (mg/L)

n: Freundlich exponent (dimensionless), 1 for linear adsorption

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(Equation 5)

In this approach, the Freundlich exponent was considered equal to 1, and  $C_w$  was equivalent to the target soil leachate concentration. USEPA concluded that the determination of a generic, single-value  $K_d$  value for each metal under consideration was inappropriate because it would not capture the range of conditions at a site.

The decision to calculate metal specific isotherms as part of the derivation of SSLs was largely based on the dependence of sorption on the system pH, presence of clay, organic matter and iron oxides, redox conditions, major ion chemistry, and chemical speciation of the metal. This was supported by a literature review conducted by the USEPA, which identified that metal specific  $K_d$  values varied by up to 7 orders–of-magnitude, depending on system conditions.

MINTEQ2A was utilized to estimate metal-specific isotherms due to the inherent difficulties in determining a generic  $K_d$  value. A general discussion of the use of the MINTEQA2 reaction code to predict contaminant sorption is provided in Section 4; detailed discussions are provided in Alison et al. (1991) and USEPA (1999).

Several assumptions were made by USEPA in creating the sorption isotherms discussed below:

- System equilibrium was assumed. This is a conservative estimate because of the kinetic dependence of desorption in natural systems;
- The redox state of the system was not considered because of the lack of reliable data when the isotherms were modeled;
- Sorbent surfaces were limited to iron oxide and soil organic matter. This assumption could under-predict sorption for soils with significant clay sorption sites, resulting in over-prediction of leachate concentrations; and,
- Metal competition was not considered.

Sorption isotherms modeled by MINTEQA2 were generated for three pH values: 4.9, 6.8 and 8.0. These pH values correspond to the 7.5<sup>th</sup>, 50<sup>th</sup> and 92.5<sup>th</sup> percentiles of 24,921 field measured values in the EPA STORET database. Iron oxide contents were varied based on the analysis of six aquifer samples from a wide geographic area. The lowest iron oxide content measured was considered as the low value, the average the medium value, and the highest the high value. These "variable" geochemical parameters are listed in Table 10.

Value	pH (s.u.)	Iron oxide content (wt.%)	Organic matter content (wt.%)
Low	4.9	0.01	
Medium	6.8	0.31	0.2
High	8.0	1.11	

**Table 10:** Geochemical parameters considered in USEPA SSL modeling effort (USEPA, 1999). Values in bold italics were used to develop parametric, metal specific isotherms.

Parametric isotherms were generated for a number of priority pollutant metals found at hazardous waste sites. Extensive MINTEQA2 modeling conducted by the USEPA indicated that metal mobility was most affected by changes in pH. Iron oxide content is not normally measured as part of site characterization programs. Therefore, parametric isotherms were developed over a range of pH (4.9 to 8.0) under constant iron oxide (0.31 wt%) and organic matter (0.2 wt%) concentrations (USEPA 1996b).

The background pore-water chemistry input into MINTEQ2A was defined based on 13 chemical constituents that commonly occur in groundwater (Table 11). A single total ion concentration was input for each chemical constituent, and pore-water chemistry was assumed to be constant. The value assigned to each pore-water constituent is a median value from a probability distribution obtained from the USEPA STORET database (USEPA, 1999).

Parameter	Concentration (mg/L)
Aluminum	0.2
Bromine	0.3
Calcium	48
Carbonate	187
Chlorine	15
Iron (+3)	0.2
Magnesium	14
Manganese (+2)	0.04
Nitrate	1
Phosphate	0.09
Potassium	2.9
Sodium	22
Sulphate	25

Table 11:	Background porewater chemistry assumed for SSL MINTEQA2 modeling
	efforts (USEPA, 1999).

USEPA isotherms are presented in Table 12, and in Figures 3 and 4. Arsenic (III), chromium (VI), selenium and thallium isotherms are based on laboratory derived, pH-dependent sorption relationships. Isotherms for all other variables were estimated using MINTEQ2A. Extended isotherms used for plots and comparisons are provided in Appendix A.

<b>Table 12:</b>	Partition Coefficients for USEPA Soil Screening Level Guidance (USEPA,
	1996b).

	Estimated K <sub>d</sub>			
Metal	рН 4.9	рН 6.8	рН 8.0	
Antimony		45		
Arsenic (+3)	25	29	31	
Barium	11	41	52	
Beryllium	23	790	100000	
Cadmium	15	75	4300	
Chromium (+3)	1200	1800000	4300000	
Chromium (+6)	31	19	14	
Cyanide		9.9		
Mercury (+2)	0.04	52	200	
Nickel	16	65	1900	
Selenium	18	5	2.2	
Silver	0.1	8.3	110	
Thallium	44	71	96	
Vanadium		1000		
Zinc	16	62	530	
	Isotherm generated using an empirical pH relationship			
	pH-dependent values not available; data taken from Superfund Chemical Data Matrix			

Experimental isotherms for arsenic (III), chromium (VI), selenium and thallium were reported in Loux et al. (1991), and are based on work published in Loux et al. (1989) (Loux, Pers. Comm, March 3, 2005). This work focused on competitive cation partitioning in Wisconsin sand aquifer material (Loux, Pers. Comm.). The physical properties of "Wisconsin Sand" are listed in Table 13. Empirical pH-dependent adsorption relationships are reported in Table 14.

Property	Unit	Measured value
Porosity		0.331
Wet density	g/cm <sup>3</sup>	2.07
Dry density	g/cm <sup>3</sup>	2.6
Specific surface area	m²/g	0.578
Total carbon content	%	0.34
Inorganic carbon content	%	0.17
Organic carbon content	%	0.17
Amorphous iron content	%	0.077
Amorphous manganese content	%	0.0089
Cation exchange capacity	cmol/kg	7.1

**Table 13:** Properties of Wisconsin Sand material used to generate empirical isotherms for As (III), Cr(VI), Se and Tl for USEPA SSL model (as reported in Loux et al. (1989)).

**Table 14:** Empirical pH-dependent adsorption relationships derived by Loux et al.(1990) (USEPA, 1996c).

Metal Species	K <sub>d</sub> (L/kg)
As(III)	10 <sup>(0.0322pH+1.24)</sup>
Cr(VI)	10 <sup>(-0.117pH + 2.07)</sup>
Sb(V)	10 <sup>(-2.07pH + 2.996)</sup>
Se(VI)	10 <sup>(-2.96pH + 2.71)</sup>
Tl	$10^{(0.110\text{pH}+1.102)}$

A discussion of the relation between USEPA-derived  $K_d$  values in 1996 and literature reported  $K_d$  values was provided in USEPA (1996b). This summary is provided as an exhibit in Appendix B.

### 5.1.2 3MRA

The USEPA developed the 3MRA system (Multimedia, Multipathway and Multireceptor Risk Assessment) in response to the 1995 Hazardous Waste Identification Rule (HWIR). The 3MRA system is a series of models for screening-level assessment of human and ecological health risks resulting from chronic exposure to contaminants. The 3MRA system consists of several components integrated into a single framework. A description of the function of the 3MRA model is beyond the scope of this document; detail is provided in USEPA (2003).

Soil matrix-water partitioning is considered within the "Vadose zone and aquifer models" of the 3MRA system. The soil-water partition coefficients are used to predict partitioning from contamination in soil to leachate in the unsaturated zone, and to estimate retardation due to sorption as groundwater migrates from a source zone. The approach to soil-water partitioning adopted for 3MRA was established in EPACMTP, a fate and transport model developed under the HWIR (EPA 1996c). A complete description of the use of partition coefficients in the context of the 3MRA model is provided in USEPA (2003).

Non-linear soil-water partition isotherms were generated using the MINTEQA2 reaction code. The purpose of modeling with MINTEQA2 was to capture the variability of  $K_d$  resulting from heterogeneity in natural systems. In order to represent the variability of geochemical conditions, concentration-dependent partition coefficients were developed for various combinations of four key parameters known to affect metal sorption (master variables). The MINTEQA2 master variables are pH, hydrous ferric oxide (HFO), particulate organic matter (POM) and labile organic matter (LOM). Representative values for master variables were calculated for conditions representing the saturated and unsaturated zones. Table 15 summarizes these values.

Unsaturated zone	pН	HFO	POM	LOM*
	s.u	Fe wt%	wt%	wt%
Low	4.9	0.009	0.034	
Medium	6.8	0.02	0.105	0.00117
High	8	0.05	0.325	

Table 15: Master variables used to calculate non-linear adsorption isotherms for 3MRA.

Saturated zone	pН	HFO	POM	LOM*
	s.u	Fe wt%	wt%	wt%
Low	4.9	0.009	0.02	
Medium	6.8	0.02	0.074	0.00117
High	8	0.05	0.275	

\* LOM held constant at "low" concentration for all model iterations.

Background water chemistry is considered a secondary input value. The background water chemistry was the same as that utilized in the USEPA SSL modeling effort (see Table 11). The ionic strength of the solution was held constant at 0.005 moles for all MINTEQA2 model runs.

Single-value partition coefficients ( $K_d$ ) were determined using the MINTEQA2 data output, where the ratio of the concentration of metal sorbed to the solid phase to the concentration of the dissolved metal at equilibrium was normalized to the mass of soil with which 1 L of solution is equilibrated (USEPA, 2003). Partition coefficients were calculated for sixteen metals, including: arsenic (III), arsenic (V), cadmium, chromium

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(III), chromium (VI), lead, zinc, thallium, selenium, vanadium, silver, barium, beryllium, mercury, nickel and antimony.

Isotherms were generated for each respective metal by MINTEQA2. Partition coefficients were calculated for a series of total metal concentrations ranging from 0.001 mg/L to 10,000 mg/L, in a range of user-defined pH, iron oxide and organic matter conditions. For example, for each model run, the organic matter, pH, and iron oxide conditions were each assigned a respective input parameter of high, medium or low; 44 K<sub>d</sub> values were generated for metal concentrations ranging from 0.001 to 10,000 mg/L based on these primary geochemical input parameters. Two sets of isotherms were developed for each definition of geochemical parameters: one representative of vadose zone (unsaturated) conditions and the other of aquifer (saturated) conditions.

Rather than using the  $K_d$  values generated by MINTEQA2 as input for the calculation of a soil screening level (as in sections 3.0 and 5.1.1.1), 3MRA utilizes data from the isotherms to develop risk assessment predictions. First, non-linear partition coefficient isotherms are plotted as  $K_d$  versus contaminant concentration. If the model is considering vadose zone conditions, a number of  $K_d$  values are averaged to generate a single  $K_d$  value based on the range of metal concentrations expected to be encountered. The aquifer model considers a single  $K_d$  value selected from an isotherm that corresponds to the geochemical conditions expected in the aquifer, and the maximum metal concentration encountered below the water table.

The approach for modeling partition coefficients adopted for 3MRA is considered by USEPA (2005) to be an improvement relative to the 1996 USEPA SSL and EPACMTP approaches, as outlined below:

- Thermodynamic data were appended to and updated within the MINTEQA2 thermodynamic database, making it possible to model the behavior of several additional metals, including arsenic(III), arsenic(V), antimony, beryllium, chromium (VI), cobalt, selenium and vanadium (The USEPA (1996b) modeling approach was restricted to empirical an empirical pH dependent relationship, as discussed in Section 5.1.1.1);
- The database of hydrous ferric oxide sorption reactions was expanded to include sorption reactions for arsenic, antimony, beryllium, chromium (VI), cobalt, selenium and vanadium;
- The database of metal-organic matter reactions was updated and expanded;
- The hydrous ferric oxide content was decreased by a factor of 10. This reduction was warranted based on comparisons of MINTEQA2 estimates of K<sub>d</sub> with literature values;

- The ionic strength was held constant at 0.005 moles for all MINTEQA2 simulations; and,
- Precipitation of trace metal solid phases was not permitted; only solid phases of major ions, such as iron and aluminum oxyhydroxides were allowed to precipitate during MINTEQA2 model runs.

### 5.2 Selected U.S. States

### 5.2.1 Washington State

In Washington State, soil concentrations protective of groundwater are defined by the Washington State Model Toxics Control Act (MTCA) Cleanup regulations, Chapter 173-740. Washington State has worked to establish soil concentrations that will not cause contamination of groundwater at levels that exceed state groundwater cleanup levels.

Under Washington Administrative Code (WAC) 173-340-747, several methods are permitted for derivation of soil concentrations. The reason for providing several methods is to tailor the method to the hazardous substance or site. Methods recommended by Washington State for deriving soil concentrations are outlined in Table 16.

**Table 16:** Washington State recommended methods for deriving soil concentrations for<br/>the protection of groundwater under WAC 173-340-747.

Method		Purpose	Site specific data/material required
1	Fixed parameter three-phase partitioning model	To establish soil concentration for any substance.	No
2	Variable parameter three-phase partitioning model	To establish soil concentration for any substance.	Yes
3	Four-phase partitioning model	Use at sites contaminated with petroleum hydrocarbons, where hazardous substances are present in soil as non-aqueous phase liquids (NAPLs)	Yes
4	Leaching tests	To establish soil concentrations for metals.	Yes
5	Alternative fate and transport models	Fate and transport models other than the three/four phase partitioning model.	Yes
6	Empirical demonstration	To prove that measured soil concentrations will not cause an exceedance of the groundwater cleanup levels.	Yes

Methods 1, 2, 4, 5 and 6 are applicable to metals. Only methods 1, 2 and 4 are considered in detail below; for further detail on legislation in Washington State, refer to WAC 2001.

Methods 1 and 2 (fixed and variable parameter three-phase partitioning model) take an approach similar to that proposed by the USEPA for the derivation of soil concentrations. The fixed approach considers input values to Equation 6 that are considered to be protective under most circumstances. The variable approach considers site-specific input parameters. Equation 6 is used to calculate protective soil concentrations. Table 17 lists input parameters used for Method 1.

$$Cs = Cw (UCF) DF \left[ Kd \; \frac{\theta w + \theta a Hcc}{\rho b} \right]$$
 (Equation 6)

Where:

C<sub>s</sub>: Soil concentration (mg/kg);

C<sub>w</sub>: Groundwater cleanup level established

under WAC 173-340-720 (µg/L);

DF: Dilution factor (dimensionless);

K<sub>d</sub>: Metal partition coefficient;

 $\Theta_w$ : Water-filled soil porosity (mL water/mL soil;

 $\Theta_a$ : Air-filled soil porosity (mL air/mL soil);

H<sub>cc</sub>: Henry's Law constant (dimensionless)

 $\rho_b$ : Dry bulk soil density (kg/L)

Par	Parameter Units		Default		
C w	Target soil leachate concentration	mg/L	Groundwater cleanup level established under WAC 173-340-720		
K <sub>d</sub>	Soil-water partition coefficient	L/kg	Chemical specific		
$\theta_{\rm w}$	Water-filled soil porosity	$L_{water}/L_s$	0.3		
$\theta_a$	Air-filled soil porosity	Lair/Lsoil	0.13		
$\rho_b$	Dry soil bulk density	kg/L	1.5		
Η'	Dimensionless Henry's law constant		Chemical-specific, 0 for all elements except mercury		

 Table 17: Default input values used in the calculation of Washington State soil screening levels (WAC, 2001).

The variable approach considers site-specific conditions, and therefore the values listed in Table 17 are not utilized in the soil concentration calculations.

Metal partition coefficients are provided by WAC 2001 (Table 18). For metals not listed in Table 18,  $K_d$  values may be developed from site data, batch tests or taken from the scientific literature. Calculating a  $K_d$  from site data considers the ratio of the concentration of metal in soil to the concentration of metal in pore water. This approach may not be conservative for all metals or all hazardous sites. The derivation of  $K_d$  values using batch tests is reviewed in Section 4.1.2.1.

<b>Table 18:</b>	Metal partition coefficients recommended for use under WAC 173-340-747
	(WAC, 2001).

Metal	$\mathbf{K_d}^*$
Arsenic	29
Cadmium	6.7
Chromium (total)	1000
Chromium (VI)	19
Copper	22
Mercury	52
Nickel	65
Lead	10000
Selenium	5
Zinc	62

\* Metal K<sub>d</sub> values compiled by Washington State Department of Ecology from multiple sources.

An alternative to using the three-phase partitioning model to determine  $K_d$  values for metals listed in Table 18 is to utilize leaching tests to derive soil concentrations. Two leaching tests are recommended by Washington State: the Synthetic Precipitation Leaching Procedure (SPLP – USEPA Method 1312) and the Toxicity Characteristic Leaching Procedure (TCLP – USEPA Method 1311) (Table 19).

Table 19:	Summary o	f leaching j	procedures	recommen	nded for	the der	ivation	of soil
	co	oncentration	n levels in	Washingto	on State.			

Method		Procedure	Overview	Limitations	
Synthetic Precipitation Leaching Procedure	SPLP	USEPA Method 1312	Soil leached with water with a pH representative of acid rain in the western US (pH 5)	May underestimate groundwater impacts under acidic conditions (pH < 6)	
Toxicity Characteristic Leaching Procedure	TCLP	USEPA Method 1311	Soil leached with water with a pH representative of organic acids generated by biological degradation (pH 4.93).	Intended to represent acidic conditions due to biological degradation in landfills. May underestimate groundwater impacts in alkaline conditions (pH 8)	

Under WAC 173-340-747, it is stated that the analytical method used for the soil leachate must be sensitive enough to quantify hazardous substances at concentrations at the groundwater cleanup level:

- For cadmium, lead and zinc, the effluent concentration must be less than or equal to 10 times the applicable groundwater cleanup level;
- For arsenic, total chromium, chromium (VI), copper, mercury, nickel and selenium, the leaching test effluent concentration must be less than or equal to the applicable groundwater cleanup level.

Further information describing the approach adopted by Washington State for the determination of soil cleanup levels is listed in Chapter 173-340 of WAC 2001.

### 5.2.2 New Jersey

Soil remediation standards protective of groundwater for mobile contaminants were developed in New Jersey in response to the Brownfield and Contaminated Site Remediation Act N.J.S.A. 58:10B-12c(1). Subsurface Soil Cleanup Standards for the Soil-to-Groundwater pathway adopted by the State of New Jersey are outlined in New Jersey Department of Environmental Protection (NJDEP)(2005), and references therein.

The NJDEP, in part, adopted the USEPA Soil Screening Level approach to develop soil cleanup standards (Equation 7). Because the Brownfield and Contaminated Site Remediation Act requires the department to avoid the use of unrealistic or conservative assumptions when determining generic remediation standards, a balance of "conservative" and "typical" values was chosen for input parameters.

- "Conservative" values are protective of groundwater and are reflective of conditions that actually occur in the state; and,
- "Typical" values reflect common conditions, or conditions that are between extremes observed in New Jersey.

As outlined in Section 5.1, the USEPA SSL Equation considers equilibrium partitioning between sorbed (solid), water and air phases. Equation 7 calculates the total amount of contaminant remaining in soil such that the aqueous phase concentration will not exceed the groundwater criteria. A dilution-attenuation factor (DAF) is included to account for soil water dilution upon mixing with groundwater.

$$\begin{split} & IGWSRS = C_{gw} \Biggl\{ K_{d} + \frac{\theta_{w} + \theta_{a} H'}{\rho_{b}} \Biggr\} DAF \\ & DAF = 1 + \frac{Kid}{IL} \end{split}$$

(Equation 7)

# Where:

IGWSRS: Impact to groundwater soil remediation standard (mg/kg)

- C<sub>gw</sub>: Health-based New Jersey groundwater quality criteria (mg/L)
- K<sub>d</sub>: Soil water partition coefficient (L/kg)
- $\Theta_{w}$ : Water-filled soil porosity (L water/L soil)
- $\Theta_a$ : Air filled soil porosity (L air/L soil)
- H<sub>cc</sub>: Henry's Law constant (dimensionless)
- $\rho_b$ : Dry bulk soil density (kg/L)
- DAF: Dilution-attenuation factor
- i: gradient (m/m)
- d: mixing zone depth (m)
- I: Infiltration rate (m/year)
- L: Length of area of concern parallel to groundwater flow (m)
- K: aquifer hydraulic conductivity (m/year)

Default values for use in Equation 7 are listed in Table 20. For parameters that do not follow region-specific trends, such as chemical properties, USEPA default values were adopted. For properties such as soil parameters, values specific to New Jersey conditions were assumed.

Paran	neter	Units	Default
$C_{gw}$	Groundwater criteria	mg/L	Groundwater quality criteria
K <sub>d</sub>	Soil-water partition coefficient	L/kg	Chemical specific
Η'	Dimensionless Henry's law constant		Chemical-specific, 0 for all elements except mercury
рН	Soil pH	s.u.	4.9 or 6.8
	Soil texture		sandy loam
Ν	Soil porosity	v/v	0.41
Foc	Fraction organic carbon	kg/kg	0.002
$\theta_{\rm w}$	Water-filled soil porosity	Lwater/Lsoil	0.23
$\theta_a$	Air-filled soil porosity	Lair/Lsoil	0.18
$\rho_b$	Dry soil bulk density	kg/L	1.5
DAF	Dilution and attenuation factor		12
K*i	Aquifer hydraulic conductivity*gradient	m/year	30
d	Mixing zone depth	m	3.05
Ι	Infiltration rate	m/year	0.28
L	Length parallel to groundwater flow	m	30.5

Table 20:	Default input values for the calculation of New Jersey soil screening levels
	(New Jersey, 2005).

The  $K_d$  values were adopted from values in the USEPA SSL guidance (see Section 5.1, and Table 12). The  $K_d$  values for inorganic contaminants are only considered for pH values of 4.9 and 6.8 (whichever value yields the lowest  $K_d$  value, which is conservative). This pH range was selected because the pH of soil in New Jersey ranges from pH 4 to 6.5. Where  $K_d$  values were not available as part of the USEPA SSL guidance, partition coefficients were adopted from the Superfund Chemical Data Matrix (New Jersey, 2005). A complete list of  $K_d$  values is provided in NJDEP (2005).

The Brownfield and Contaminated Site Remediation Act authorizes the use of Impact to Groundwater Alternative Remediation Standards (IGWARS). The purpose of utilizing IGWARS instead of IGWSRS is to generate site-specific characteristics that produce more accurate remediation values. Site-specific remediation standards recommended in NJDEP (2005) include:

- a. Modification of input parameters to Equation 7 to reflect site-specific data (including pH, soil organic carbon and the DAF) in order to calculate a site specific remediation standard;
- b. Determination if the contaminant of concern is on the Department's list of immobile chemicals; immobile chemicals may not require remediation as they generally do not result in exceedances of groundwater quality criteria;

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- c. Perform the Synthetic Precipitation Leaching Procedure (SPLP) to determine the sitespecific leaching potential for metals. SPLP measures desorption, rather than adsorption, accounting for irreversible adsorption of contaminants to soil. A complete description of how New Jersey utilizes the results of SPLP tests for soil screening level determination is provided as an exhibit in Appendix C;
- d. Conduct transport modeling to calculate a site-specific remediation standard;
- e. Conduct vadose zone and groundwater modeling to calculate a soil remediation standard;
- f. Evaluate site specific groundwater, soil analytical results and water table conditions; if no groundwater impacts are observed, site remediation may not be required.

A complete description of the recommended use of the six alternative strategies for deriving soil standards is provided in NJDEP (2005).

### 5.2.3 New Mexico

The New Mexico Environment Department (NMED) adopted two approaches to develop soil screening levels: a generic model, and a site-specific model (NMED, 2000). Both models use the same set of equations to calculate SSLs based on scenarios that are protective of groundwater. The generic model calculates SSLs using default parameter conditions representative of those expected in New Mexico. The site-specific model utilizes site specific meteorological, soil and hydrological data to calculate SSLs.

Soil leachate SSLs are developed by defining a DAF that accounts for leachate mixing in the aquifer. A leachate concentration protective of groundwater is calculated by multiplying the groundwater standard concentration by the DAF (Equation 8). This leachate concentration is used to calculate a SSL protective of groundwater using an equilibrium partition coefficient ( $K_d$ ). New Mexico utilizes the approach developed by USEPA (1996b) to derive soil-water partition coefficients for input to the leaching to groundwater pathway (Equation 9, Table 21). Further detail related to the development of New Mexico soil screening guidelines is provided in NMED (2000).

 $C_w = WQCC * DAF$ 

(Equation 8)

### Where:

Cw: Target soil leachate concentrations; mg/L WQCC: Water quality control concentration (water quality standard); mg/L DAF: Dilution attenuation factor SSL =  $C_w[K_d + \frac{(\theta_w + \theta_a H')}{\rho_b}]$ Where: SSL: Soil Screening Level (mg/kg)  $C_w$ : Target soil leachate concentration (L/kg)  $K_d$ : Partition coefficient for a chemical (cm<sup>3</sup>/g)  $\theta_w$ : Water-filled soil porosity (L<sub>water</sub>/L<sub>soil</sub>)  $\theta_a$ : Air-filled soil porosity (L<sub>air</sub>/L<sub>soil</sub>) H': Henry's law constant (where H' = H\*42.3)  $\rho_b$ : soil particle density (kg/L)

**Table 21:** Default input values used in the calculation of New Mexico soil screening levels (NMED, 2000).

Parameter		Units	Default
$C_{\rm w}$	Target soil leachate concentration	mg/L	Chemical specific maximum contaminant level
K <sub>d</sub>	Soil-water partition coefficient	L/kg	Chemical specific
$\theta_{\rm w}$	Water-filled soil porosity	L <sub>water</sub> /L <sub>soil</sub>	0.26
$\theta_{a}$	Air-filled soil porosity	L <sub>air</sub> /L <sub>soil</sub>	$n-\theta_w$
$\rho_b$	Dry soil bulk density	kg/L	1.5
n	Soil porosity	L <sub>pore</sub> /L <sub>soil</sub>	$1-(\rho_b/\rho_s)$
$\rho_{s}$	Soil particle density	kg/L	2.65
Η'	Dimensionless Henry's law constant		Chemical-specific, 0 for all elements except mercury

# 6.0 SUMMARY, EVALUATION AND IMPLICATIONS OF REGULATORY APPROACHES FOR THE METAL-GROUNDWATER PATHWAY

The purpose of this section is to summarize and compare methods for estimating soilmetal partition coefficients used to derive soil screening levels. The intent is to evaluate the current CSST protocol in light of scientifically-defensible methods utilized in other jurisdictions. The implications of adopting similar approaches to determine soil-water partition coefficients are considered and recommendations are provided.

# 6.1 Overview of regulatory methods of soil-water metal partition coefficient determination

Soil screening levels are calculated based on unsaturated zone partitioning of metals from soil to pore-water. Appendix D presents a comparison of three regulatory approaches of deriving soil-water partitioning coefficients. The province of British Columbia utilized

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the Contaminated Sites Soil Task group (CSST) protocol to generate soil screening levels for six metals. The CSST protocol is based on draft USEPA Soil Screening guidance published in 1994 (CSST 1996).

In 1996, USEPA published a protocol for derivation of soil screening standards for 15 metals based on soil-water partitioning coefficients calculated for standard geochemical conditions (USEPA, 1996b). This effort utilized MINTEQA2 to develop soil-water partitioning coefficients based on surface complexation of metals to charged iron oxide surfaces. The USEPA developed  $K_d$  values for three specific pH conditions: 4.9, 6.8 and 8.0.

The CSST (1996) / USEPA (1996b) approach was developed with the intent of developing standard site/soil independent metal partitioning coefficients for soil screening level prediction. A downfall of the USEPA / CSST approach is that metal Kd results were parameterized only for pH under a set of standard iron oxide and organic matter input representative of average conditions in the United States. Sorbtive substrates including clay minerals, Mn-oxides and carbonate minerals were not considered.

The 3MRA approach of deriving  $K_d$  values is the most transparent of all methods reviewed (USEPA 1996c, USEPA 2003). Soil-water metal partition coefficients are utilized in 3MRA for multi-pathway risk assessment. The 3MRA model utilized MINTEQA2 to calculate partitioning coefficients for metal concentrations ranging from 0.001 to 10,000 mg/L. The results were further parameterized according to hydrous ferric oxide (HFO), particulate organic matter (POM) and labile organic matter (LOM) content. The advantage of the 3MRA approach is that the results are parameterized for a variety of site conditions, and all modeling was completed with MINTEQA2 to generate non-linear isotherms.

Regulatory jurisdictions within the United States, including Washington State, New Jersey, and New Mexico have adopted parts of the USEPA SSL method of soil screening level prediction. All three jurisdictions use variations of Equation 4 to generate soil screening levels. The approach to metal partitioning for the purpose of generic soil screening levels is approximately the same in all jurisdictions: New Jersey uses a combination of USEPA SSL and Superfund Chemical Data Matrix partition coefficients, New Mexico has adopted the USEPA SSL partition coefficients and Washington State provides a set of non-parameterized partition coefficients developed by the Washington Department of Ecology. In addition, New Jersey and Washington State provide a number of options for developing site-specific soil screening levels. Site-specific soil screening level may be generated by utilizing site specific data in the USEPA soil screening level equation, or by conducting chemical mobility. Site-specific soil screening levels are

based on the behavior of a given metal under specific physical and chemical conditions, therefore this method is limited by the fact that values cannot be used to generate generic soil screening levels.

A comparison of partitioning coefficients utilized by CSST (1996), USEPA (1996b), 3MRA (2003) and standard literature values is presented in Table 22. It should be noted that the literature values presented in Table 22 were generated for a wide variety of site conditions, using various testing methods.

### 6.2 Evaluation of CSST soil-water partitioning coefficients

6.2.1 Chromium (VI)

Metal-water partitioning coefficients for chromium (VI) presented in CSST (1996) and USEPA (1996b) are fundamentally similar, as they were developed based on results of empirical pH-K<sub>d</sub> relationships (Figure 5). This isotherm was developed in an empirical system that contained 0.34 % total carbon (0.17 wt% total organic carbon), and 0.077 wt% amorphous iron oxide (Loux, Pers. Comm., March 3, 2005). In summary:

- CSST and USEPA isotherms show very little variation with pH. The Cr(VI)  $K_d$  varies from 31.4 to 13.6 L/kg over a pH range from 4.9 to 8.
- Literature K<sub>d</sub> values for chromium (VI) are orders of magnitude higher than those reported in CSST / USEPA (Table 22). This reflects the variability of soil-water partitioning in response to site-specific conditions.

Chromium (VI) isotherms generated as part of 3MRA are presented in Figures 6 and 7. The USEPA input assumptions correspond roughly to medium particulate organic matter and high hydrous ferric oxide conditions simulated in 3MRA. The purpose of these plots is to demonstrate the dependence of Cr (VI) sorption on site-specific parameters. Chromium (VI) sorption is complex and appears to be affected by both iron oxide and POM concentrations. In summary:

• 3MRA K<sub>d</sub> values decrease with increasing pH. 3MRA K<sub>d</sub>s are less than the CSST isotherms in circumneutral to weakly alkaline pH conditions with 0.05 wt% Fe This relationship is outlined in Table 22. 3MRA Kd values are less than CSST values under the range of modeled pH conditions where the iron oxide concentration equals 0.0009 wt%.

### 6.2.2 Arsenic (III)

Metal-water partitioning coefficients for arsenic (III) were also developed based on results of empirical pH-K<sub>d</sub> relationships (Figure 8). As for Cr(VI), the isotherm was developed in an empirical system that contained 0.34 % total carbon (0.17 wt% total

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organic carbon), and 0.077 wt% amorphous iron oxide (Loux, Pers. Comm., March 3, 2005). In summary:

- The arsenic (III)  $K_d$  varies from 25 to 31.4 L/kg over a pH range from 4.9 to 8.
- Literature  $K_d$  values for arsenic (III) may be up to 25 times greater than those recommended in CSST / USEPA guidance (Table 22).

Arsenic (III) isotherms generated as part of 3MRA are presented in Figure 9. The USEPA input assumptions correspond roughly to medium particulate organic matter and high hydrous ferric oxide conditions simulated in 3MRA. Arsenic (III) sorption appears to be controlled primarily by the iron oxide content, and secondarily by the pH of the system; POM has little impact on arsenic sorption. In summary:

- 3MRA Kd values are lower than the CSST / USEPA isotherms where the iron oxide concentration equals 0.0009 wt%.
- 3MRA  $K_d$  values are greater than the CSST isotherms in circumneutral to weakly alkaline pH conditions with 0.02 to 0.05 wt% Fe, as outlined in Table 22.

### 6.2.3 Zinc

Figure 10 compares the CSST-recommended isotherms for zinc to the USEPA (1996b) isotherm. Generally, at pH less than 6, USEPA  $K_d$  values are higher than CSST, and are less conservative. In higher pH conditions, CSST isotherms are slightly less conservative than USEPA (1996b) recommended values. In summary:

• The wide range of partitioning coefficients adopted by CSST (1.6 to 15849 L/kg) corresponds well with the range presented in literature (Table 22).

Zinc was further analyzed to summarize the impact of conservative input estimates for metal  $K_d$  generation. Figures 11 and 12 present isotherms developed for a number of iron oxide, particulate and pH conditions in the vadose zone. As demonstrated in Figures 12 and 13, zinc sorption behavior varies as a function of iron oxide and particulate organic matter concentrations, and pH. General comparisons of zinc isotherms as developed using pH as the sole variable parameter, and POM / HFO / pH as variable parameters are provided below. In summary:

• Zinc soil-water partitioning coefficients generated by USEPA (1996b)/3MRA are generally lower than the CSST values in circumneutral to weakly alkaline pH conditions, and are therefore more conservative. In low pH conditions (pH 4.8), the 3MRA and USEPA K<sub>d</sub> values are generally greater than the CSST values.

### 6.2.4 Cadmium

Figure 13 compares the CSST-recommended isotherms for cadmium to the USEPA (1996b) isotherms. Generally, at pH less than 6.6, USEPA  $K_d$  values are higher than CSST, and are less conservative. CSST isotherms are slightly less conservative than USEPA(1996b) recommended values where the pH is greater than 6.6. In summary:

• Cadmium partitioning coefficients reported by CSST for a pH range of 4.9 to 8.0 range from 0.6 to 4597 L/kg, which agrees well with USEPA values ranging from 0.61 to 4467 L/kg. However, CSST (1996) reports a cadmium  $K_d$  of 56234 L/kg for pH 8.1, which does not correlate with either the trend reported by CSST or the USEPA (1996b) values.

### 6.2.5 Copper

Copper isotherms were not generated as part of the USEPA SSL or 3MRA efforts. USEPA SSLs were intended for use in modeling fate and transport at waste disposal facilities where copper was not considered a priority pollutant (Jerry Allison, Pers. Comm.).

There is no background information describing the derivation of CSST copper partitioning coefficients. CSST copper Kd values range from 39.8 L/kg (pH 4.9) to 25119 L/kg (pH 8). Further, CSST recommends the use of copper isotherms as surrogates for lead  $K_d$  values. Copper is generally more mobile than lead in aqueous systems.

### 6.2.6 Lead

Lead isotherms were not generated as part of the USEPA SSL effort. However, 3MRA considered lead soil-water partitioning. Results of 3MRA modeling are presented as part of Figures 14 through 16. Lead has the highest  $K_d$  values of all metals modeled as part of the 3MRA (Jerry Allison, Pers. Comm). 3MRA lead partition coefficients presented in Table 23 are generally less conservative than CSST isotherms. Therefore, the use of copper  $K_d$  values as surrogates for lead partitioning is not defensible or conservative.

The CSST recommended lead  $K_d$  values range from 39.8 to 25119 L/kg. As outlined in Figure 14, 3MRA lead partition coefficients are generally higher than those predicted by CSST. In comparison to the parameterized results generated by 3MRA, CSST lead partition coefficients are overly conservative (ie. Lower  $K_d$  values) in circumneutral to weakly alkaline pH (6.8 to 8), medium to high iron oxide concentration (0.02 to 0.05 wt %) systems (Figures 15, 16). 3MRA  $K_d$  values are generally greater than those proposed by CSST.

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### 6.3 Limitations to current regulatory approaches

Several limitations exist with respect to the use of empirical and MINTEQA2-derived soil-water partition coefficients:

- The result of the USEPA (1996b) modeling effort has been the creation of a generic partition coefficient "look-up table", parameterized for pH assuming constant geochemical conditions. Not taking into account the diversity in site conditions may result in under- or over-estimation of actual partition coefficients in natural soils.
- The result of the 3MRA modeling effort (USEPA 2003) was a more transparent, parametric approach to Kd determination, conducted for a large dataset of metals, where the effect of varying different master geochemical parameters was evaluated. The 3MRA assumptions may not necessarily be suited for site conditions in British Columbia.
- In many cases, the Kd values generated using average HFO and POM concentrations during the USEPA SSL effort vary over orders-of-magnitude from those predicted using parameterized HFO and POM in the 3MRA effort. This highlights the difficulty in predicting metal mobility based on certain default geochemical conditions and input parameters.
- Neither the USEPA or 3MRA approaches account for metal sorption on clays, manganese oxides or carbonate minerals. Therefore, these models may under-predict sorption with respect to natural conditions.
- As illustrated in Table 22, the natural variability of empirical K<sub>d</sub> values is quite large for each metal. The USEPA (1996b) and 3MRA MINTEQA-2 isotherms are both higher and lower than the empirical values. This highlights the uncertainty in defining a standard K<sub>d</sub> parameter set. Varying K<sub>d</sub> parametrically with respect to pH (as in CSST, 1996 and USEPA 1996b) in some cases fails to produce results with a range comparable to literature values. However, this does not necessarily indicate a failure on the part of the CSST / USEPA approach, as literature values may also be biased towards conditions that may not be representative of "typical" sites.

### 6.4 Discussion and Recommendations

The USEPA (1996b) partition coefficients were developed following an in-depth review of methods for predicting metals partitioning and comparison to empirical data, although the database of test data used to estimate the mean HFO (six samples) was limited. There are significant limitations associated with the USEPA approach, as described above; however, for the purposes of deriving generic soil standards, there does not appear to be a

better approach that would be practical for use in British Columbia. This is reflected in guidance from several other regulatory jurisdictions, which essentially have adopted the USEPA pH-dependent isotherms. Discussions with the experts (Jerry Allison, Allison Geoscience; Robert Truesdale, RTI International) who were instrumental in developing the USEPA and 3MRA guidance over the past decade also indicate for generic standard purposes, it would be difficult to improve upon the USEPA approach, in the absence of site specific data for key geochemical parameters.

The 3MRA isotherms provide additional flexibility through a parameterized approach based on site-specific pH, pore-water metal concentration, iron oxide concentration, and organic matter concentrations. While use of the 3MRA approach could be useful for sitespecific development of standards, it is not considered practical for development of generic soil standards since parameters such as iron oxide and organic matter content are not measured in typical site investigations in British Columbia. Also, it is noted that the 3MRA iron oxide contents are considerably lower than those presented in literature (Battelle, 1989) and in previous models (USEPA, 1996b). These lower iron oxide contents may be overly conservative with respect to natural conditions in British Columbia.

The 3MRA isotherms are useful in a general sense in terms of providing information that could be used to benchmark the USEPA isotherms. In approximate terms, the 3MRA isotherms are similar the USEPA isotherms for similar input values and low concentration ranges.

Neither USEPA or 3MRA include isotherms for copper. CSST recommends an isotherm for copper, however it's genesis is not documented. It is not suggested that the current CSST isotherm be adopted for further modeling efforts. Rather, it is recommended that a suitable isotherm be developed for copper partitioning using the MINTEQA2 thermodynamic database (1996b). Iron oxide and organic matter concentrations should be based on average concentrations detected in B.C. soils.

The CSST protocol assumed that the  $K_d$  isotherm for copper could be used as a surrogate for lead partitioning. This is not considered scientifically defensible, as copper and lead behave quite differently in natural environments. Copper is considerably more mobile than lead and therefore, the lead isotherms recommended by CSST are not conservative. There is no USEPA isotherm for lead; therefore, it is recommended that a suitable isotherm be developed for lead partitioning using the MINTEQA2 thermodynamic database. Iron oxide and organic matter concentrations should be based on average concentrations detected in B.C. soils.

An alternative approach is to adopt a "multi-tiered" system of site investigation, such as those in place in Washington State and New Jersey. In these jurisdictions, regulations provide the option of using a generic set of soil screening levels (USEPA SSLs in New Jersey, or single value  $K_{ds}$  recommended by the Department of Ecology in Washington State). However, several other site-specific methods of developing soil screening levels are provided for use, including the option of using site-specific geochemical parameters to develop partitioning coefficients, or the use of leach tests to develop soil screening levels or partitioning coefficients. A similar protocol involving leaching tests to evaluate metals partitioning has been developed by the Science Advisory Board (SAB) of British Columbia. However, this type of framework can not be easily used to develop generic soil standards.

### Recommendations

- Adopt the partition coefficients recommended by USEPA (1996b) for the following metals: antimony; arsenic(III); barium; beryllium; cadmium; chromium(III); chromium (VI); cyanide; mercury (II); nickel; selenium; silver; thallium; vanadium; and, zinc (Tables 22a and 22b).
- Develop an isotherm for lead using the MINTEQA2 thermodynamic database, assuming iron oxide and organic matter input values representative of conditions encountered at contaminated sites in British Columbia. An interim K<sub>d</sub> isotherm was derived using 3MRA isotherms for "mid-range" iron oxide and "high range" organic matter conditions, with an iron oxide concentration of 0.05 wt% and organic matter concentration of 0.33 wt%.
- Develop an isotherm for copper partitioning using MINTEQA2 thermodynamic database, assuming conditions representative of iron oxide and organic matter concentrations at contaminated sites in British Columbia.

### 6.5 Implications

The implications of the above recommendations are evaluated through comparison of example soil standards for protection of aquatic life pathway, calculated using the CSST-recommended metal partitioning coefficients and USEPA Soil Screening Level partitioning coefficients (Table 23). The soil standards in Table 23 are developed for pH ranges recommended in the CSR matrix standards (Schedule 5). The soil standard was back-calculated using Equation 11, using a dilution attenuation factor (DAF) of 3.29, which was the factor using for the CSST derivation of soil standards.

The comparison in Table 23 present both the CSST and USEPA  $K_{ds}$  used as input (Columns 6 and 10), and the calculated soil standards (Columns 7 and 11). The soil standards are equal to the sum of the soil-based standard and the background soil concentration.

(Equation 11)

$$C_{s} = C_{L} * DAF * \left\{ K_{d} + \left(\frac{n_{u}}{\rho_{b}}\right) \right\}$$

## Where:

C<sub>s</sub>: Calculated toxicity based soil standard (Columns 6 and 10)

C<sub>L</sub>: Receptor groundwater concentration

DAF: Dilution attenuation factor (3.29)

K<sub>d</sub>: Soil-water metal partition coefficient (L/kg) (Columns 5

and 9)

- n<sub>u</sub>: Water filled porosity (0.1)
- $\rho_b$ : Dry bulk density of soil (g/cm<sup>3</sup>) (1.75)

For metals that were considered by both CSST and USEPA (1996b), the comparison indicates:

- 1. The example soil standards for arsenic (III) and chromium (VI) are virtually identical within a pH range of 5 to 8.
- 2. The example soil standards for cadmium and chromium (III), calculated using the USEPA K<sub>d</sub> values, are higher than the CSST derived standards.
- 3. The example lead soil standards, calculated using 3MRA isotherms based on an iron concentration of 0.05 wt% and an organic matter concentration of 0.33 wt%, are lower than the CSST derived standards.
- 4. The example zinc soil standard, calculated using the USEPA  $K_d$  values, is slightly greater than the CSST derived standard at pH less than 6.0, but are less than the CSST standards above pH of 6.0.

USEPA  $K_d$  values and example soil standards for chromium (III), mercury and nickel, which are not included in the CSST (1996) protocol, are provided in Table 23.

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- Washington Administrative Code, 2001. Model Toxics Control Act, Cleanup Regulation, Chapter 173-340 WAC. Publication No. 94-06. Amended February 12, 2001.

 Table 3

 Partition Coefficients for BCE Groundwater Model (CSST, 1996).

	K <sub>d</sub> **	K <sub>d</sub>	K <sub>d</sub> **	K <sub>d</sub>	K <sub>d</sub> *	K <sub>d</sub>
рн	As(+3)	Cd	Cr(+6)	Cu(+2)	Pb	Zn (+2)
4.5	24.3		35			
4.6	24.4		34			
4.7	24.6		33.1			
4.8	24.8		32.2			
4.9	25	0.8	31.4	39.8	*	1.6
5.0	25.2	0.9	30.5	50.1	*	1.8
5.1	25.4	1	29.7	63.1	*	2
5.2	25.6	1.1	28.9	79.4	*	2.2
5.3	25.7	1.3	28.2	100	*	2.5
5.4	25.9	1.5	27.4	126	*	3.2
5.5	26.1	1.7	26.7	158	*	4
5.6	26.3	2	26	219	*	5
5.7	26.5	2.5	25.3	302	*	6.3
5.8	26.7	3.2	24.6	417	*	8.6
5.9	26.9	4	24	575	*	11.7
6.0	27.1	5	23.3	794	*	15.8
6.1	27.3	7.5	22.7	1148	*	24
6.2	27.5	11.2	22.1	1660	*	36.3
6.3	27.7	16.8	21.5	2399	*	55
6.4	27.9	25.1	21	3467	*	83.2
6.5	28.1	36.9	20.4	5012	*	126
6.6	28.3	54.1	19.9	6310	*	191
6.7	28.6	79.4	19.3	7943	*	288
6.8	28.8	117	18.8	10000	*	437
6.9	29	171	18.3	12589	*	661
7.0	29.2	251	17.8	15849	*	1000
7.1	29.4	355	17.4	17783	*	1380
7.2	29.6	501	16.9	19953	*	1905
7.3	29.9	708	16.4	22387	*	2630
7.4	30.1	972	16	25119	*	3631
7.5	30.3	1334	15.6	25119	*	5012
7.6	30.5	1830	15.2	25119	*	6310
7.7	30.8	5512	14.8	25119	*	7943
7.8	31	3073	14.4	25119	*	10000
7.9	31.2	3758	14	25119	*	12589
8.0	31.4	4597	13.6	25119	*	15849
8.1	31.7	56234	13.3			19953
8.2	31.9		12.9			
8.3	32.2		12.6			
8.4	32.4		12.2			
8.5	32.6		11.9			

\* Pb values assumed to be the same as those presented for copper.

\*\* Derived based on empirical Kd-pH relationship.

Kd values equal to those presented in USEPA 1996b.

Kd values less than USEPA 1996b.

Kd values greater than USEPA 1996b.

Summary of the use of batch tests and flow through column methods to developing soil-water partition coefficients (adopted from USEPA, 1999).

Model	Assumptions	Formula	Advantages	Disadvantages
Batch tests	<ol> <li>The rate of adsorption is assumed to equal the rate of desorption;</li> <li>Only one type of adsorption site, and one type of dissolved contaminant exists;</li> <li>The activity of the solid is equal to 1;</li> <li>Equilibrium is maintained during the mixing period;</li> <li>No adsorption on suspended colloids occurs; and,</li> <li>No precipitation of the contaminant phase occurs.</li> </ol>	$\begin{split} \mathbf{K}_{d} &= \frac{\mathbf{V}_{w}(\mathbf{C}_{o} - \mathbf{C}_{i})}{\mathbf{M}_{sed}\mathbf{C}_{i}} \\ \textbf{Where:} \\ \mathbf{K}_{d}:  \text{Partition coefficient} \\ \mathbf{V}_{w}:  \text{Solution volume} \\ \mathbf{C}_{o}:  \text{Initial concentration of} \\ \text{contaminant in solution} \\ \mathbf{C}_{i}:  \text{Final concentration of} \\ \text{contaminant in solution} \\ \mathbf{M}_{sed}:  \text{Mass of soil sample} \end{split}$	<ul> <li>Inexpensive, fast, and simple methodology.</li> <li>Procedure is easily varied to address the system in question</li> <li>If a number of batch tests are performed using a variable input concentration, an isotherm can be generated which can be input to the Langmuir or Freundlich models.</li> </ul>	<ul> <li>No distinction of how the sorbate is associated with the soil (adsorption, absorption or precipitation).</li> <li>Equilibrium and reaction reversibility, are rarely maintained when adsorption is measured in the lab.</li> <li>Physical variations such as particle size distribution, method of solute addition, solid-solution separation methods, and temperature can result in large variability in results.</li> <li>Mixing is rarely achieved.</li> <li>Desorption is the dominant process in contaminant transport, and desorption processes are much slower than adsorption. Therefore, the measurement of adsorption in solution may result in overly conservative estimates of K<sub>d</sub>.</li> <li>The speciation of the inorganic phase in solution may impact it's sorption tendency in natural systems.</li> </ul>
Flow through columns	<ol> <li>There is a relationship between Kd and the retardation factor (Rf); and,</li> <li>Water flow and contaminant dispersion in the system are constant.</li> </ol>	$\begin{split} R_{f} &= \frac{n}{n_{e}} + \frac{K_{d}\rho_{b}}{n_{e}} \\ R_{f} &= 1 + \frac{K_{d}\rho_{b}}{n_{e}} \\ R_{f} &= 1 + \frac{K_{d}\rho_{b}}{n} \\ R_{f} &= 1 + \frac{K_{d}\rho_{b}}{\theta} \\ \hline \textbf{Where:} \\ R_{f} &= Retardation factor \\ K_{d}: Partition coefficient \\ n: Total porosity \\ n_{e}: Effective porosity \\ \theta: Volumetric water content in \\ vadose zone \\ \rho_{\circ}: Bulk density \end{split}$	- Sorption can be measured under the simulation of field conditions, hydrodynamic effects (dispersion) and chemical phenomena (multiple species and reaction reversibility).	<ul> <li>Flow through systems are rarely at equilibrium therefore results are specific to the flow conditions the experiment was performed under.</li> <li>It is known that measured Kd varies with flow velocity and column dimensions.</li> <li>Equipment is expensive, and experiments are complicated and time consuming (USEPA, 1999).</li> </ul>

# Table 22 Comparison of $K_d$ values reported in literature to CSST, USEPA and 3MRA $K_d$ values (adapted from USEPA 1996b).

	AECL	Baes and Sh	arn (1983) or	Coughtrey et al	Batelle	CSST*	USEDA*	
Metal	(1990) <sup>a</sup>	Baes et al (1984) <sup>b</sup>		(1985) <sup>c</sup>	(1989) <sup>d</sup>	(1996)	(1996b)	3MRA**
	Range	Geometric mean	Range	Range	Range	Range	Range	Range
Antimony	45-550	45 <sup>f</sup>			2.0-15.9			
Arsenic <sup>e</sup>		$200^{\rm f}$			5.86-19.4			
Arsenic (+3)		3.3 <sup>g</sup>	1.0-8.3			24.3 - 32.6	23.4 - 33.9	0.64 - 343 <sup>i</sup>
Arsenic (+5)		6.7 <sup>g</sup>	1.9-18					
Barium		60 <sup>f</sup>			530-16000		2.7 - 53.1	
Beryllium	250 - 3000	650 <sup>f</sup>			70-8000		6.6 - 112202	
Cadmium	2.7 - 17000	6.4 <sup>h</sup>	1.26-26.8	32-50	14.9-567	0.8 - 56234	4.1 - 4467	
Chromium	1.7 - 2517	850 <sup>f</sup>						
Chromium (+2)		2200 <sup>g</sup>	470-150000					
Chromium (+3)					168-3600		60.3 - 4216965	
Chromium (+6)		37 <sup>g</sup>	1.2-1800		16.8-360	11.9 - 35	10.5 - 40	0.02 - 10587 <sup>i</sup>
Copper						39.8 - 25119		
Lead						39.8 - 25119		39 - 738031 <sup>j</sup>
Mercury <sup>e</sup>		$10^{\rm f}$			322-5280		0.001 - 200	
Nickel	60 - 4700	150 <sup>f</sup>		~20	12.2-650		4.1 - 1884	
Selenium	150 - 1800	300 <sup>f</sup>		<9	5.9-14.9			
Silver	2.7 - 33000	46 <sup>h</sup>	10-1000	50	0.4-40.0		0.01 - 112.2	
Thallium		1500 <sup>f</sup>			0.0-0.8		35.1 - 123	
Vanadium		1000 <sup>f</sup>			50-100.0			
Zinc	0.1 - 100000	38 <sup>h</sup>	0.1-8000	>/= 20		1.6 - 19953	5.3 - 531	0.65 - 3678 <sup>j</sup>

a The Atomic Energy of Canada, Limited (AECL, 1990) presents the distribution of Kd values according to four major soil types-sand, silt, clay, and organic material. Their data were obtained from available literature.

**b** Bases et al. (1984) present Kd values for approximately 220 agricultural soils in the **pH** range of 4.5 to 9. Their data were derived from available literature and represent a diverse mixture of soils, extracting solutions, and laboratory techniques.

c Coughtrey et al. (1985) report best estimates and ranges of measured soil Kd values for a limited number of metals.

**d** Battelle Memorial Institute (Battelle, 1989) reports a range in Kd values as a function of **pH** (*5 to 9*) and **sorbent content** (a combination of clay, aluminum and iron oxyhydroxides, and organic matter content). The sorbent content ranges were <10 percent, 10 to 30 percent, and >30 percent sorbent . Their data were based on available literature.

e The valence of these metals is not reported in the documents.

f Estimated based on the correlation between Kd and soil-to-plant concentration factor (Bv).

g Average value reported by Baes and Sharp (1983).

h Represents the median of the logarithms of the observed values.

\* CSST and USEPA isotherms reported for a pH range of 4.5 to 8.5 and 4 to 9, respectively.

\*\* 3MRA isotherms only presented for 4 metals for the purpose of comparison. Note that isotherms are available for 16 metals as part of 3MRA database. **i HFO** 0.0009 to 0.05 wt%, **POM** 0.11 wt%, **pH** 4.8 - 8

j HFO 0.0009 to 0.05 wt%, POM 0.03 to 0.33 wt%, pH 4.8 - 8

Table 23
Comparison of soil screening levels calculated with CSST- and USEPA-recommended soil-water partition coefficients

		1	2	3	4	5	6	7	8	9	10	11	12	13
		CSR Standards			CSST Inputs (Transient Model)						USEPA SSL 1996 (Steady State Model)			
	Receptor	Background	pH for	CSR	pН	CSST	DAF	DAF	Calc. Tox	Calculated	pН	USEPA	Calc. Tox	Calculated
	Groundwater	Soil	Matrix	Matrix	for Kd	1996	@ 100	@ 2200	based Soil	CSST Input	USEPA	SSL	based Soil	USEPA Input
Metal	Concentration'	Concentration <sup>2</sup>	Standard	Standard <sup>®</sup>	Table B-2*	K <sub>d</sub> ⁴	years	years	Standard <sup>®</sup>	Standard <sup>®</sup>	SSL	K <sub>d</sub> ′	Standard	Standard <sup>®</sup>
	(mg/L)	(mg/kg)		(mg/kg)		(L/kg)			(mg/kg)	(mg/kg)		(L/kg)	(mg/kg)	(mg/kg)
Arsenic	0.05	14.9	N/A	20	5	25.2	3.29	3.29	4.15	19.1	5	27.0	4.45	19.3
111	0.05	14.9	N/A	20	6	27.1	3.29	3.29	4.47	19.4	6	29.1	4.80	19.7
	0.05	14.9	N/A	20	7	29.2	3.29	3.29	4.81	19.7	7	29.5	4.86	19.8
	0.05	14.9	N/A	20	8	31.4	3.29	3.29	5.17	20.1	8	31.6	5.21	20.1
Cadmium	0.0006 9	1.3	<7	2	7	251	125	3.29	0.50	1.8	7	118.9	0.23	1.5
	0.0006	1.3	7 to < 7.5	2.5	7.25	604.5	4.65E+05	3.29	1.2	2.5	7.25	251.2	0.50	1.8
	0.0006	1.3	7.5 to 8	25	7.75	2792.5	Out of range	9.13	15	17	7.75	1631.2	3.2	4.5
	0.0006	1.3	>= 8	150	8	4597	Out of range	49.2	136	137	8	4466.8	8.8	10
Chromium	0.09	58.9	N/A	65	N/A	N/A	N/A	N/A	N/A	N/A	5	1995.3	591	650
111	0.09	58.9	N/A	65	N/A	N/A	N/A	N/A	N/A	N/A	6	211348.9	62580	62639
	0.09	58.9	N/A	65	N/A	N/A	N/A	N/A	N/A	N/A	7	2511886.4	743770	743828
	0.09	58.9	N/A	65	N/A	N/A	N/A	N/A	N/A	N/A	8	4466835.9	1322630	1322689
Chromium	0.01	58.9	N/A	60	5	30.5	3.29	3.29	1.01	59.9	5	30.7	1.01	60
VI	0.01	58.9	N/A	60	6	23.3	3.29	3.29	0.77	59.7	6	29.9	0.99	60
	0.01	58.9	N/A	60	7	17.8	3.29	3.29	0.59	59.5	7	18.0	0.59	59
	0.01	58.9	N/A	60	8	13.6	3.29	3.29	0.45	59.3	8	13.9	0.46	59
Copper	0.09 10	74	<5.0	90	5	50.1	3.42	3.29	14.9	88.9	N/A	N/A	N/A	N/A
	0.09	74	5.0 to 5.5	100	5.25	89.7	4.98	3.29	26.6	101	N/A	N/A	N/A	N/A
	0.09	74	5.5 to 6	200	5.75	359.5	1511	3.29	106	180	N/A	N/A	N/A	N/A
	0.09	74	6 to <6.5	1500	6.25	2029.5	Out of range	5.15	940.70	1015	N/A	N/A	N/A	N/A
	0.09	74	>=6.5	30000	6.5	5012	Out of range	74	33380.30	33454	N/A	N/A	N/A	N/A
Nickel	1.1	N/A	N/A	100 to 500	N/A	N/A	N/A	N/A	N/A	N/A	5	17.4	63.2	63.2
	1.1	N/A	N/A	100 to 500	N/A	N/A	N/A	N/A	N/A	N/A	6	38.9	141.0	141
	1.1	N/A	N/A	100 to 500	N/A	N/A	N/A	N/A	N/A	N/A	7	87.1	315	315
	1.1	N/A	N/A	100 to 500	N/A	N/A	N/A	N/A	N/A	N/A	8	1883.6	6817	6817
Lead	0.11 11	108.6	<5.5	150	5.5	158	16.7	3.29	57.20	166	5.5	280	101.4	210
	0.11	108.6	5.5 to 6	250	5.75	359.5	1494	3.29	130.12	239	5.75	700	253.4	362
	0.11	108.6	6 to <6.5	2000	6.25	2029.5	Out of range	5.15	1149.74	1258	6.25	3000	1085.7	1194
	0.11	108.6	>=6.5	40000	6.5	5012	Out of range	74	40798.15	40907	6.5	10200	3691.4	3800
Zinc	0.9 12	138.1	<6.0	150	6	7.45	3.29	3.29	22.23	160	6	37.6	111.5	250
	0.9	138.1	6 to <6.5	300	6.25	45.65	3.37	3.29	135.34	273	6.25	43.4	129	267
	0.9	138.1	>6.5 to <7	1500	6.75	362.5	1650	3.29	1073.53	1212	6.75	61.3	182	320
	0.9	138.1	>=7	3000	7	1000	Out of range	6.06	5454.31	5592	7	75.0	222	360

Notes:

Notes: 1. Receptor groundwater concentration is CSR AW freshwater standard (Schedule 6), unless otherwise noted. 2. Background soil concentration is that referenced in CSR matrix soil standard (Schedule 4). 3. CSR Schedule 5, freshwater standard 4. Table B-2 Overview of CSST Procedures for the Derivation of Soil Quality Matrix Standards for Contaminated Sites.

Table B-2 Overview of CSST Procedures for the Derivation of Soil Quality Matrix Standards for Contaminated Sites.
 Tox Based Soil Standard = Q<sub>a</sub>\* DAF\* (K<sub>a</sub>\* 6/p<sub>b</sub>) where C<sub>b</sub> is groundwater concentration. DAF = dilution attenuation factor (3.29)0<sub>u</sub> is water-filled porosity (0.1), p<sub>b</sub> = bulk dry density (1.75)
 Calc. CSST Input Standard = Tox. Based Standard + Background Soil Conc. (freshwater standard)
 USEPA Soil Screening Guidance (USEPA, 1996) cadmium, chromium III, zinc, mercury, nickel (Figure 11), Arsenic (III), chromium (VI) (Figure 10). For lead the approximate interpolated values obtained from 3MRA isotherms using a using a mid-range HFO (0.05 % wt) and mid-range POM (0.11% wt) for a dissolved lead concentration of 0.06 mg/L were used.
 Calc. USEPA Input Standard = Tox. Based Standard + Background Soil Conc. (freshwater standard)
 Based on correspondance from George Szefer, April 8, 2005
 Based on hardness equal H>200, default value in SSS model, March 2005 version
 Based on hardness equal H>200, default usine in SSC model, March 2005 version
 Based on hardness equal H>100-200, based on footnote 7 in Schedule 5 for zinc.






























## **APPENDIX A**

EXTENDED LIST OF PARTITION COEFFICIENTS FOR USEPA SOIL SCREENING LEVEL GUIDANCE (USEPA, 1996B)

	K <sub>d</sub>											
рН	Ni	Cd	Be	Cr(III)	TI*	As(III)*	Cr(VI)*	Se*	Zn	Hg	Ag	Ba
4	4.1	4.1	6.6	60.3	35.1	23.4	39.8	33.5	5.3	0.001	0.01	2.7
4.1	5.1	5.1	7.8	70.8					6.0	0.002	0.01	3.3
4.2	6.0	6.0	9.1	87.1					7.1	0.003	0.02	3.8
4.3	6.6	6.6	10.5	112.2					7.9	0.004	0.02	4.5
4.4	7.9	7.9	12.3	154.9					8.9	0.006	0.03	5.3
4.5	9.3	9.3	13.8	213.8	39.8				10.6	0.008	0.04	6.3
4.6	10.7	10.7	16.2	327.3					11.9	0.012	0.05	7.1
4.7	12.0	12.0	18.6	478.6					13.3	0.019	0.06	7.9
4.8	13.8	13.8	20.9	741.3					14.1	0.027	0.08	9.4
4.9	15.8	15.8	23.7	1174.9		25.1	31.6		16.8	0.040	0.11	10.6
5	17.4	17.4	25.7	1995.3					17.8	0.063	0.13	11.9
5.1	19.5	19.5	29.9	3162.3				15.8	20.0	0.094	0.16	14.1
5.2	21.9	21.9	31.6	5308.8					21.1	0.141	0.21	15.8
5.3	24.0	24.0	35.5	8414.0					23.7	0.211	0.27	16.8
5.4	26.0	26.0	37.6	14125.4					25.1	0.316	0.33	18.8
5.5	27.9	27.9	42.2	22387.2					26.6	0.473	0.42	21.1
5.6	30.2	30.2	47.3	37583.7					28.2	0.668	0.53	22.4
5.7	32.4	32.4	53.1	59566.2					29.9	1.1	0.67	25.1
5.8	34.7	34.7	59.6	94406.1					31.6	1.6	0.84	26.6
5.9	37.2	37.2	70.8	141253.8					33.5	2.4	1.1	28.2
6	38.9	38.9	84.1	211348.9					37.6	3.5	1.4	29.9
6.1	39.8	39.8	100.0	298538.3					39.8	5.3	1.7	31.6
6.2	41.7	41.7	125.9	446683.6					42.2	7.5	2.2	33.5
6.3	44.7	44.7	158.5	595662.1	63.1				44.7	11.2	2.7	35.5
6.4	47.9	47.9	223.9	794328.2					47.3	15.8	3.3	37.6
6.5	50.7	50.7	298.5	1059253.7		28.2			53.1	22.4	4.2	39.8
6.6	56.2	59.6	398.1	1258925.4			20.0		56.2	29.9	5.3	38.9
6.7	60.3	66.8	562.3	1496235.7					59.6	39.8	6.7	39.8
6.8	64.6	79.4	794.3	1778279.4				5.0	63.1	53.1	8.4	40.7
6.9	72.4	94.4	1188.5	2238721.1					66.8	66.8	10.6	42.2
7	87.1	118.9	1678.8	2511886.4					75.0	84.1	13.3	42.2
7.1	112.2	149.6	2660.7	2818382.9					84.1	100.0	15.8	44.7
7.2	149.6	211.3	3758.4	3162277.7					94.4	118.9	21.1	44.7
7.3	188.4	298.5	5956.6	3548133.9					112.2	133.4	25.1	44.7
7.4	251.2	421.7	8912.5	3758374.0					133.4	149.6	29.9	45.2
7.5	354.8	631.0	14125.4	3981071.7					158.5	158.5	39.8	45.2
7.6	501.2	891.3	21134.9	4216965.0					188.4	167.9	47.3	45.2
7.7	749.9	1258.9	31622.8	4466835.9					251.2	177.8	59.6	45.7
7.8	1000.0	2113.5	47315.1	4731512.6				2.5	316.2	188.4	75.0	47.3
7.9	1496.2	2985.4	70794.6	4466835.9					421.7	188.4	89.1	50.1
8	1883.6	4466.8	112201.8	4466835.9		31.6			530.9	199.5	112.2	53.1
8.1				4216965.0								
8.2					100.0							
8.3							12.6					
8.4												
8.5												
8.6												
8.7	ļ		ļ						ļ			
8.8												
8.9												
9	1	1	1		123.0	33.9	10.5	1.1			1	

al isotherms presented in USEPA 1996b

I-pH relationship of Loux et al, 1991

## **APPENDIX B**

EXHIBIT: COMPARISON OF LITERATURE REPORTED KD VALUES AND USEPA SOIL SCREENING GUIDANCE  $K_D$  VALUES (FROM USEPA, 1996B)

#### Exhibit

Comparison of literature reported Kd values and USEPA Soil Screening Guidance K<sub>d</sub> values (from USEPA, 1996b).

**5.4.4 Results and Discussion.** MINTEQ model results indicate that metal mobility is most affected by changes in pH. Based on this observation and because iron oxide content is not routinely measured in site characterization efforts, pH-dependent Kds for metals were developed for SSL application by fixing iron oxide at its medium value and fraction organic carbon at 0.002. For arsenic (+3), chromium (+6), selenium, and thallium, the empirical pH-dependent Kds were used.

Table 46 shows the SSL Kd values at high, medium, and low subsurface pH conditions. Figure 11 plots MINTEQ-derived metal Kd values over this pH range. Figure 10 shows the same for the empirically derived metal Kds. These results are discussed below by metal and compared with measured values. See RTI (1994) for more information. pH-dependent values are not available for antimony, cyanide, and vanadium. The estimated Kd values shown in Table 46 for antimony and vanadium are reported by Baes et al. (1984) and the Kd value for cyanide is obtained from SCDM.

**Arsenic.** Values developed using the empirical equation for arsenic (+3) range from 25 to 31 L/kg for pH values of 4.9 to 8.0, respectively. These values correlate fairly well with the range of measured values reported by Battelle (1989)-5.86 to 19.4 L/kg. They are slightly above the range reported by Baes and Sharp (1983) for arsenic (+3) (1. 0-8.3). The estimated \_ values for arsenic (+3) do not correlate well with the value of 200 L/kg presented by Baes et al. (1984). Oxidation state is not specified in Baes et al. (1984), and the difference between the empirical-derived Kd values presented here and the value presented by Baes et al. (1984) may reflect differences in oxidation states (arsenic (+3) is the most mobile species).

**Barium.** For ground water pH conditions, MINTEQ-estimated Kd values for barium range from 11 to 52 L/kg. This range correlates well with the value of 60 L/kg reported by Baes et aI. (1984). Battelle (1989) reports a range in Kd values from 530 to 16,000 L/kg for a pH range of 5 to 9. The model-predicted Kd values for barium are several orders of magnitude less than the measured values, possibly due to the lower sorptive potential of iron oxide, used as the modeled sorbent, relative to clay, a sorbent present in the experimental systems reported by Battelle (1989).

**Beryllium.** The Kd values estimated for beryllium range from 23 to 100,000 L/kg for the conditions studied. AECL (1990) reports medians of observed values for Kd ranging from 250 L/kg for sand to 3,000 L/kg for organic matter. Base et al. (1984) report a value of 650 L/kg. Battelle (1989) reports a range of Kd values from 70 L/kg for sand to 8,000 L/kg for clay. MINTEQ results for medium ground water pH (i.e., a value of 6.8) yields a Kd value of 790 L/kg. Hence, there is reasonable agreement between the MINTEQ-predicted Kd values and values reported in the literature.

**Cadmium.** For the three pH conditions, MINTEQ Kd values for cadmium range from 15 to 4000 L/kg, with a value of 75 at a pH of 6.8. The range in experimentally determined Kd values for cadmium is as follows: 1.26 to 26.8 L/kg (Baes et al., 1983), 32 to 50 L/kg (Coughtrey et al., 1985), 14.9 to 567 L/kg (Battelle, 1989), and 2.7 to 17,000 L/kg (AECL, 1990). Thus the MINTEQ estimates are generally within the range of measured values.

**Chromium** (+3). MINTEQ-estimated Kd values for chromium (+3) range from 1000 to 4,300,000 L/kg. Battelle (1989) reports a range of Kd values of 168 to 3,600 L/kg, orders of magnitude lower than the MINTEQ values. This difference may reflect the measurements of mixed systems comprised of both chromium (+3) and (+6). The incorporation of chromium (+6) would tend to lower the Kd. Because the model-predicted values may overpredict sorption, the user should exercise care in the use of these values. Values for chromium (+6) should be used where speciation is mixed or uncertain.

#### **Golder Associates**

**Chromium** (+6). Chromium (+6) Kd values estimated using the empirical pH-dependent adsorption relationship range from 31 to 14 L/kg for pH values of 4.9 to 8.0. Battelle (1989) reports a range of 16.8 to 360 L/kg for chromium (+6) and Baes and Sharp (1983) *report* a range of 1.2 to 1,800. The predicted chromium (+6) \_ values thus generally agree with the lower end of the range of measured values (37) reported by Baes and Sharp (1983). These values represent conservative estimates of mobility the more toxic of the chromium species.

**Mercury** (+2). MINTEQ-estimated values for mercury (+2) range from 0.04 to 200 L/kg. These modelpredicted estimates are less than the measured range of 322 to 5,280 L/kg reported by Battelle (1989). This difference may reflect the limited thermodynamic database with respect to mercury and/or that only the divalent oxidation state is considered in the simulation. Allison (1993) reviewed the model results in comparison to the measured values reported by Battelle (1989) and found reasonable agreement between the two sets of data, given the uncertainty associated with laboratory measurements and model precision.

**Nickel.** MINTEQ-estimated Kd values for nickel range from 16 to 1,900 L/kg. These values agree well with measured values of approximately 20 L/kg (mean) and 12.2 to 650 L/kg, reported by Coughtrey et aI. (1985) and Battelle (1989), respectively. These values also agree well with the value of 150 L/kg reported by Baes et aI. (1984). However, the predicted values are at the low end of the range reported by the AECL (1990) - 60 to 4,700 L/kg.

**Selenium.** Empirically derived Kd values for selenium range from 2.2 to 18 L/kg for pH values of 8.0 to 4.9. The range in experimentally determined values for selenium is as follows: less than 9 L/kg (Coughtrey et al., 1985), 5.9 to 14.9 L/kg (Battelle, 1989), and 150 to 1,800 L/kg (AECL, 1990). Baes et al. (1984) reported a value of 300 L/kg. Although they are significantly below the values presented by the AECL (1990) and Baes et al. (1984), the MINTEQ-predicted Kd values correlate well with the values reported by Coughtrey et al. (1985) and Battelle (1989).

**Silver.** The Kd values estimated for silver range from 0.10 to 110 L/kg for the conditions studied. The range in experimentally determined Kd values for silver is as follows: 2.7 to 33,000 L/kg (AECL, 1990), 10 to 1,000 L/kg (Baes et al., 1984), 50 L/kg (Coughtrey et al., 1985), and 0.4 to 40 L/kg (Battelle, 1989). The model-predicted Kd values agree well with the values reported by Coughtrey et al. (1985) and Battelle (1989) but are at the lower end of the ranges reported by AECL (1990) and Baes et al. (1984).

**Thallium.** Empirically derived Kd values for thallium range from 44 to 96 L/kg for pH values of 4.9 to 8.0. Generally, these values are about an order of magnitude greater than those reported by Battelle (1989)-0.0 to 0.8 L/kg - but are well below the value predicted by Baes et al. (1984).

**Zinc.** MINTEQ-estimated values for zinc range from 16 to 530 L/kg. These estimated Kd values are within the range of measured values reported by the AECL (1990) (0.1 to 100,000 L/kg) and Baes et aI. (1984) (0.1 to 8,000 L/kg). Coughtrey et aI. (1985) reported a value for zinc of greater than or equal to 20 L/kg.

## **APPENDIX C**

EXHIBIT: USE OF SYNTHETIC PRECIPITATION LEACHING PROCEDURE RESULTS TO DEVELOP SITE SPECIFIC SOIL SCREENING LEVELS, AS RECOMMENDED BY THE STATE OF NEW JERSEY (FROM NEW JERSEY, 2005)

#### **Option C. Synthetic Precipitation Leaching Procedure**

#### Introduction

The Synthetic Precipitation Leaching Procedure (SPLP) is an EPA SW-846 analytical method (Method 1312) that can be used to determine the concentration of contaminant that will leach from soil (USEPA, 1998). The results of this procedure can be used directly to determine an AOC specific impact to ground water standard, or may be used indirectly to determine an AOC specific adsorption constant ( $K_d$ ). This  $K_d$  value may then be substituted into the simple partitioning equation to calculate a sample-specific impact to ground water remediation standard. SPLP offers a quick and inexpensive method to develop site-specific alternative remediation standards for inorganic, semi-volatile and pesticide contaminants that will be protective of ground water.

A particularly useful aspect of the SPLP procedure is that it measures desorption, rather than adsorption, of contaminants from soil. It is well known that adsorption of many chemicals to soil increases as contact time increases (Loehr and Webster, 1996; Alexander, 1995; Pavlostathis and Mathavan, 1992). This is particularly true for less mobile contaminants. In some cases, contaminants may become irreversibly adsorbed to soil and therefore immobile. Soil adsorption coefficients (and  $K_{oc}$  values) used in the USEPA SSL partitioning equation do not consider these processes. While the USEPA partitioning equation could be used with desorption, rather than adsorption coefficients, values for desorption coefficients are not generally available and if they are available they are likely to be site-specific. Therefore, generic standards are determined using adsorption coefficients and are therefore often conservative.

Because the SPLP procedure uses the soil on site, it addresses species-specific issues regarding inorganic contaminants, particularly metals. The USEPA's simple partitioning equation assumes the most mobile form of an inorganic contaminant to estimate an adsorption coefficient for use in the partitioning equation (USEPA, 1996b). Because the actual species (redox state, salt, or complex) of an inorganic contaminant at a discharge site is typically not known after the site investigation phase, this assumption is necessary for generic analysis in order to be adequately protective of all situations that may occur. The SPLP procedure, on the other hand, measures the leaching potential of the actual species of the contaminant present at the discharge site.

species of metals can have widely varying mobility. Speciation is generally not known because standard analytical methods usually measure total metals only. The SPLP test will measure the actual mobility, regardless of species. While a detailed assessment of the results of this test may be complex when mixtures of different species of the same metal are present, the procedure nonetheless provides a much-improved estimate of leaching tendency relative to the generic level assumptions.

The conditions of the SPLP test simulate actual environmental precipitation, in that the leaching solution is a simulation of mid-Atlantic rainfall (pH 4.2). Thus, the test more realistically estimates the leaching potential of contaminants that may occur under field conditions in New Jersey (Brown et al., 1996; Lackovic et al., 1997). Because the leaching test is conducted with actual soil samples taken from the site, remediation standards developed using this test are expected to be much more representative of site conditions than standards determined via other methods.

The utility of SPLP for case processing can be significant. SPLP can be easily and quickly conducted on samples during the site investigation in a time and cost efficient manner.

For all of the reasons above, it is recommended that the SPLP ARS option be used during the site investigation (SI) for cases involving semi-volatile chemical, pesticide and inorganic contaminants. The processing of these cases is likely to be considerably accelerated when SPLP results are available.

The limitations of the SPLP test are as follows. First, because leachate is filtered through a  $0.6 - 0.8 \mu m$  filter, the concentration of colloidal metals above this pore size may be underestimated. Second, because the oxidation/reduction potential of the sample is not preserved when the test is conducted, the interconversion of metal species with multiple oxidation states may occur. Third, at this time the Department is not allowing the use of the SPLP procedure to determine the leaching potential of volatile organic compounds. The Department requires that volatile organic soil samples be collected using either methanol preservation or the Encore<sup>®</sup> sampler. Methanol cannot be added to an SPLP sample because it affects contaminant desorption. The Encore<sup>®</sup> sampler comes in 5 or 25 gram sizes, which would require the collection of several samples to achieve the required sample size for the SPLP test and total soil analysis. These separate samples would need to be composited, which is difficult without loss of volatiles. Furthermore, volatiles are weakly adsorbed to soil, so the use of the SPLP test will usually not significantly increase the calculated standard.

The IGWARS generated by this option may result in no further action, thus would not require monitoring, deed notices or other restrictions.

#### Sampling procedures required for SPLP

When using SPLP during the investigation of an AOC, the number of samples collected should be determined by the size of the area initially being investigated pursuant to the Department's Technical Requirements for Site Remediation, N.J.A.C. 7:26E. At a minimum, three samples must be taken per AOC. Ideally, the samples must be chosen to target the highest concentrations of the chemicals. Furthermore, the samples should be representative of the variation in soil conditions over the area of concern, including variation with soil depth.

Samples taken for SPLP analysis must be split, because the calculation of a site-specific remediation standard, or a site-specific  $K_d$  value requires knowledge of the total contaminant concentration in the soil sample. One sample must be analyzed for total contaminant concentration, and the other for SPLP analysis. When reporting SPLP results, the total contaminant contaminant concentration in the soil, the leachate concentration, and the pH of leachate must be reported.

The following situations (not inclusive) may require that additional soil samples be collected for SPLP testing to refine an AOC specific IGWARS:

Contamination extends to a depth not investigated during Site Investigation. Because soil
properties often vary with depth, subsurface soil samples should be included if the
contamination extends below the surface soil.

2. Contaminant concentrations measured during the Remedial Investigation are found to be higher than those measured during the Site Investigation.

#### **Using SPLP Results**

#### 1. Pass/Fail

This option was developed for cases where all SPLP leachate results are below a "Target Ground Water Concentration" or the Practical Quantitation Limit (PQL), as specified in the Department's GWQS N.J.A.C. 7:9-6. The target ground water concentration, (TGWC) is the Ground Water Quality Criterion pursuant to N.J.A.C. 7:9-6 *et seq.* multiplied by the generic DAF of 12.

Therefore, if all SPLP samples taken from an area of concern yield leachate concentrations that are below the higher of the TGWC or the PQL, no remediation of the soil is necessary for the impact to ground water exposure pathway for that specific AOC. See examples below:

To determine if further remediation is needed, compare SPLP results with the PQL and the TGWC, which is the Ground Water Quality Criterion that has been multiplied by the generic DAF of 12. If all SPLP results are lower than the PQL and the GWQC x 12 then no further remediation of the soil is necessary for the impact to ground water exposure pathway. This analysis should be done for each AOC. See examples below:

Chemical	GWQC	TGWC (GWQC*DAF)	PQL
Lead	5 µg/L	60 µg/L	10 µg/L
Toxaphene	0.03 µg/L	0.36 µg/L	3 µg/L

**Target Ground Water Concentration** (*TGWC*) = the Ground Water Quality Criteria (GWQC) unadjusted for PQLs x the DAF

GWQC = Ground Water Quality Criterion from N.J.A.C. 7:9-6

**DAF** = Dilution-attenuation factor (default DAF=12)

**PQL** = Practical Quantitation Levels from N.J.A.C. 7:9-6

For the chemical lead, the TGWC is 60 ug/L (GWQC of 5  $\mu$ g/L multiplied by the generic DAF,12). According to the Department's Ground Water Quality Standards, the PQL for lead is 10  $\mu$ g/L. The calculated TGWC is higher than the PQL; therefore, if the leachate concentrations from the SPLP tests are less than the TGWC of 60  $\mu$ g/L, soil remediation for lead is not necessary for this exposure pathway.

For the chemical toxaphene, the TGWC is 0.36  $\mu$ g/L. According to the Department's Ground Water Quality Standards, the PQL for toxaphene is 3  $\mu$ g/L. The calculated TGWC is lower than the PQL; therefore, if the leachate concentrations from the SPLP tests are less than the PQL of 3  $\mu$ g/L, soil remediation for toxaphene is not necessary for this exposure pathway.

If some or all samples yield leachate concentrations above the TGWC or PQL, continue to Option 2 or 3 below.

NOTE: In cases where contaminants are weakly adsorbed to soil, an adjustment to the SPLP leachate concentration may be necessary (see section "Adjustment of leachate concentration for weakly adsorbed chemicals" below).

2. Procedure when SPLP results vary by more than an order of magnitude, or when SPLP results are above the TGWC/PQL

This option allows the user to develop an IGWARS by identifying the highest soil concentration at which all leachate concentrations when divided by the DAF are at or below the GWQC.

The SPLP leachate results represent the concentration of contaminant in soil pore water before dilution by the saturated zone. Therefore, the SPLP leachate concentration is divided by the DAF (12) to represent the instantaneous dilution of contamination as it enters the saturated zone. The soil concentration may be used as an IGWARS.

$$\frac{C_L}{DAF} \le GWQC$$

To develop an IGWARS using this option divide all SPLP leachate concentrations by the DAF (12) and compare the resulting numbers to the GWQC. The examples below illustrate this approach:

Example 1.

$C_T(mg/kg)$	$C_L(\mu g/L)$	$C_L$ /DAF	GWQC (µg/L)
5	900	75	200
10	1200	100	200
30	2280	190	200
50	1680	140	200
75	2700	225	200

where:

 $C_L$  = Concentration of contaminant in the SPLP leachate (µg/L)

**DAF** = Dilution attenuation factor (default DAF=12)

**GWQC** = the Ground Water Quality Criterion, N.J.A.C. 7:9-6

 $C_T$  = the total concentration of the contaminant in the SPLP soil sample (mg/kg)

In the example above, the GWQC for the chemical of concern is 200  $\mu$ g/L, the IGWARS would be 50 mg/kg because it is the highest soil concentration at which all leachate concentrations when divided by the DAF are at or below the GWQC.

Example 2.

$C_{\rm T}(\rm mg/kg)$	$C_{\rm L}(\mu g/{\rm L})$	$C_{\rm L}/{\rm DAF}$	GWQC (µg/L)
5	900	75	150
10	1200	100	150
30	2280	190	150
50	1680	140	150
75	2700	225	150

where:

 $C_{\rm L}$  = the concentration of contaminant in the SPLP leachate (µg/L)

**DAF** = the dilution attenuation factor (default DAF=12)

**GWQC** = the Ground Water Quality Criterion, N.J.A.C. 7:9-6

 $C_{\rm T}$  = the total concentration of the contaminant in the SPLP soil sample (mg/kg)

In the example above, the GWQC for the chemical of concern is  $150 \mu g/L$ , the acceptable IGWARS would be 10 ppm. Although the sample with a total concentration of 50 mg/kg yields an acceptable leachate result, the 30 ppm sample does not, and the IGWARS would default to the highest soil concentration at which all leachate concentrations when divided by the DAF are at or below the GWQC, in this case 10 mg/kg.

NOTE: In cases where contaminants are weakly adsorbed to soil, an adjustment to the SPLP leachate concentration may be necessary (see section "Adjustment of leachate concentration for weakly adsorbed chemicals" below).

#### 3. Calculate Sample-Specific Alternative Remediation Standard

A sample-specific IGWARS may be calculated using the total contaminant concentration in a soil sample ( $C_T$ ), and the SPLP leachate concentration ( $C_L$ ). These results and other sample specific data are used to calculate a sample-specific soil-water partition coefficient ( $K_d$ ), which is then substituted into the USEPA simple partitioning equation. See below:

#### Step 1. Calculate Sample Specific Kd

For each sample where the SPLP leachate concentration is above the Minimum Detection Limit (MDL), calculate a  $K_d$  value using the formula below:

$$Kd = \left[\frac{(C_T M_s - C_L V_L) / M_s}{C_L}\right]$$
 Equation (6)

The equation is derived in Appendix H, where:

 $K_{d}$  = soil water partition coefficient (L/kg)

 $C_{\rm T}$  = the total concentration of the contaminant in the SPLP soil sample (mg/kg)

 $M_{\rm S}$  = the total weight of the soil sample submitted for SPLP analysis (kg)

 $C_{\rm L}$  = the concentration of contaminant in the SPLP leachate (mg/L)

 $V_{\rm L}$  = the volume of the SPLP leachate (L)

If the  $K_d$  values vary by less than an order of magnitude, the results may be averaged and this average substituted into the simple partitioning equation.

If the  $K_d$  values vary by more than an order of magnitude, they may not be averaged. In this case, the lowest calculated  $K_d$  value may be used in the simple partitioning equation.

Step 2. Substitute Sample Specific  $K_d$  values in the Simple Partitioning Equation Calculate the IGWARS for the impact to ground water pathway using the following equation:

Simple Partitioning Equation:

where:

$$ARS = C_{gw} \left\{ \left[ K_{d} \right] + \frac{\theta_{w} + \theta_{a} H'}{\rho_{b}} \right\} DAF$$

**ARS** = alternative remediation standard (mg/kg)

 $K_d$  = is the average, or lowest, calculated sample specific soil-water partition coefficient (L/kg)

 $\theta_{\rm w}$  = the volume fraction of water in the original soil sample (v/v, assume generic value of 0.23 unless sitespecific data indicates otherwise)

 $\theta_a$  = the volume fraction of air in the original water sample (v/v, assume generic value of 0.18 unless sitespecific data indicates otherwise)

H' = the dimensionless Henry's law constant for the contaminant of interest

 $\rho_{\rm b}$  = the dry bulk density of the soil (1.5 kg/L)

DAF = the dilution-attenuation factor (default DAF = 12)

 $C_{gw}$  = the ground water criteria for the contaminant (mg/L)

## 4. Use of Regression analysis to calculate IGWARS using results from the Synthetic

#### Precipitation Leaching Procedure

If an adequate linear correlation is observed between observed leachate concentrations and their corresponding total soil concentrations, a linear regression technique may be used to determine the acceptable total soil concentration.

 Plot the leachate concentration versus total soil concentration for all samples where both concentrations are above the detection limit. The x-axis (independent variable) is the total soil concentration and the y-axis (dependent variable) is the leachate concentration.

- 2. At least half of the points must lie at or above the midpoint of the range of total soil concentrations, and the Target Ground Water Concentration (TGWC) must lie within the range of measured leachate concentrations.
- Do a linear least-squares regression analysis of the plotted points. If the R-square value is
   0.8 or higher, the calculated linear regression line may be used to determine the acceptable total soil concentration.
- 4. Calculate the acceptable total soil concentration:

$$IGWARS = \frac{TGWC - b}{m}$$

where IGWARS is the impact-to-ground water alternative remediation standard, TGWC is the target ground water concentration, and m and b are the slope and intercept of the best fit line obtained via linear regression.

NOTE: For cases where contaminants are weakly adsorbed to soil, an adjustment to the SPLP leachate concentration may be necessary (see below).



Example Linear Regression and Calculations

If Target Groundwater Concentration (TGWC) is 10 $\mu$ g/L, then

#### Adjustment of leachate concentration for weakly adsorbed chemicals

Normally, contaminants subjected to the SPLP tests are highly adsorbed to the soil. For hazardous waste sites that have existed for many years, contaminants that are weakly adsorbed have already migrated away from the site.

In cases where discharges are recent or very large in size, contaminants may still be relatively mobile (i.e., weakly adsorbed to soil) at the time of the Site Investigation. In these situations, the leachate concentration determined using the SPLP test may underestimate concentrations that would be observed under natural conditions because the large amount of extracting solution used dilutes the contaminant. The ratio of extracting solution weight to the soil weight employed in the SPLP test is 20 to 1. In contrast, a representative soil water to soil solids ratio in saturated sandy loam soil in New Jersey (the field conditions under which leaching would occur) is approximately 0.41 ml moisture to 1.5 grams of soil. The dilution error in the SPLP test becomes significant when approximately 25% of the contaminant is found in the leachate solution, or when the  $K_d$  is less than or equal to 50 L/kg:

Leachate concentration (mg/L) as a function of leaching volume						
Kd (L/kg)	Natural conditions 0.41mL water per 1.5gram of soil	SPLP conditions (20mL extractant per gram of soil)	% of contaminant in leachate			
1	11.6	0.64	96			
10	1.3	0.44	66			
20	0.66	0.33	50			
20	0.66	0.33	50			
50	0.27	0.19	28			
100	0.13	0.11	16			
Total contaminant concentration (dry soil basis):13.3mg/kg						

Note that when  $K_d$  is less than 50 L/kg, the difference between the SPLP concentration and the natural field leachate concentration becomes significant.

For this reason, when using Options 1, 2, and 4, the total mass of contaminant in the leachate should be compared to the total mass of contaminant in the soil sample. When the mass of contaminant in the leachate exceeds 25% of the total mass, an adjustment of the leachate concentration is necessary.

Equation to check % of contaminant in the leachate:

 $(C_{\rm L} \times V_{\rm L})/(C_{\rm T} \times M_{\rm S}) \times 100$  This should be less than 25.

Where  $V_L$  is the volume of leachate in liters (often 2 L),  $M_S$  is the mass of the soil sample in kilograms (often 0.1 kg), and  $C_L$  and  $C_T$  are the leachate concentration (mg/L) and the total soil concentration (mg/kg), respectively.

When a leachate concentration adjustment is necessary, a  $K_d$  is first calculated for the chemical for each sample using Equation (6) under Option 3:

$$Kd = \left[\frac{\left(C_T M_S - C_L V_L\right) / M_S}{C_L}\right]$$

where:

 $K_d$  = is the soil water partition coefficient (L/kg)  $C_T$  = the total concentration of the contaminant in the SPLP soil sample (mg/kg)  $M_S$  = the total weight of the soil sample submitted for SPLP analysis (kg)  $C_L$  = the concentration of contaminant in the SPLP leachate (mg/L)  $V_{\rm L}$  = the volume of the SPLP leachate (L)

This  $K_d$  value is then substituted in the following equation, which is a simple rearrangement of the USEPA simple partitioning equation (no air phase):

$$C_{\rm adj} = C_{\rm T}[\rho_{\rm b}/(K_{\rm d} \ge \rho_{\rm b} \ge \theta_{\rm w})]$$

Where  $\rho_{\rm b}$  is the bulk density of the soil (1.5 kg/L), and  $\theta_{\rm w}$  is the soil moisture (0.23), and  $C_{\rm adj}$  is the adjusted leachate concentration (mg/L).

## APPENDIX D

## COMPARISON OF METHODS OF ISOTHERM DEVELOPMENT FOR THE PURPOSE OF SOIL SCREENING LEVEL CALCULATION

	CSST	USEPA	3MRA
Primary reference	CSST, 1996	USEPA, 1996a, b	USEPA 1996c, 2003
Number of metals considered	6	15	16
Method of isotherm	Empirical pH-Kd relationships (As (III) and Cr	Empirical pH-Kd relationships (As (III), Cr (VI),	MINTEQA2
development	(VI)), and MINTEQA2 (?)	Se, TI, Sb, V), and MINTEQA2	
Level of transparency	Low	Moderate to High	High
	Ma	ister input values	
pН	4.9, 6.8, 8	4.9, 6.8, 8	4.9, 6.8, 8
Organic matter	Unknown	0.2 wt%	0.034 to 0.325 wt%
Iron oxide	Unknown	0.31 wt% Fe	0.009 to 0.05 wt% Fe
Metal input concentration	Unknown	Unknown	0.001 to 10000 mg/L
Advantages	Current method utilized to develop soil screening levels in British Columbia.	Soil-water partitioning isotherms are currently used in a number of jurisdictions in the United States. Scientific approach is well documented and easy to use.	Well documented isotherms are parameterized under a variety of geochemical conditions. All metals modeled with MINTEQA2 to generate non-linear isotherms over a range of concentrations.
Disadvantages	<ul> <li>Poor documentation of isotherm generation.</li> <li>Isotherms are generic, and don't consider a number of metals of environmental concern.</li> <li>Linear, empirical pH-Kd relationships developed for As(III) and Cr(VI) may not be representative of site conditions.</li> <li>Assumptions regarding iron oxide content, and neglect of sorption onto clays, Mn-oxides and carbonates are conservative.</li> </ul>	<ul> <li>Generic isotherms may not be representative of the actual geochemical conditions at a site, and K<sub>d</sub> values may be overly conservative.</li> <li>Linear, empirical pH-Kd relationships developed for As(III), Cr(VI), Se and TI may not be representative of site conditions.</li> </ul>	<ul> <li>Isotherms are complicated to use, and require knowledge site specific geochemical conditions whose measurement is not required in routine site evaluations.</li> <li>Even with parameterized results, some sites may not be well represented.</li> </ul>

## **APPENDIX II**

## OVERVIEW OF CSST PROCEDURES FOR THE DERIVATION OF SOIL QUALITY MATRIX STANDARDS FOR CONTAMINATED SITES

## Overview of CSST Procedures for the Derivation of Soil Quality Matrix Standards for Contaminated Sites

Risk Assessment Unit Environmental Protection Department BC Environment

January 31, 1996

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#### <u>PART A</u>

A1

# THE CONTAMINATED SITES SOIL TASK GROUP (CSST) HISTORY AND OBJECTIVES

## A1.1 CSST History

The Contaminated Sites Soil Task Group (CSST) was formed in November of 1994 and completed its work in November 1995. Under its terms of reference (BC Ministry of Environment, Lands and Parks, 1994), CSST was charged with the development of scientifically defensible environmental quality standards to protect human and environmental health from contaminants present in the soil of contaminated sites. The members of CSST represented health and environment experts providing assistance to the BC Ministry of Environment, Lands and Parks in the derivation of appropriate soil quality standards for use in the Contaminated Sites Regulation (BC Ministry of Environment, Lands and Parks, 1995a). In conducting this work, CSST encouraged open communication between its members and sought advice and support from other knowledgeable professionals. CSST reported regularly to a steering committee composed of representatives from the Ministry of Environment, Lands and Parks, the Ministry of Health and the province's Medical and Environmental Health Officers. (See Appendix A for a listing of CSST members.)

In developing its policy recommendations, CSST started with two documents provided by the CCME's Subcommittee on Environmental Quality Criteria for Contaminated Sites (SEQCCS); "A Protocol for the Derivation of Ecological Effects-based and Human Health-based Soil Quality Criteria for Contaminated Sites" (CCME, 1994a) and "Guidance Manual for Developing Site Specific Soil Quality Remediation Objectives for Contaminated Sites in Canada" (CCME, 1994b). CSST's considered all aspects of the CCME's documents, including the stated goals and principles, levels of protection and scope of receptors to which protection is to be accorded as well as specific derivation formulas. In some cases CSST accepted CCME recommendations while in other cases CSST policy recommendations differ from those of CCME. The rationale behind CSST science policies are recorded in the document, "CSST Policy Decision Summary"(BC Ministry of Environment, Lands and Parks, 1996). The soil quality standard derivation procedures provided herein are based on CSST's science policy decisions as documented in the CSST Policy Decision Summary.

## A1.2 CSST Objectives

Recognizing that both scientific and policy considerations must be addressed, CSST's challenge was to derive soil quality standards which serve the following objectives under British Columbia's contaminated sites legislation:

- to determine when a site is considered to be contaminated,
- to determine when remediation has been adequately performed at a site, and
- to control the relocation of contaminated soils.

Developing procedures to derive soil quality standards to address the above objectives formed the basis of the work of CSST.

# A2 THE CSST PROCEDURES AND THE CCME NATIONAL SOIL QUALITY CRITERIA PROTOCOL

#### A2.1 Relationship to CCME Protocol

The proposed CCME Protocol was developed by the SEQCCS to provide National criteria for the assessment and remediation of contaminated sites in Canada. The common goal of both CCME and CSST was to produce scientifically defensible and "transparent" risk-based defined exposure scenario soil quality numbers. CSST accepted the fundamental methodology represented in the CCME Protocol as guidance and developed derivation procedures for soil quality standards using CCME policy as the foundation for its work. However, CSST also recommended adoption of a number of different policies regarding certain aspects of the CCME Protocol, such as the level of protection afforded receptors.

CSST adapted the CCME Protocol because it believed that for many parameters, the CCME Protocol produced both human and ecological health criteria which provided a level of protection which would not be workable within the contaminated site remediation and management program envisioned for British Columbia. CSST was of the opinion that soil quality standards derived from the CCME Protocol would be generally more appropriate for use in the prevention of new contaminated sites than in the remediation of existing sites.

# A2.2 Comparison to CCME Protocol

Both the CCME protocol and the CSST procedures emphasize the derivation of standards which reflect acceptable concentrations of contaminants in soil. The alterations made to the CCME Protocol by CSST centre primarily around the levels of protection, the defined exposure scenarios, reasonable critical receptors, and the use of "checks" in derivations. The levels of protection, exposure scenarios and receptors used in the CSST methods reflect policies considered appropriate within the context of contaminated site management in British Columbia. New equations have been added by CSST to address some site specific factors not considered by CCME. In addition, derivation methods in the CSST procedures are often simpler than those proposed by the CCME. This reflects CSST's judgement that some of the CCME procedures use default assumptions of questionable scientific veracity or are overly complex.

The derivation of soil criteria in the CCME protocol to protect groundwater for use as drinking water has been expanded by CSST to also address the protection of aquatic life, irrigation and livestock watering. CSST also considered the possibility of deriving standards to address potential "physical hazards" and organoleptic concerns posed by some contaminants. As a result, CSST developed procedures to derive standards to address concerns relating to objectionable odours associated with some contaminants. Standards relating to other physical hazards (i.e. explosivity, flammability) are more appropriately addressed and evaluated through reference to the Special Waste Regulation.

As a result of the incorporation of mechanisms to account for common site specific factors, the soil quality standards derived under the CSST protocol are designed to be both flexible and easy to use. BC Environment has opted to present all derived soil quality standards as discrete components of substancespecific "matrices" which contain human, environmental and "other" protective standards.

## CSST PROCEDURES FOR THE DERIVATION OF BRITISH COLUMBIA SOIL QUALITY STANDARDS FOR CONTAMINATED SITES

#### A3.1 Summary of CSST Methods

A3 .

This overview of CSST Procedures provides the basic concepts and methods employed by CSST in developing soil quality matrix standards. The derivation procedures as detailed herein provide the basic steps needed to generate risk-based soil remediation standards for the defined exposure scenarios presented. In this summary, the general rationale, methodology and equations used by CSST to derive the soil quality standards is outlined and referenced.

#### A3.1.1 Environmental Protection Standards

For the protection of the non-human components of the terrestrial ecosystem, the derivation procedures consider primarily adverse effects from exposure to soil-based contaminants at point-of-contact. Potential exposure pathways, receptor arrays, and exposure scenarios are described for major land uses. As in the CCME procedures, CSST generally believes that derivation of soil contact standards, protective of plants and soil invertebrates, will act to sustain the ecological receptors thought critical to the primary activities associated with the identified land use categories. Additionally, groundwater protection soil quality standards for nonpolar and polar organic and heavy metal contaminants are also derived for the protection of aquatic life, irrigation and livestock watering. These indirect exposure routes are evaluated through the application of simplified transport and redistribution models using specified site default characteristics. The models were constructed to protect a wide variety of site specific conditions.

#### A3.1.2 Human Health Protective Standards

For the protection of human health, derivation procedures for threshold and non-threshold toxicants are differentiated. Receptors and exposure periods are chosen to be generally representative of each land use scenario. Also provided is CSST's procedure to derive soil standards to protect groundwater for use as drinking water.

#### A3.2 Limitations of CSST Methodology

CSST's methodology does not generally attempt to account for the important factor of contaminant depth in the soil. This issue is a management consideration which is addressed in the Contaminated Sites Regulation (BC Ministry of Environment, Lands and Parks, 1995a).

The defined exposure scenarios used to develop the soil quality standards are necessarily limited in scope and do not cover the full spectrum of the types of sites, environments and organism-site interactions that can exist. For example, the effects of exposure to mixtures of chemicals cannot be addressed, as the bulk of toxicological data are concerned with the effects of isolated chemicals. However, it is believed, on the basis of professional judgement and the scientific literature on contaminated site exposures, that the defined exposure scenarios used by CSST can address the majority of hazardous and potentially hazardous exposures likely to occur.

It is also recognised that each chemical will offer specific characteristics that cannot be adequately documented in this summary. These substance specific characteristics have been identified and discussed in supporting substance assessment documents produced by the CCME. In addition, it is recognized that new data will come to light as the science of toxicology and soil contaminant exposure develops.

A3.3 Land Use Based Differential Protection.

Toxicological effects-based soil quality standards were derived according to broad land use categories. These are: Agricultural, Residential/Urban

Parkland, Commercial and Industrial land uses. For provincial regulatory purposes, the Residential/Urban Parkland group was separated to give two discrete land use categories. Standards were derived to protect human and key ecological receptors that sustain 'normal' activities carried out on these lands. Specific land use scenarios were defined for each category based on the representative "normal" activities carried out on these lands. Sensitivity to contamination varies among the land uses, reflecting CSST's policy decisions made regarding the differential level of protection to be accorded to the ecological or human health components. Thus, Agricultural and Residential/Urban Parkland land uses are accorded a greater level of protection from contamination than Commercial or Industrial land uses. This differential protection was deemed necessary to sustain the specified land use activities. It should be noted however, that the land use scenario envisioned for each category may not always occur on a site-specific basis.

#### A3.3.1 Land Use Definitions

The definition of each land use must be broad enough to be generally representative of the likely conditions encountered. However, the definition provided for each land use also acts to "bound" or limit the receptors and exposure pathways considered in the derivation of soil quality standards for that land use. CSST's definitions of the four land use categories are provided below:

Agricultural: land where the primary activity is related to food production, such as using the land for growing crops and producing livestock. This also includes lands categorised as agricultural that provide habitat for resident and transitory wildlife and native flora (e.g. transition zones).

Residential/ lands where the primary activity is occupation of the land for Urban residency and lands used for the purpose of recreational Parkland: activity. This also includes parkland and residential lands used by wildlife, such as buffer zones between areas of residences, but does not include "wildlands" such as national or provincial parks.

Commercial: lands where the primary activity is related to commercial operations (e.g. shopping mall) and occupancy is not for residential or manufacturing purposes. This does not include operations where the growing of food is the primary activity.

Industrial: lands where the primary activity involves the production, manufacture or construction of goods.

#### <u>part b</u>

**B2** 

# B1 THE DERIVATION OF ENVIRONMENTAL PROTECTIVE MATRIX SOIL QUALITY STANDARDS

#### B1.1 Introduction

CSST developed derivation procedures for the following six discrete Environmental Protective matrix standards;

- Toxicity to soil invertebrates and plants
- 2. Livestock ingesting soil and fodder
- 3. Major microbial functional impairment
- 4. Groundwater flow to surface water used by aquatic life
- 5. Groundwater used for livestock watering
- 6. Groundwater used for irrigation watering

The derivation procedures for each of these discrete standards is detailed below.

# DERIVATION OF TOXICITY TO SOIL INVERTEBRATES AND PLANTS STANDARD

#### B2.1 General Considerations

The "Toxicity to soil invertebrates and plants" standard represents the primary soil standard for the protection of ecological health. This standard represents a "mandatory" matrix standard which is required to be applied at every site.

In deriving substance "Toxicity to soil invertebrates and plants" standards for the protection of ecological health, CSST focused its attention primarily on the effects of chemical stressors to the biotic component of the terrestrial ecosystem. The ecological effects-based "Toxicity to soil invertebrates and plants" standard ( $SQS_{EE}$ ) was derived through the use of sensitive measurement endpoint data from key receptors which are considered to act as predictive sentinel species. Primary acceptable endpoints for  $SQS_{EE}$  derivation include mortality, reproduction and growth. CSST considered the complete set of such endpoint measurements as given in draft unpublished CCME Ecological Health Substance Assessment documents as the raw data from which to derive the SQS\_{EE} matrix standards.

B2.1.1 Ecological Receptors and Exposure Pathways

In determining the critical ecological receptors and exposure pathways for use in deriving environmental protection matrix standards, CSST

believed that the selected receptors should reflect the important characteristics of the ecosystem for each land use and should be compatible with the system attributes. Thus, although the level of protection provided is less rigorous for industrial and commercial sites, CSST believed that even these lands should be able to support a reasonable level of ecological function (i.e. at least be able to grow unsupplemented grass). The paucity of ecological effects information available for terrestrial organisms required that selection of ecological receptors be focused only on those receptors considered key to the maintenance of land use activities.

Similar data limitations restricted the pathways of soil exposure that could be considered for these receptors. Possible direct exposure pathways considered were:

Direct Soil Contact- by microbes, soil invertebrates and plants
 Food Ingestion- by livestock eating contaminated plants

3) Soil Ingestion- by livestock eating soil

Ultimately, CSST decided to focus on direct soil contact as the appropriate exposure pathway to derive the primary ecological health protective standard. This choice was thought appropriate as these organisms may receive the greatest threat from contaminated soil. Consequently, this pathway is considered in all land uses and is used to calculate the "toxicity to soil invertebrates and plants" standard. Due to the lack of data regarding dermal contact with contaminated soil by other organisms, it is assumed that the level of protection provided for soil dependent species will also be generally adequate for the protection of livestock and wildlife. This assumption holds except in the case where explicit evidence to the contrary exists.

In addition to the above direct exposure pathways, CSST acknowledged the need to protect against indirect contamination of ground water which may affect aquatic life or transfer contamination to water used for irrigation or livestock watering. Table 1 summarizes the receptors and exposure pathways considered for each land use.

#### Table 1

Ecological Receptors and Exposure Pathways Considered for Specific Land-use Categories in the Derivation of Ecological Effects Soil Quality Standards -

LAND USE	RECEPTORS	DIRECT EXPOSURE PATHWAYS	INDIRECT EXPOSURE PATHWAYS
Agricultural	- soil nutrient cycling	- direct soil contact	- transfer of contaminant
	processes (microbes)	- soil and fodder	to groundwater affecting:
	- crops/plants	ingestion by	- aquatic life
	- Soil invertebrates	livestock	- livestock
Residential/	- nvestock		- plants
Urban	- soil invertebrates	- direct soil contact	to groundwater affecting
Parkland 🖓			- aquatic life
			- plants
Commercial	- plants		- transfer of contaminant
	- Sou invertebrates	- direct soil contact	to groundwater affecting:
			- aquatic life
Industrial	- plants		- transfer of contaminant
	- soil invertebrates	- direct soil contact	to groundwater affecting
	n in 1990 and an		- aquatic life
		1 1. A 1.	1 A second state of the

## B2.1.2 Details

"Toxicity to soil invertebrates and plants" soil quality standards were calculated for all land uses to protect plants and soil dependent invertebrates from the adverse effects of direct contact with contaminants in soil. As described below, both LC20 and EC50-NL values were estimated for each substance. For Agricultural, Residential and Urban Parkland uses, the concentration corresponding to the more stringent of the LC20 and the EC50-NL values was chosen as the appropriate "Toxicity to soil invertebrates and plants" soil quality matrix standard. For Commercial and Industrial land uses, the concentration representing the less stringent of the LC20 and the EC50-NL values was chosen as the appropriate "Toxicity to soil invertebrates and plants" matrix standard. The "Toxicity to soil invertebrates and plants" standard is derived according to the five step procedure below:

- 1. Consider all appropriate invertebrate and plant toxicity data from CCME "Substance Assessment" documents
- Separate data into discrete lethal and non-lethal effect distributions
   Calculate median effects concentrations for lethal and non-lethal
  - distributions

6.5%

- Fit linear regression lines to lethal and non-lethal median distributions. If lethal or non-lethal regression correlation coefficient < 0.25 use "Empirical Exception" rule<sup>1</sup>.
- 5. Determine regression intercepts for EC50-NL and LC20 and apply appropriate level of protection rule for:
  - A/R/P lesser of EC50-NL or LC20
    - C/I greater of EC50-NL or LC20

"Empirical Exception" rule: Estimate EC50-NL and/or LC20 via empirical extrapolation from median effects distributions.

# B2.2 Site-Specific Factors For Agricultural Land

CSST recognized that in some circumstances the "Toxicity to soil invertebrates and plants" standard derived above might not adequately protect livestock raised on remediated agricultural sites. In consequence, CSST developed the procedure detailed below to derive a "Livestock ingesting soil and fodder" standard. This standard is applicable to agricultural land use only.

B2.2.1 Livestock Ingesting Soil and Fodder Standard

Wherever sufficient livestock toxicity data was available, a "Livestock ingesting soil and fodder" standard was derived to ensure that remediated agricultural sites would not pose health risks for domestic livestock directly ingesting soil and foraging on vegetation grown on these sites. Livestock exposures to both contaminated soil and plants grown in contaminated soil are assessed through this site specific factor. Where data indicated a particular or unique species sensitivity to the contaminant in question, the standard was derived using parameters relevant to that species, otherwise cattle were generally assumed as the default receptor of concern.

#### B2.2.2 Details

The CSST "Livestock ingesting soil and fodder" standard derivation procedure is detailed below (Exhibit 1).

Exhibit 1 - Doriver	on of Livestock incosting coil and fordat	an atom dan 1 (Cu)
LATION I - Dellvati	ion of Livestock ingesting soll and fodde	er standard (Cs)
Cs =	$1 \text{RV} \times \text{BW}$	_
	$[(Bv \times IR_{t}) + IR_{s}] \times AB \times ED \times AUF$	
<u>Parameter</u>	Definition (units)	<u>Default</u>
C,	= Livestock ingesting soil and fodder standard	
TRV	= toxicity reference value	chemical specific <sup>1</sup>
BW	= receptor body weight (kg)	600 <sup>2</sup>
Bv	= soil to plant transfer coefficient for vegetative tissue	chemical specific <sup>3</sup>
IR <sub>f</sub>	= food ingestion rate (kg/d) or 0.687 x BW <sup>0.651</sup>	13.5²
IR <sub>s</sub>	= soil ingestion rate (kg/d) or 0.083 x DMIR	1.5 <sup>2</sup>
AB	= bioavailability	1.0 (i.e. 100%)
ED	= duration of exposure	1.0 <sup>4</sup> (і.е365d/ут)
AUF	= area use function; ratio of affected area	1.0 <sup>5</sup> (i.e. 100%)
	eren en e	
DMIR	= dry matter intake rate (kg/d)	15 <sup>2</sup>

= see Exhibit 2

= default value for cattle

= point estimate from Oak Ridge National Laboratory , ORNL, 1984

<sup>4</sup> = ÊD is climate specific because the duration of exposure to the contaminant is dependent to a variable extent on the climate of the given region.
 <sup>5</sup> = AUF is area specific since the receptors may not occupy the entire given area and the contaminant might not be uniformly distributed throughout the given area

The substance toxicity reference values (TRV) of Exhibit 1 are calculated as detailed in Exhibit 2 and are generally derived using the lower bound of the estimated high dietary concentration range for the contaminant as reported in Puls (1994).

Exhibit 2 - C	Calculation of Toxicity Reference Value (TRV) for Use in Derivation of CSST Livestock ingesting soil and fodder standard
	$TRV = \frac{CD \times IR}{BW}$
Parameter TRV CD IR <sub>i</sub> BW	Definition (units)Default= toxicity reference value= lower bound of the high dietary concentration (mg/kg)chemical specific= fodder ingestion rate (kg/d)13.51= body weight (kg)6001

The estimated TRVs represent dosages where frank adverse effects to the receptor are not expected to occur. Calculated copper and lead livestock soil quality standards based on this approach resulted in soil standard concentrations at or below reported background levels. To remedy this, the upper bound of the high dietary range was used to derive "Livestock ingesting soil and fodder" matrix standards for these two contaminants (Macfarlane, 1995a).

The CSST "Livestock ingesting soil and fodder" standard derivation procedure is generally consistent with a similar procedure presented in the CCME Protocol (CCME 1994a). However, CSST has modified the CCME method to make use of the dietary toxicity data available for livestock species documented in Puls (1994). In addition, the CSST procedure considers the potential exposure of a receptor via ingestion of both contaminated soil (IR<sub>s</sub>) and contaminated fodder (IR<sub>s</sub>) at a site. Estimates of contaminant uptake by plants (fodder) were derived using the soil-to-plant transfer coefficients for the vegetative portion of plants (Bv) referenced in the 1984 Oak Ridge National Laboratory report "A Review and Analysis of Parameters for Assessing Transport of Environmentally Released Radionuclides through Agriculture" (ORNL, 1984).

B2.3 Derivation of Major Microbial Functional Impairment Soil Quality Standard

As a matter of policy, CSST decided to ensure additional protection for microbial functional processes in agricultural soils. In consequence, CSST has recommended simple adoption of the CCME "major microbial function check" criterion as the "Major microbial functional impairment" standard. The reader is referred to the CCME Protocol document (see pages 40-56 and Appendix A of that document) for details of the derivation procedure (CCME, 1995a). Where sufficient data exists, Environment Canada has calculated microbial protective criteria for inclusion in CCME substance assessment documents.

# B2.4 Environmental Soil Quality Standards for the Protection of Groundwater

CSST recognized that groundwater is a valuable resource. Groundwater is a source of recharge to our streams, rivers and lakes, and is a source of drinking water and irrigation water. The discharge and use of groundwater can affect the health of humans and aquatic life, and influence the aesthetic quality of the environment. In consequence, CSST developed procedures to derive soil-groundwater protective standards for the protection of drinking water, livestock watering, irrigation watering and use by aquatic life.

#### B2.4.1 General Considerations

Matrix soil standards for the protection of groundwater were derived using a groundwater transport model approved by CSST. This model simulates the movement of a contaminant from the soil to the groundwater, and the subsequent movement of the contaminant in the groundwater to a receptor. Contaminant transport is modelled through four chemical/ physical components, including: contaminant partitioning between soil, soil pore air, and soil pore water; contaminant leachate movement and attenuation through the unsaturated soil zone; contaminant leachate mixing with the groundwater, and contaminant movement and attenuation through the saturated groundwater zone to a receptor.

CSST considered many of the groundwater models available, including that described in the CCME protocol (CCME, 1994a; CCME, 1995a). Ultimately however, CSST recommended the use of a relatively simple model proposed by BC Environment.

#### B2.4.2 Details

BC Environment, with the assistance of Golder Associates Ltd., compiled a model in which flow is assumed to be essentially one dimensional, while still incorporating the major transport and attenuation processes affecting contaminant movement. The draft "Soil Screening Guidance, 1994" produced by the US Environment Protection Agency was used as the framework to develop the model (EPA, 1994). The mathematical code for the saturated groundwater transport is based on work by Domenico and Robbins, (Domenico and Robbins, 1984). Model assumptions however, are based on work by BC Environment. BC Environment recommended its four component model because:

- the major transport processes are represented,
- the major variables affecting each of the transport components are included, can be identified, and can be modified,
- physical and chemical affects are considered,
- model assumptions and criteria derivations are "transparent,"
- the model can be calibrated,
- the model performs with reasonable accuracy using a small set of input parameters,
- the accuracy and reliability of the model increases as site specific information increases,
- the model can be used with assumed site characteristics or use site specific data, and
- the model is scientifically based and defensible.

The BC Environment Transport Model as approved by CSST has been used to develop soil matrix standards for the protection of groundwater for both organic and inorganic contaminants. The model best simulates the transport of non-polar organic contaminants, and with modifications the model is used to simulate the transport of weakly ionizing substances. Metal transport modelling must be augmented by using an equilibrium geochemical speciation model, such as MINTEQ2.

In all transport models, the proportionment or partitioning of a chemical between soil, soil pore air, and soil pore water is critical. In the CSST approved model, the partitioning for non-polar organic contaminants is primarily a function of the organic carbon coefficient of the contaminant and the amount of organic carbon in the soil. For weakly ionizing substances, such as pentachlorophenols, partitioning in the model is additionally influenced by the pH of the soil. Partitioning of inorganics is considerably. more complex, being additionally dependent on factors such as pH, sorption to clays, organic matter, iron oxides, oxidation/reduction conditions, major ion chemistry and the chemical form of the metal. This model uses distribution coefficients (Kd) calculated as a function of pH, and as a function of an idealised soil with assigned physical and chemical characteristics. For inorganic contaminants modelling flexibility is limited in that distribution coefficients are only allowed to vary with respect to changes in soil pH. Soil pH, however, is only one of many geochemical parameters that actually can affect and change the distribution coefficient.

Attenuation within the model is essentially confined to adsorptiondesorption reactions (partitioning), dilution (mixing between contaminated leachate and groundwater, biological degradation (for organics only) and dispersion.

The transport model derives soil concentration standards to ensure that the contaminant concentrations in the groundwater discharging and in contact with a receptor are less than or equal to established substance specific water quality criteria for the receptor (i.e. aquatic life) or water use (i.e. irrigation watering, livestock watering or drinking water) of concern. Thus, allowable concentrations in the groundwater at the point of contact with a receptor are based on either the aquatic life criteria, or for irrigation and livestock water uses, the respective irrigation or livestock watering criteria, presented in the CCME "Interim Canadian Environmental Quality Criteria for Contaminated Sites" (CCME, 1991), or "Canadian Water Quality Guidelines" (CCME, 1995b) and/or BC Environment's "Approved and Working Criteria for Water Quality" (BC Ministry of Environment, Lands and Parks, 1995b). Soil standards to protect groundwater for use as drinking water are based on the drinking water criteria presented in "Guidelines for Canadian Drinking Water Quality" (Health Canada, 1993) and/or "Approved and Working Criteria for Water Quality" (BC Ministry of Environment, Lands and Parks, 1995b) documents.

The Groundwater Protection Transport Model is based on assumptions generally typical of the climatic conditions of the lower Fraser River/ Vancouver area of British Columbia, and assumed groundwater characteristics typical of those found within the Fraser River sands of the Fraser River delta area. Other assumptions include:

的一个,这种问题是我的意思。"他们的"是是"的话题。

- the site is medium sized (between 1500  $m^2$  and 12000  $m^2$ ),
- the total volume of contaminated soil is less than 450 cubic metres  $(5m \times 30 m \times 3 m)$ ,
- the depth to groundwater is not more than three (3) metres,
- the distance to the receptor is at least 10 metres,
- the soil is physically and chemically homogeneous,
- the organic content of the soil is at least 0.6 percent,
- the moisture content is uniform throughout the unsaturated zone,
- the porosity of the soil is 30 percent, and 10 percent of the pore volume is water filled,
- the infiltration rate is uniform throughout the unsaturated zone,
- flow in the unsaturated zone is assumed to be one dimensional and downward only, with dispersion, retardation and biological degradation,
  - the contaminant is not present as a free product phase (i.e. a non-aqueous phase liquid),

- the maximum concentration in the leachate is equivalent to the solubility limit of the chemical in water under the defined site conditions,
- the groundwater aquifer is unconfined,
- the groundwater flow is uniform and steady,
- co-solubility and oxidation/reduction effects are not considered,
- attenuation in the saturated zone is assumed to be one dimensional with respect to retardation, dispersion and biodegradation,
- dispersion is assumed to occur in the longitudinal and horizontal transverse directions only, and diffusion is not considered,
- mixing of the leachate with the groundwater is assumed to occur through mixing of leachate and groundwater mass fluxes, and
- dilution by groundwater recharge down gradient of the source is not included.

Refer to Schematic drawing 1 for a typical transverse section through a contaminated source.

The mathematical equations for each of the four model components are presented below in Exhibits 3, 4, 5, 6 and 7. The soil/leachate partitioning component is presented in Exhibit 3. The flow component in the unsaturated soil zone is presented in Exhibit 4. The mixing of unsaturated and saturated zone waters is presented in Exhibit 5. The flow component in the saturated groundwater zone is presented in Exhibit 6. Conditions relating to the contaminant concentration in the saturated groundwater zone are provided in Exhibit 7. Exhibit 8 provides definitions for parameters, and corresponding default values, used in modelling to produce matrix soil groundwater protective standards.

For each of the chemicals for which matrix soil-groundwater protection standards have been derived, the chemical characteristics used in the model are presented in Appendix B. Chemical characteristics provided include solubility, organic:water and other distribution coefficients, biological degradation rates, and Henry's Law constants.

# Schematic drawing 1 - Transverse section of contaminated source in various layers of soil

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Aquitard - Permeability less than unconfined aquifer

- Z = thickness of contaminated source
- d = depth from ground surface to uncontaminated groundwater surface
- b = thickness of the unsaturated zone
- da = thickness of unconfined groundwater aquifer
- Za = thickness of mixing zone

da

Exhibit 3 - S	Soil/Leachate Partitioning Model	
	$C_{s} = C_{L} \{K_{d} + (\underline{n_{u} + H'n_{s}})\}$	
<u>Parameter</u>	Definition (units)	<u>Default</u>
Cs CL K₄	= soil concentration at source (mg/kg) = leachate concentration at source (mg/L) = distribution coefficient for a chemical (cm³/g)	calculated value chemical/physical specific <sup>1</sup>
n, H'	<ul> <li>= water filled porosity (dimensionless)</li> <li>= dimensionless Henry's Law constant for the chemical</li> </ul>	0.1 H x 42.3 <sup>2</sup>
H n,	= Henry's Law constant (atm-m <sup>3</sup> /mol) = air filled porosity (dimensionless):	chemical specific 0.2
P <sub>b</sub>	$r_{b} = n - n_{u}$ = dry bulk density of soil (g/cm <sup>3</sup> )	1.75 <sup>3</sup>
$^{1}$ = see Append $^{2}$ = where 42.3 $^{3}$ = based on "	lix B is a units conversion factor for 15°C Fraser River sand" characteristics	

Я

	Onsaturated Groundwater Zone	
	$C_{1} = C_{1} \exp[b - b \{1 + (4\partial_{1}L_{10})\}^{1/2}]$	
	27 27 27 V	
2 C		
· · ·		
	$V_{ii} = \underline{I}_{ii}; R_{ii} = 1 + \underline{P}_{ii} \times K_{ii};$	
	nR n	
	tru ±tu	·
Donomotor	Definition (control	
alameter	<u>Demution (units)</u>	<u>Default</u>
e a ser e		
C <sub>z</sub>	= chemical concentration of the leachate at the	and the second second
	watertable (mg/L)	
C.	= leachate concentration at the source $(mg/I)$	calculated value
<b>)</b>	= thickness of the unsaturated zone (m).	n
10 - C	b = d - Z	•
4	= depth from surface to uncontaminated	· • .
	eroundwater surface (m)	3
7	= depth of contaminated soil (m)	<b>.</b>
	- deput or containinated soil (iii)	3
τ <u>α</u>	= degret constant for shorting (started 2000 (m)	0.1x5
-Us	- decay constant for chemical (seconds ·) in	
1	The officer of the second seco	calculated value
	$L_{US} = 0.691 \times (e^{-10.42}) \times (1 - (D_{1/2US}))$	en a sur en anter a setter a
	1/2US 365	
1/2 US	= chemical half-life in unsaturated zone	chemical specific <sup>1</sup>
U <sub>1/2US</sub>	= frost free days	365
V <sub>u</sub>	= average linear leachate velocity (m/s)	calculated value
[	= infiltration rate ( m/yr):	0.55
1	I = P - (RO + EV)	· · ·
P	= precipitation rate (m/yr)	1
(RO + EV)	= sum of runoff rate (RO) + surface	0.45
	evapotranspiration rate (EV) (m/vr)	
n.,	= water-filled porosity (dimensionless)	01
R.	= retardation factor in unsaturated zone	calculated value
	(dimensionless)	calculated value
P.	= dry bulk density of soil (kg /i)	1 7=2
ĸ	= distribution coefficient for a chemical $(am^3/a)$ .	1.70 -
	for organics $K = K \times f$	cnemical specific-
Carlos de la carlo de la c	for models $K = function of call matrix is$	
	to interais $K_d = 101000000000000000000000000000000000$	
· ·	pH, redox conditions, iron oxide	
	content, cation exchange capacity	
r	and major ion chemistry	
Noc 1	= organic carbon partitioning coefficient (cm <sup>3</sup> /g)	chemical specific <sup>1</sup>
oc	= weight fraction of organic carbon in soil	0.006 -
	(dimensionless)	

= based on "Fraser River sand" characteristics

÷

			н н Т
•			
	Exhibit 5 - Mixing Zone Unsaturated (Saturated		,. ],
	$C = C + 1 + (7 \times 37)$		1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
	$C_z = C_{gw} \left\{ 1 + \left( \frac{Z_d \times V}{Z_d} \right) \right\}$		
	<u>perinition (units)</u>	<u>Default</u>	•
	- chamical concentration of the least-to at		
	the water table (mg/L)		
· .	$C_{rw}$ = chemical concentration in the groundwater	calculated value	
	at source (mg/L)		
	$Z_d$ = average thickness of mixing zone (m)	0.5 <sup>1</sup>	· .
	Darcy velocity in groundwater (m/year)	12.6	
	I = infiltration rate $(m/s)$	2×108 ) + 1/20 0	12000
	X = length of contaminated soils (m) for point source	5	
· · · ·			· ·
	$f = z_d$ is a function of mixing zone depths available due to dispersion/diff infiltration and underground flow rates. Son Exhibit 6	fusion and due to	
	- Autoritation and Entactigiounity now rates. See Exhibit 6.		]
·			
	Exhibit 6 - Calculation of Average Thickness of Mixing Zor	7	7
		ie, Zd	· · ·
	$Z_{r} = r + s$		
1997 - D.			
	Parameter Definition (units)	<u>D</u> efault	
	$Z_{d}$ = average thickness of mixing zone (m)		
	= mixing deput available due to dispersion		
	$r = 0.01 \times X$	calculated value	
	X = length of contaminated soils (m)	5	1
	s = mixing depth available due to infiltration		
	rate and groundwater flow rate (m): calculat $f = \frac{1}{2} 1$	ed value	
	$d_{1} = unconfined groundwater aquifer (m)$	E	
	(used to calculate Z,)	<b>J</b>	· ·
	I = infiltration rate (m/yr):	0.55	
	I = P - (RO + EV)		· ·
- 126	= precipitation rate  (m/yr)	1	
	evapotranspiration rate (RV) (m/vr)	U.45	. • . •
	V = Darcy velocity (m/yr)	12.6	
·			. L

Ì	TT 1 11 14 P		•			
Ì	Exhibit 7 - Saturated Groundwater Zone					
	$C_{w}(x,y)$	$(z,t) = (C_{-1})\exp\{(x_{1})[1-(1+4L\partial_{1})^{1/2}]\} \exp\{(x-v_{1}t/1)$	$+41.2 /77)^{1/2}$			
		4  73  77  77	$(3 \text{ m+})^{1/2}$			
1	1 April 1	$2 \qquad 20_{\rm X} \qquad 0 \qquad 2$	$(\mathbf{O}_{\mathbf{x}},\mathbf{O}_{\mathbf{y}})$			
	1	$\operatorname{err}\left[\frac{ y+1/2 }{ y-1/2 }\right]$				
		$2(\partial_y \mathbf{x})^{n/2} = 2(\partial_y \mathbf{x})^{n/2}$				
		$V = Ki$ ; $v = V$ ; $R_s = 1 + (P_s K_s)$ ; $K_s = K_s f$				
	Parameter	Definition (unite)	<b>.</b>			
	<u>i alailicici</u>	<u>Deminon (umis)</u>	<u>Default</u>			
•	C <sub>w</sub>	= chemical concentration in groundwater	applicable water			
	(1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,	flow at receptor (mg/L)	quality standard			
	×	= distance to source (m)	10			
	x,y,z	= Cartesian coordinates that coincide with principle	x is site specific			
		directions of the dispersivity tensor (m)				
	t	= time since contaminant release (years)	100			
	C <sub>gw</sub>	= chemical concentration in the groundwater	calculated value			
		at source (mg/L)				
ć,	$\partial_{x'} \partial_{y'} \partial_z$	= principle values of the dispersivity tensor (m):	calculated values			
Ż		$\partial_x=0.1_X$				
i,	·	∂ <sub>y</sub> =0.1∂ <sub>x</sub>				
	Ls .	= decay constant (seconds') in saturated zone:	chemical/depth			
		$L_{s} = 0.691 \times (e^{-0.07 \times a})$	specific			
·	4	t <sub>1/25</sub>				
	<b>"</b>	= depth from surface to uncontaminated groundwater	3			
		surface (m)				
· ;	t <sub>1/2s</sub>	= decay (biodegradation) half-life (s)	chemical specific <sup>1</sup>			
•• •	<b>D</b>	= velocity of the contaminant (m/s)	$v = V/n_r R_r$			
	V	= Darcy velocity or specific discharge (m/yr):	12.6			
		$\mathbf{V} = \mathbf{K}\mathbf{i}$				
	K	= hydraulic conductivity (m/s):	calculated value			
		is that $\mathbf{K} = \mathbf{V} / \mathbf{i}$ . The second function $\mathbf{K}$ with every $\mathbf{K}$ is the second state $\mathbf{k}$	1995 - A.			
· .	i	= groundwater gradient (dimensionless):	calculated value			
•		i = V/K				
	n	= porosity of contaminated soil	0.3			
	n <sub>e</sub>	= effective porosity (dimensionless) <sup>1</sup>	0.2			
	Y	= source's width (m) - perpendicular to ground-	- 30			
· ·		water flow				
	R <sub>r</sub>	= Retardation factor (dimensionless)	calculated value			
1.	Pb	= bulk density of soil (g/cm <sup>3</sup> )	1.75			
•	K <sub>d</sub>	= distribution coefficient for chemical and	chemical/soil			
		soil (cm³/g) and in the second sec	specific <sup>1</sup>			
		$K_{d} = K_{re} \times f_{re}$				

(see over)



= see Appendix B

Exhibit 8 - L	Default Groundwater Model Parameters		
<u>Parameter</u>	Definition (units)	<u>Default</u>	
G	= maximum solubility	chemical specific <sup>1</sup>	· · · ·
n	= total porosity (dimensionless)	0.3	
n,	= water filled porosity	0.1	
n,	= air filled porosity (dimensionless):	calculated value	<u> </u>
	n₃ ≖ n - n,	0.2	
$\mathbf{P}_{\mathbf{b}}$ . The first field	= dry bulk density of soil (g/cm <sup>3</sup> )	1.75	
H	= Henry's Law constant	chemical specific <sup>1</sup>	:
H'	= dimensionless Henry's Law constant	chemical specific <sup>1</sup>	
<b>∂</b> _	= dispersivity in unsaturated zone	0.1 x b	
for	= fraction of organic carbon in soil	0.006	
V	= Darcy velocity in saturated zone (m/yr)	12.6	
Z	= thickness of mixing zone (m)	0.5	
K	= distribution coefficient for a chemical $(cm^3/g)$	chemical specific <sup>1</sup>	
K	= organic carbon partitioning coefficient (cm <sup>3</sup> /g)	chemical specific <sup>1</sup>	
5	= dispersivity in x-direction	$\partial_x = 0.1 \times$	
9,	= dispersivity in y-direction	$\partial_y = 0.1 \partial_x$	
d	= unconfined groundwater aquifer (m)	5	
b	= thickness of the unsaturated zone	0	
	note: $b = d - Z$		
a	= depth from surface to uncontaminated	3	1
	groundwater surface (m)		
x	= distance from source to receptor (m)	10	
n,	= effective porosity (dimensionless)	0.2	
t <sub>1/2 US</sub>	= decay (biodegradation)	chemical specific <sup>1</sup>	· .
	half-life at unsaturated sites		
t <sub>1/2 5</sub>	= decay (biodegradation)	chemical specific <sup>1</sup>	1
	half-life at saturated sites		
I	= infiltration rate (m/yr)	0.55	
	Note: $I = P - (RO + EV)$	(1 - 0.45)	
P	= precipitation rate (m/yr)	1	
(RO + EV)	= runoff rate plus surface	0.45	
	evapotranspiration rate (m/yr)		· .
X	= source dimension length (m)	5	
Y	= source dimension width (m)	30	. i.
Z	= source dimension thickness (m)	3	
D <sub>1/2U5</sub>	= frost free days	365	
<sup>1</sup> = reference	e values provided in Appendix B		

#### HUMAN HEALTH PROTECTIVE STANDARDS <u>PART C</u>

#### DERIVATION OF HUMAN HEALTH BASED-SOIL QUALITY C1 . STANDARDS (SQS<sub>HH</sub>)

# C1.1 Introduction

CSST has developed derivation procedures for two human health protection soil quality matrix standards;

1. Intake of contaminated soil, and

2. Groundwater used for drinking water.

The derivation of the "Groundwater used for drinking water" soil standard has been detailed in section B2.4 above. Procedures to derive the "Intake of contaminated soil" standard are provided below.

#### C1.2 General Considerations

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The derivation of the "Intake of contaminated soil" quality standard involved four basic components:

determination of a critical human reference dose representative of a defined acceptable toxicological hazard or risk posed by a chemical, definition of appropriate critical human receptors for the specified land uses.

development of defined exposure scenarios for the specific land uses, and integration of exposure scenarios and toxicity information with CSST policy decisions to calculate soil quality standards.

- Q.

والمراجع والمراجع والمتعالية المحاج والمحاج والمحاج والمحاج والمحاج والمحاج والمحاج والمحاج والمحاج والمحاج وا The "Intake of contaminated soil" human health soil quality standard is intended to ensure that human exposure to a contaminant resulting from the ingestion of contaminated soil would not exceed a specified level of acceptable hazard or risk established by CSST. Consequently, soil quality standards were developed by considering exposure to contamination through the direct soil ingestion pathway. Other potential exposure pathways such as the inhalation of dust or vapours and the consumption of contaminated vegetables, milk and meat produced on contaminated soils were also considered by CSST.

In the case of dermal exposure, sufficient data to derive standards is lacking. In the case of exposures to dust or vapours and milk and meat produced on contaminated sites, CSST was of the opinion that either the models or default parameters used to estimate such exposures lacked sufficient scientific validation. Thus, these additional indirect human exposure pathways were excluded from standard derivation procedures.

However, for most non-volatile substances direct ingestion of soil contaminants was believed to be the quantitatively most significant human exposure pathway of concern for use in deriving human health protective standards. In addition, CSST believed that for some contaminants, empirical information linking soil contaminant exposure with health outcomes might exist. Consequently, CSST contracted a study with independent health experts to review such information. The results of that study were used to adjust, where necessary and scientifically defensible, substance "Intake of contaminated soil" standards derived on the basis of toxicological models (see section C3 below).

#### C1.3 Threshold and Non-threshold Contaminants

Environmental contaminants were classified with respect to their potential carcinogenicity and mutagenicity based on the quantity, quality and nature of the available toxicological and epidemiological studies. Health Canada (1992) separates substances into two broad categories, non-threshold and threshold contaminants using this information. Non-threshold contaminants, such as carcinogens or germ cell mutagens are those for which it is assumed that there is some probability of harm to human health at any level of exposure. Consequently for such substances, it is not possible to determine a dose below which adverse affects may not occur. Threshold substances are those for which a level may be set below which no adverse effects are expected to be produced. The critical endpoints usually considered for deriving reference doses for threshold substances are either NOAEL. (No Observed Adverse Effect Level) or LOAEL (Lowest Observed Adverse Effect Level) based.

For threshold and non-threshold contaminants a "reference dose" has been determined. This is the Tolerable Daily Intake (TDI) for threshold substances and the Risk Specific Dose (RsD) for non-threshold substances. For a threshold substance, exposure less than the TDI should pose essentially a negligible probability of incidence of an adverse effect in the population. For a non-threshold substance, the RsD used by CSST corresponds to an expected excess lifetime cancer incidence of  $1 \times 10^{-5}$  (i.e. 1 in 100,000).

C2 LEVEL OF PROTECTION, RECEPTORS AND PATHWAYS

C2.1 Levels of Protection for the Protection of Human Health

For the purpose of deriving the "Intake of contaminated soil" quality standards to protect human health, CSST determined that contaminated site related risks arising from human exposure to non-threshold carcinogenic substances should not exceed a risk level of 1x10<sup>5</sup>. The matrix standard derived for such substances, therefore reflects this level of risk. In order to derive matrix soil quality standards for threshold contaminants, it was necessary to ascribe some allowable proportion of the total exposure to contaminants present at a site to the soil medium. Considering the five sources to which people are exposed (i.e. air, water, soil, food and consumer products) CSST recommended that 20% of the total TDI for threshold contaminants be allotted to soil.

CCME recommended that the Estimated Daily Intake (EDI) for a particular contaminant due to normal background exposure (i.e. not including exposure which may occur at a contaminated site) also be accounted for in deriving soil quality criteria to protect human health (CCME, 1994a; CCME, 1995a). CCME reasons that as we are constantly exposed to this background contamination, risks posed by a contaminated site should be determined in addition to the background exposure. Thus, CCME soil criteria are calculated in consideration of the background soil exposure as well as the soil allocation (20%) of tolerable daily intake. CSST recognized the potential impact of normal background (i.e. EDI) exposures. However, since estimation of generic EDIs is both difficult and of questionable relevance for any specific site, CSST recommended that the CCME methodology incorporating background EDIs not be followed. Rather, CSST believed that a simple 20% apportionment of the TDI to soil would ensure an adequate level of protection. CSST also noted that incorporation of consideration of background EDIs in the CCME methodology often resulted in the derivation of soil quality values which typically approximate or, on occasion, are actually less than that of the usual background soil concentration of ubiquitous. substances. As noted in section E1 below, the proposed Contaminated Sites Regulation, as a matter of policy, does not force clean up of contaminated site soil concentrations to less than local background levels.

C2.2 Choice of Exposure Pathways and Receptors for Land Uses

For the purposes of deriving intake of contaminated soil standards, CSST assumed a chronic human exposure scenario (i.e. lifetime exposure to a remediated site). This assumption acts to overestimate actual exposure and helps ensure that no site usage limitations will exist within a defined land use.

· 是你不知道,你还是你们的事情。""你们就是你不能。"

The choice of sensitive receptors was linked to land use considerations and was primarily dependent on the ages of the human receptors reasonably expected to be associated with those land uses. Studies have indicated that children are likely to ingest much larger quantities of soil and have greater general exposure to soil contaminants than adults. These factors, as well as lower average body weights for younger individuals, create a broad range of receptor characteristics which might be considered in derivation of soil quality standards (Table 2).

Table 2 Typical Average Receptor Characteristic Values for the Canadian General Population (sources: Angus Environmental, 1991; Newhook, 1992; MENVIQ, 1992)

Age classes (years)	Body weight (kg)	Air intake (m³/day)	Water intake (L/day)	Soil intake (mg/day)	Skin surface areas <sup>1,2</sup> (m <sup>2</sup> )
0-0.5	. 7.	<b>2</b>	0.75	20	0.30
0.6-4	13	5	0.8	80	0.26
5-11	27	12	0.9	20	0.41
12-19	57	21	1.3	20	0.43
20+	70	23	1.5	20	0.43

skin surface areas for different age classes based on: 0-0.5: total body; 0.6-4 and 5-11: head, arms, hands, lower legs; 12-19 and 20+:head, arms, hands. the amount of dirt assumed to be covering skin surfaces for all age classes is 1.0 mg/cm<sup>2</sup>; taken from EPA (1990), Interim Guidance for Dermal Exposure Assessment.

In considering Table 2, CSST decided that in the case of non-threshold substances, hazard would be assessed using an adult as the critical receptor for all land uses, and exposure was assumed to be continuous over 70 years.

For threshold substances, ideally, exposure would be averaged over, and TDIs measured against, the most sensitive life stages. As such "agestepping" is a complex procedure for which data is lacking for many substances, CSST decided to derive standards for scenarios (eg. Agricultural, Residential/Urban Parkland, and Commercial) in which the 0.6-4 year old child was assumed to be both the critical receptor and the critical age class. CSST recognized that for some specific chemicals, different receptors and age classes than those assumed may be more appropriate. State Part of

The land use defined exposure scenarios envisioned by CSST in deriving human health protective standards are outlined in Table 3.

			·
	Agricultural	Residential/ Urban Parkland	Commercial
Defined Land Use Scenario	<ul> <li>a multi-functional farm with a family living on- site</li> <li>children are present</li> <li>groundwater is used as drinking water</li> </ul>	<ul> <li>single family home with a backyard</li> <li>children are present</li> <li>groundwater may be used as drinking water</li> </ul>	<ul> <li>urban commercial property</li> <li>children have access to property</li> <li>groundwater may be used as drinking water</li> </ul>
Sensitive Receptor	- child (threshold contaminants) - adult (non-threshold contaminants)	- child (threshold contaminants) - adult (non-threshold contaminants)	- child (threshold contaminants) - adult (non-threshold contaminants)
Exposure Period	See Table 4	See Table 4	See Table 4
Direct Soil Exposure Pathways	- soil ingestion	- soil ingestion	- soil ingestion
Indirect Soil Exposure Pathways	- ingestion of groundwater as drinking water	- ingestion of groundwater as drinking water	- ingestion of groundwater as drinking water

Table 3 CSST Human Health Land-use Defined Exposure Scenarios

No land use defined exposure scenario for Industrial land is provided in Table 3. CSST recognized that issues relating to soil quality for human health protection on industrial sites is the mandate and responsibility of the Workers' Compensation Board of British Columbia. Consequently, Industrial "Intake of contaminated soil" standards have not been derived by CSST.

DERIVATION EQUATIONS FOR INTAKE OF CONTAMINATED SOIL STANDARDS

C3

The equations detailed below were used to derive toxicological risk based soil quality standards for direct ingestion of contaminants in soil. A "Real World Clinical Health Experience" review was conducted for CSST by the University of British Columbia, Department of Health Care and Epidemiology to determine the extent of correlation between exposure to arsenic, benzene, cadmium, chromium and lead in soil and "real world" adverse health outcomes (Jin and Teschke, 1995). Based on the review results presented in the UBC final report (Jin and Teschke, 1995), Ministry of Health members of CSST were able to provide rationales to justify the "adjustment" of toxicological-derived intake of contaminated soil standards for arsenic, cadmium and lead.

# C3.1 Intake of Contaminated Soil Standards

The equations used to derive "Intake of contaminated soil" standards for threshold and non-threshold substances are presented below.

C3.1.1 Derivation of Intake of Contaminated Soil Standards for Threshold Substances

The general theoretical equation for calculating preliminary human health soil quality standard (PSQS<sub>HH</sub>) is shown in Exhibit 9A. This equation is simplified, as described below, to yield the equation in Exhibit 9B which was used by CSST to calculate  $PSQS_{HH}$ .

Estatist OA	Dealer to a state of the second state of the s
EXHIDIT 9A -	Prenminary Human Health IDI-based "Intake of contaminated
	soil" Standard (PSQS <sub>HH</sub> ) - Threshold Substances
	a sugarta da serie de la companya en la companya de la companya de la companya de la companya de la companya d La companya da companya de la company
	$PSQS_{HH} = $ [SAF × TDI] × BW
	$[(AF_X IR) + (AF_X DR) + (AF_X SR)] \times FT$
Parameter	Definition (unite)
<u>Xarumeter</u>	<u>Default</u>
DCOC	
r SQS <sub>HH</sub>	= preliminary human health TDI-based soil
	quality standard (mg/kg)
SAF	= soil allocation factor $0.2$
TDI	= tolerable daily intake (mg/kg BW day) chemical specific
BW	= body weight (kg)
	ter de se <b>chald</b> de l'arte de la companie de la chald de la companie de la compa
	e se la adult de la seconda de la contra de la la seconda de la seconda de la seconda de la seconda de la secon
AF,	= absorption factor for out (unitless)
IR	= soil ingestion rate (mg/day)
	child
	SU SU
AF	
קרו D	= absorption factor for lung (unifiess)
	= soli innaiation rate (kg/day)
Ars	= absorption factor for skin (unitless) 1.0
SR	= soil dermal contact rate (kg/day)
ET	= exposure term (unitless)
1	= see Table 4

The exposure term parameter (ET) of Table 4, is a ratio of the assumed land use defined exposure period versus the maximum possible lifetime exposure period (i.e. 24 hours/day x 7 days/week x 52 weeks/year x 70 years).

Table 4	Exposure Ter	ms for	Various	Classes	of	Toxic	Substa	nces	and
	Land Uses				1			· · · ·	

Class of Toxic Substance	Receptor	Land Use	Exposure Term (ET)
Non-threshold	Adult	Agricultural, Residential, Urban Parkland	1.01
		Commerical	0.33²
Threshold	Child	Agricultural, Residential, Urban Parkland	1.0 <sup>3</sup>
		Commerical	0.334

 $^{1}ET = (24hr/24hr \times 7d/7d \times 52wk/52wk \times 70yr/70yr)$ 

 $^{2}$ ET = (12hr/24hr × 5d/7d × 48wk/52wk × 70yr/70yr)

<sup>3</sup>ET =  $(24hr/24hr \times 7d/7d \times 52wk/52wk \times 3.5yr/3.5yr)$ 

 $^{4}$ ET = (12hr/24hr × 5d/7d × 48wk/52wk × 3.5yr/3.5yr)

Although the equation provided in Exhibit 9A provides terms to deal with other possible routes of exposure (i.e. inhalation and dermal), currently only the direct soil ingestion route is used to derive standards. Unless verifiable scientific data indicates otherwise, the absorption factor parameter,  $AF_1$ , is assumed to equal 100%. Consequently, the equation of Exhibit 9A for direct soil ingestion of threshold substances reduces to that of Exhibit 9B.

Exhibit 9B -	Simplified Human Health TDI-based "Intak soil" Standard (PSQS <sub>HH</sub> ) - Threshold Substar	e of contaminated
	$PSQS_{HH} = \frac{[SAF \times TDI] \times BW}{(AF_1 \times IR) \times ET}$	
<u>Parameter</u>	Definition (units)	<u>Default</u>
PSQS <sub>HH</sub>	= preliminary human health TDI-based soil quality standard (mg/kg)	
SAF TDI BW	= soil allocation factor = tolerable daily intake (mg/kg BW-day) = body weight (kg)	0.2 chemical specific
AT	child adult	13 70
IR	= absorption factor for gut (unitless) = soil ingestion rate (mg/day)	1.0
ET	adult ≃ exposure term (unitless)	80 20 land use specific <sup>1</sup>
L.	= see Table 4	

If published Health Canada data for both background EDI and National generic background soil concentrations are available, the following equation (Exhibit 10) is used to derive an additional value, PSQN<sub>HH(EDI)</sub>:

<u>_</u>		
Exhibit 10 -	Preliminary Human Health EDI-based "Intal	ke of contaminated
	Soil Standard (PSQS <sub>HH(EDi)</sub> - Threshold Subst	ances
PSQS	$HH(EDI) = (TDI - EDI) \times SAF \times BW + [BSC]$	
	$(AF_{I} \times IR) \times ET$	
Bowern etc.	entre in all and an anna an a	
<u>r arameter</u>	<u>Definition (units)</u>	<u>Default</u>
PSQSHHIEDIN	= preliminary human health EDI-based soil	en a Martine, en la compañía de la com Referencia
	quality standard (mg/kg)	
TDI	= tolerable daily intake (mg/kg BW day)	chemical specific
SAF	= estimated daily intake (mg/kg BW-day)	chemical specific
BW	≈ body weight (kg)	0.2
	child	13
BSC	adult	70
550	(mg/kg)	chamical specific
AF	= absorption factor for gut (unitless)	1.0
IR	= soil ingestion rate (mg/day)	
	child	80
ET	= exposure term (unitless)	20 land use specific <sup>1</sup>
	= see Table 4	with the specific

It should be noted that for all substances for which matrix standards have been calculated to date, there are either no published Health Canada EDIs or background soil concentrations which would enable calculation of a PSQS<sub>HH(EDI)</sub> value using the equation in Exhibit 10.

If a  $PSQS_{HH(EDI)}$  value could be calculated it would then be compared with the  $PSQS_{HH}$  value calculated from CSST's preferred simplified formula (Exhibit 9B). CSST recommends that the final "Intake of contaminated soil" standard should be based on the "more reasonable" of the two preliminary values derived above.

# C3.1.2 Derivation of Intake of Contaminated Soil Standards for Nonthreshold Substances

The calculation of RsD-based "Intake of contaminated soil" quality standards for non-threshold substances is similar to that given for threshold substances. The general theoretical equation for calculating this human health soil quality standard  $SQS_{HH}$  is shown in Exhibit 11A. This equation is simplified, as described below, to yield the equation in Exhibit 11B which was used by CSST to calculate  $SQS_{HH}$ .

$SQS_{HH} = \frac{RsD \times BW}{[(AF_1 \times IR) + (AF_D \times DR) + (AF_S \times SR)] \times ET}$ $SQS_{HH} = \frac{RsD \times BW}{[(AF_1 \times IR) + (AF_D \times DR) + (AF_S \times SR)] \times ET}$ $\frac{Parameter}{Definition (units)} \qquad Default$ $SQS_{HH} = human health RsD-based soil quality$ $standard (mg/kg)$ $RsD = risk specific dose (mg/kg day)$ $BW = body weight (kg)$ $RsD = absorption factor for gut (unitless)$ $I.0$ $R = absorption rate (mg/day)$ $R = body = absorption rate (mg/day)$
$SQS_{HH} = \frac{RsD \times BW}{[(AF_{I} \times IR) + (AF_{D} \times DR) + (AF_{S} \times SR)] \times ET}$ $Parameter \qquad Definition (units) \qquad Default$ $SQS_{HH} = human health RsD-based soil quality$ $SQS_{HH} = $
Substances $SQS_{HH} = \underline{RsD \times BW}$ $[(AF_1 \times IR) \neq (AF_D \times DR) + (AF_S \times SR)] \times ET$ ParameterDefinition (units)Default $SQS_{HH}$ = human health RsD-based soil quality standard (mg/kg)RsD= nisk specific dose (mg/kg-day)chemical specificBW= body weight (kg)70AF_1= absorption factor for gut (unitless)1.0IR= soil ingestion rate (mg/day)20
$\begin{split} SQS_{HH} &= \frac{RsD \times BW}{[(AF_I \times IR) + (AF_D \times DR) + (AF_s \times SR)] \times ET} \\ \hline \underline{Parameter} & \underline{Definition (units)} & \underline{Default} \\ \\ SQS_{HH} &= human health RsD-based soil quality \\ standard (mg/kg) \\ \\ RsD &= risk specific dose (mg/kg day) \\ \\ BW &= body weight (kg) \\ \\ AF_I &= absorption factor for gut (unitless) \\ \\ I.0 \\ \\ 20 \\ \\ \end{split}$
$\begin{split} SQS_{HH} &= \frac{RsD \times BW}{[(AF_{I} \times IR) + (AF_{D} \times DR) + (AF_{S} \times SR)] \times ET} \\ \hline \underline{Parameter} & \underline{Definition (units)} & \underline{Default} \\ \\ SQS_{HH} &= human health RsD-based soil quality \\ standard (mg/kg) \\ \\ RsD &= risk specific dose (mg/kg day) \\ \\ BW &= body weight (kg) \\ \\ AF_{I} &= absorption factor for gut (unitless) \\ \\ RsD &= soil ingestion rate (mg/day) \\ \\ AF_{I} &= absorption factor for gut (unitless) \\ \\ RsD &= soil ingestion rate (mg/day) \\ \\ RsD &= absorption factor for gut (unitless) \\ \\ RsD &= soil ingestion rate (mg/day) \\ \\ RsD &= body Weight (kg) \\ \\ RsD &= soil ingestion rate (mg/day) \\ \\ RsD &= body Weight (kg) \\ \\ $
$SQS_{HH} = \frac{RsD \times BW}{[(AF_I \times IR) + (AF_D \times DR) + (AF_s \times SR)] \times ET}$ $\frac{Parameter}{Definition (units)} \qquad \frac{Default}{Default}$ $SQS_{HH} = human health RsD-based soil quality$ $standard (mg/kg)$ $RsD = risk specific dose (mg/kg day)$ $BW = body weight (kg)$ $aborption factor for gut (unitless)$ $I.0$ $RsD = soil ingestion rate (mg/day)$ $AE = body = body = body$
$[(AF_{I} \times IR) + (AF_{D} \times DR) + (AF_{s} \times SR)] \times ET$ $\underline{Parameter} \qquad \underline{Definition (units)} \qquad \underline{Default}$ $SQS_{HH} = human health RsD-based soil quality$ $standard (mg/kg)$ $RsD = risk specific dose (mg/kg day) \qquad chemical specific$ $BW = body weight (kg) \qquad 70$ $AF_{I} = absorption factor for gut (unitless) \qquad 1.0$ $RsD = soil ingestion rate (mg/day) \qquad 20$
ParameterDefinition (units)Default $SQS_{HH}$ = human health RsD-based soil quality standard (mg/kg)standard (mg/kg)RsD= risk specific dose (mg/kg.day) = body weight (kg)chemical specific 70BW= body weight (kg) = absorption factor for gut (unitless) = soil ingestion rate (mg/day)1.0 20
ParameterDefinition (units)Default $SQS_{HH}$ = human health RsD-based soil quality standard (mg/kg)standard (mg/kg)RsD= risk specific dose (mg/kg day) = body weight (kg)chemical specificBW= body weight (kg)70AF_1= absorption factor for gut (unitless) = soil ingestion rate (mg/day)1.0AF_2= soil ingestion rate (mg/day)20
$\begin{array}{llllllllllllllllllllllllllllllllllll$
SQS <sub>HH</sub> = human health RsD-based soil quality         standard (mg/kg)       standard (mg/kg)         RsD       = risk specific dose (mg/kg day)       chemical specific         BW       = body weight (kg)       70         AF <sub>I</sub> = absorption factor for gut (unitless)       1.0         IR       = soil ingestion rate (mg/day)       20
$ \begin{array}{ll} standard (mg/kg) \\ RsD &= risk specific dose (mg/kg day) \\ BW &= body weight (kg) \\ AF_{I} &= absorption factor for gut (unitless) \\ IR &= soil ingestion rate (mg/day) \\ AF_{I} &= absorption factor for gut (unitless) \\ IR &= soil ingestion rate (mg/day) \\ Chemical specific dose (mg/kg day) \\ Chemi$
RsD= risk specific dose (mg/kg day)chemical specificBW= body weight (kg)70AF1= absorption factor for gut (unitless)1.0IR= soil ingestion rate (mg/day)20
$\begin{array}{llllllllllllllllllllllllllllllllllll$
AF1       = absorption factor for gut (unitless)       1.0         IR       = soil ingestion rate (mg/day)       20         AF-       = absorption factor for lung (day)       20
$\frac{1R}{4F} = \text{soil ingestion rate (mg/day)}$
$AF_{-}$ = physical factor for the factor for $C_{-}$
$\rightarrow$ absorption factor for lung (unitiess) 1.0
$AF_s$ = absorption factor for skin (unitless) 10
SR = soil dermal contact rate $(kg/day)$
DR = soil inhalation rate (kg/day)
FT ( Son indiadation rate (kg/day)
= exposure term (unifiess) land use specific <sup>1</sup>
= see Table 4

Again, although the Exhibit 11A equation makes provision for other possible routes of exposure (i.e. inhalation and dermal), currently only direct soil ingestion exposure is considered in deriving SQS<sub>HH</sub> for non-threshold substances. In accordance with CSST policy, SQS<sub>HH</sub> is derived using chemical specific RsDs based on a maximal acceptable risk from soil exposure of 1x10<sup>-5</sup>.

Thus, the equation of Exhibit 11A for direct soil ingestion of nonthreshold substances reduces tothat of Exhibit 11B.

Exhibit 11B - Simplified Derivation of Human Health RsD-based "Intake of contaminated soil" Standard, (SQS<sub>HH</sub>) - Non-threshold Substances

$$SQS_{HH} = \frac{RsD \times BW}{(AF_{I} \times IR) \times ET}$$

<u>Parameter</u>	Definition (units) Default
SQS <sub>HH</sub>	= human health RsD-based soil quality standard (mg/kg)
RsD	= risk specific dose (mg/kg-day) chemical specific
AF	= body weight (kg) 70 = absorption factor for gut (unitless) 1.0
IR	= soil ingestion rate (mg/day) 20
<b>E</b> 1	= exposure term (unitless) land use specific <sup>1</sup>
1	= see Table 4

C3.2

Toxicity from Transfer of Contaminants to Groundwater Used as Drinking Water

As detailed in Part B, a standard was also derived to insure that the calculated "Intake of contaminated soil" standard would not lead to excessive re-distribution of soil contaminant into groundwater used as drinking water. This groundwater protective soil standard was derived using the same groundwater transfer model and equations described in Part B. However in this case, C<sub>w</sub> corresponds to either the appropriate substance specific Canadian drinking water guideline (Health Canada, 1993) or the Ministry approved drinking water criteria (BC Ministry of Environment, Lands and Parks, 1995b) for the substance, as detailed in "Procedure to Establish Water Quality Standards used in Contaminated Sites Regulation" (Fox, 1995a). This soil standard to protect groundwater used for drinking water was calculated for all land uses.

#### PART D

# D1 "OTHER" SOIL QUALITY STANDARDS

CSST recognized that contaminated site matrix soil quality standards should also provide protection against the occurrence of physical hazards (i.e. explosivity or flammability) and objectionable odours. CSST was advised that physical hazards associated with contaminants in soil could be adequately addressed by existing standards which would qualify such soil as a special waste under the Special Waste Regulation. Consequently, the "other" protective "Odour" standard is designed to account only for objectionable odour as an aesthetic concern. The "odour" soil quality standard therefore represents soil contaminant concentrations at which existing guidelines for odour control would not be expected to be exceeded.

# D2 SOIL ODOUR QUALITY STANDARDS

Substance specific soil "Odour" standards have been derived to ensure that volatile contaminants present on site do not give rise to contaminant concentrations in air which exceed reported odour threshold limits.

Substance specific odour threshold limits were obtained from several sources, (Macfarlane, 1995b) and on the advice of CSST, the lowest available substance specific odour threshold limit was used for standard derivation purposes. For Residential sites an exposure duration of one second was used to calculate "soil odour" standards, while an exposure duration of five minutes was assumed for Agricultural, Urban Park and Commercial sites. No soil "Odour" standards were calculated for the Industrial land use category, as standards to protect workers are established under the authority of the Workers' Compensation Board of British Columbia. The soil "Odour" protective standard derivation equation is given in Exhibit 12.

The soil odour threshold pathway is based on the volatilization of contaminants from the soil surface to a receptor on the site. The derivation uses the equation presented in Exhibit 12 which is based on the methodology outlined in U.S. EPA documents, (EPA, 1990; EPA, 1994) for the evaluation of outdoor inhalation exposure from wind-blown dust and volatiles from surficial contaminated soil. Surficial soil is defined as soil within 0.5 m of the ground surface. (BC Environment is currently evaluating the applicability of other models for evaluating volatility to air where contamination exists at depth.)

The volatilization factor (VF) of Exhibit 13 defines the relationship between concentration of contaminants in soil and volatilized contaminants in air and is based on the Hwang and Falco (1986) model. Substance specific diffusivity coefficients may be calculated using the equation of Exhibit 14. An important premise of the model is that the soil contaminant must be at or below the soil saturation concentration. The soil saturation concentration is derived as described in Exhibit 15 which uses equations from the U.S. EPA's draft Soil Screening Guidance (EPA, 1994).



= where 42.3 is a units conversion factor for T=15°C

ુ 36
# Exhibit 14 - Diffusivity Coefficient (D<sub>i</sub>)

Calculated using Fuller's method (EPA, 1988)

$$D_{i} = \frac{0.001 T_{p}^{1.75} \sqrt{[(1/MW_{i}) + (1/MW_{a})]}}{P_{a}[\sqrt[3]{(\Sigma V_{i})} + \sqrt[3]{(\Sigma V_{a})}]^{2}}$$

<u>Parameter</u>	Definition (units)	<u>Default</u>
Di	= diffusivity coefficient (cm²/s)	
Tp MW <sub>i</sub> MW <sub>*</sub> P <sub>a</sub>	= absolute temperature (°K) = molecular weight of substance = molecular weight of air = absolute pressure (atm)	288 chemical specific 28.8 1
∑Vi ∑Va	= molecular diffusion volume of substance = molecular diffusion volume of air	chemical specific 20.1

Exhibit 15 - Determination of Soil Saturation Concentration for a Given Chemical

$$= \frac{S}{P_b} (K_d P_b + n_u + H' n_a)$$

<u>Parameter</u> Definition (units)

' Y.

 $C_{sat}$ 

Section and a

C <sub>sat</sub>	= soil saturation concentration (mg/kg)	
S	= solubility in water (ing/L-water)	chemical specific
РЪ	= soil dry bulk density (kg-soil/L-soil)	1.5
K <sub>d</sub>	= soil-water partition coefficient	chemical specific
	(mg/kg-soil per mg/L-water)	
n,	= water-filled soil porosity (unitless)	0.20
H	= demensionless Henry's law constant	$H \times 42.3^{1}$
н	= Henry's law constant	chemical specific
na	= air-filled soil porosity (unitless)	0.20
<sup>1</sup> = where 42.3 i	s a units conversion factor for 15°C	

## PART E ANCILLARY ISSUES/DETAILS CONCERNING DERIVATION PROCEDURES

### GENERAL ANCILLARY ISSUES

In addition to specific adjustments made to some derived standards (e.g. real world adjustment to "Intake of contaminated soil" standards for arsenic, cadmium and lead detailed in section C3 above) several more general adjustments were commonly made to CSST toxicological-derived standards.

## E1.1 CSST "Rounding-off" Rule

**E1** 

All soil quality standards derived by CSST methods were subjected to a "rounding-off" rule which states that standards are to be expressed to no more than one significant digit which must always be rounded to either 0 or 5, whichever is closer.

## E1.2 CSST "Background" Adjustment

As noted in Section C2.1 above CSST recognized that, as a matter of policy, site owners should not be expected to clean to soil concentrations below that typical of local background soil concentrations.

Consequently, proposed toxicological-derived CSST soil standards for the following non-anthropogenic pollutants; arsenic, cadmium, copper, lead and zinc were compared to "background" soil concentrations for the Lower Mainland of the Province as detailed in "Changes to Schedule 5 Matrices in Draft 3 of the Contaminated Sites Regulation" (Ward, 1995). As a result, standards for the above parameters were "capped" at contaminant concentrations equivalent to no less than the 90th percentile of the Lower Mainland background soil concentrations. Lower Mainland soil concentrations were used in this procedure, since these soils are generally representative of the soil characteristics assumed in CSST models.

### E1.3. Groundwater Standard Adjustments

Where necessary, some soil-groundwater matrix standards were adjusted to incorporate variation relating to differential soil pH, as predicted by the groundwater models used to derive the standards. This effect of variable soil pH to affect modelled contaminant mobility and transport, and hence modify toxicological-derived soil-groundwater protective standards is perhaps most apparent in the standards for pentachlorophenol (PCP).

### E1.4 "Detection Limit" Adjustment

CSST noted that it was also necessary to consider contaminant analytical detection limits in establishing soil quality standards. For some of the toxicological-derived soil quality standards calculated for benzene, PCP and trichloroethylene it was noted that the standards were in fact less than analytical detection limits. Consequently, as detailed in (Ward, 1995), these soil quality matrix standards were "adjusted" to equal corresponding substance specific analytical detection limits.

## E1.5 Derivation of CSST Soil Quality Matrix Standards for Substances for Which No CCME Assessment Documents Will be Generated

CCME is committed to producing Ecological and Human Health Assessment documents for only 15 of the total 18 CSST "Most Commonly Found Contaminants" (BC Ministry of Environment, Lands and Parks, 1995c). In addition, CCME has no commitment to produce any such documents for the approximately 80 substances remaining in the CCME's "Interim Canadian Environmental Quality Criteria for Contaminated Sites" document (CCME, 1991a). Since the CSST derivation process for soil quality numbers relies on the CCME substance assessment documents for ecological data sets and human health reference values, the lack of requisite assessment documents posed a serious impediment to the generation of soil quality matrix numbers for some substances.

After examining several options to overcome this difficulty, CSST recommended the following courses of action to derive soil quality numbers for substances which lack CCME assessment documents (Fox, 1995b):

For Protection of Human Health -

That BC Environment access requisite human health toxicity reference values from sources other than the CCME, as detailed in the CSST document "Hierarchy of Preferred Sources of Toxicity Reference Values for Use in Calculation of CSST Numbers for Use in Contaminated Sites Regulation" (Fox, 1995c), to calculate soil quality matrix numbers in accordance with CSST recommended procedures.

#### For Protection of Ecological Health -

That BC Environment use the CCME interim criteria as listed in "Interim Canadian Environmental Quality Criteria for Contaminated Sites" as ecologically protective  $SQS_{EE}$  matrix standards (for soil invertebrates and plants) until such time that requisite ecological data sets become available to allow calculation of ecologically protective soil quality numbers in accordance with CSST recommended procedures.

## E2 SITE-SPECIFIC SOIL QUALITY REMEDIATION STANDARDS BASED ON CSST PROCEDURES

The CSST procedures provide a consistent methodology necessary for deriving effects-based soil quality matrix standards under defined exposure scenarios for both ecological and human receptors. Site-specific numerical standards (SSS) can be derived using the equations and procedures detailed herein. Derivation of site specific numerical standards provides an alternative to the matrix standards, to more appropriately reflect site-specific conditions. A protocol detailing SSS derivation procedures is currently under development by BC Environment. This protocol will specify how to use CSST's equations and models to develop site specific numerical standards.

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## APPENDIX A

## Contaminated Sites Soil Task Group Members

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APPENDIX B

Table B-1 Values for BCE Groundwater Model

Substance	Hd	RE	(EPTOR	ABUTER)	VI	Solubility	Koc	(1020)	t1/2 (sat.)	H'	and the second second
er Stelle Scala State State State	Range	AW (mg/L)	lrr (mg/L)	Lstk (mg/L)	(1)/5(U)) M(C	نې (mg/L)		(Days)	(Days)	[] =H*42.3	obbio e
Benzene		0.3			0,005	1745	. 83.2	183	365	2.32E-01	
Ethylbenzene		0.7		•	0.0024	152	1096.5	114	114	3.67E-01	
Toluene		0.3	1	-	0.024	515	302.0	99 20	105	2.85E-01	_
Xylenes Xylenes					0.3	0.1	289.0	183	183	2.26E-01	
Benzo(a)pyrene		0.00001	•	1	0.00001	0.004	891250.9	529	1059	1.02E-04	, .
Naphthalene		0.001				32	1288.2	33	129	2.60E-02	
Pyrene		0.00002				<u>1110</u>	72443.6	1898	3796	1.04E-03	_
Pentachlorophenol	<6.9	0.00002		0.03	0,03	5000	pH*	383	191	6.01E-04	
	6.7.9	0.0001	-	0,03	0.03	5000	pH*	383	191	6.01E-04	
	>7.9	0.0003		0,03	0.03	5000	*Hd	383	- 191	6.01E-04	
<u>l'etrachlorcethylene</u>		0,11	•			150	158.5	411	821	7.61È-01	
l'richloroethylene		0.02		0.05	0.05	1070	107.2	411	821	8.46E-01	
CBs		0,000001	0.0005						~	•	
)ioxins/Furans											
trsenic (As+3)		0.05	0.1	0.5	0.025	p.H*	Kd**	1	. "		
Cadmium (Cd+2)		0.0018	0.01	0.02	0.005	*Hq .	Kd**	1		•	
hromium (Cr+3) 🦳						pH*					
Mromium (Cr+6)				•		pH*	Kd**	. 1		•	
Mromium (Total)		0.002	0.1	1	0.05	pH*		ŀ	1	- -	
Sopper (Cu+2)		0.008	0.2	0,3		pH*	Kd)**	4			
ead (Pb+2)		0.011	0.2	0.1	0.01	pH*				4	
inc (Zn+2)		0.03	1.0 - 5.0	50		pH*	Kd**		•		

Rule: 11/2 unsaturated (ORGANICS) - Greater of the anaerobic rate high (lowest number of days) and 25 % of anaerobic rate low (highest number of days). Unless, t1/2 unsaturated > t1/2 saturated - then, t1/2 unsaturated equals t1/2 saturated. Rule: t1/2 saturated (ORGANICS) - Equals to 50 percent of anaerobic rate low (highest number of days).

PH dependent
\*\* Kd calculated

								8.9 <u>.9</u> .
рH	Koc PCP	Kd PCP foc=0.006	Kd As(+3)	Kd Cd	Kd Cr(+6)	Kd Cu(+2)	K#*/ 15	* Kđ Zn(+2)
4.5	20,303	121.82	24.3		35.0			· ·
4.6	18,454	110.73	24.4		34.0			
4.7	16,557	99.34	24.6		33.1			
4.8	14,659	87.95	24.8		32.2			
4.9	"12,810	76.86	- 25.0	0.8	31.4	39.8	*	1.6
5.0	11,055	66.33	25.2	0.9	S0.5	50.1		1.8
5.1	9,429	56.57	25.4	1.0	29.7	63.1	.*	2.0
5.2	. 7,956	47.73	25.6	1.1	28.9	79.4	*	2.2
5.3	6,648	39.89	25.7	1.3	28.2	100	5a 🐐	2.5
5.4	5,508	33.05	25.9	1.5	27.4	126	*	3.2
5.5	4,530	27.18	26.1		26.7	158		4.0
5.6	3,703	22.22	26.3	2.0	26.0	219	*	5.0
5.7	3,010	18.06	26.5	2.5	25.3	302	*	6.3
5.8	2,437	14.62	26.7	3.2	24.6	417	*	8.6
5.9	1,965	11.79	26.9	.4.0	24.0	575	*	11.7
6.0	1,580	9:482	27.1	5.0	23.3	794		15.8
6.1	1,268	7.607	27.3	7.5	22.7	1,148	*	. 24.0
6.2	1,015	6.090	27.5	11.2	22.1	1,660	*	36.3
6.3	811	4.868	27.7	16.8	21.5	2,399	19 <b>4</b>	55.0
6.4	648	3.887	27.9	25.1	21.0	3,467	*	83.2
6.5	517	3:100	28 1	36.9	20.4	5,012		126
6.6	. 412	2.470	28.3	54.1	19.9	6,310	*	191
6.7	328	1.967	28.6	79.4	19.3	7,943	*	288
6.8	261	1.566	28.8	117	18.8	10,000	*	437
6.9	208	1.246	29.0	171	18.3	12,589	*	661
7.0	165	0.991	29.2	251	17.8	15,849	*	1,000
7.1	131	0.788	29.4	355	17.4	17,783	*	1,380
7.2	104	0.626	29.6	501	16.9	19,953	*	1,905
7.3	83.0	0.498	29.9	708	16.4	22,387	*	2,630
7.4	65.9	0.396	30.1	972	16.0	25,119	*	3,631
7.5	52.4	0.314	30.3	1,334	15.6	25,119		5,012
7.6	41.6	0.250	30.5	1,830	15.2	25,119	*	6,310
7.7	33.1	0.198	30.8	2,512	_14.8	25,119	*	7,943
7.8	26.3	0.158	31.0	3,073	14.4	25,119	*	10,000
7.9	20.9	0.125	31.2	3,758	14.0	25,119	*	12,589
8.0	16.6	0:100	31.4	4,597	13.6	25,119		15,849
8.1	13.2	0.079	31.7	56,234	13.3			19,953
8.2	10.5	0.063	31.9	1	12.9		1. 1	
8.3	8.3	0.050	32.2		12.6		1.1	- · · ·
8.4	6.6	0.040	32.4		12.2			
8.5	5.2	0.031	32.6	1	11.9			

## Table B-2 Koc and Kd values for BCE Groundwater Model

\* Copper Kd values used as surrogates for lead Kd values.