

# **BCELQAAC Technical Recommendations to BC MOE for Vapour Standards**

Mark Hugdahl,  
Chair, BCELQAAC

BC Soil Vapour Forum,  
July 8, 2009

***BCELQAAC***

# What is BCELQAAC?

## ◆ BC Environmental Laboratory Quality Assurance Advisory Committee

- Liaison Committee between BC MOE, BC Commercial Labs, Environment Canada, and other industry stakeholders.
- Focus: Laboratory issues pertinent to BC MOE regulatory framework (CSR, HWR).
- Guidance and recommendations to BC MOE on laboratory and analytical chemistry topics.
- BC Laboratory Manual development.

# BCELQAAC Membership

## ◆ Current Committee Representation:

- BC MOE – Glyn Fox, Steve Horvath
- Commercial BC Laboratories:
  - ALS Environmental
  - Bodycote
  - Cantest
  - Caro Analytical Services
  - Maxxam Analytics
- Environment Canada
- Industry / Consultant representative
  - Hazco

# BCELQAAC Technical Recommendations Re Vapour Standards / Schedule 11

MOE Requested our assistance with the following:

- ◆ Definition of Volatile Substance
- ◆ Recommended Analytical Methods for Vapour Testing
  - Discrete substances
  - Hydrocarbons
- ◆ Development of BC Lab Manual Vapour Methods
- ◆ Detection Limit Issues for selected Schedule 11 Compounds

# Definition of "Volatile Substance"

- ✦ MOE needs a simple physical / chemical definition of "volatile substance".
  - Required to finalize new Schedule 11 Vapour Stds list.
  - "Volatile" substances from Schedules 4,5,6,9,10 to be added to ACC list.
- ✦ Starting point: EPA Region 9 Def'n:
  - Henry's Law constant  $> 1.0 \times 10^{-5}$  atm-m<sup>3</sup>/mol
  - Molecular weight  $< 200$  g/mol
- ✦ BCELQAAC proposed definition:
  - Henry's Law constant  $> 1.0 \times 10^{-5}$  atm-m<sup>3</sup>/mol
  - Vapour Pressure  $> 0.05$  Torr @ 25C

# BCELQAAC Proposed Volatile Definition: Part 1 - Henry's Law Constant

Reqm't #1:  $H_{pc} > 1.0 \times 10^{-5} \text{ atm-m}^3/\text{mol}$

- ✦  $H_{pc}$  = Partial Pressure / Water Solubility.
- ✦ Related to the tendency of a substance to volatilize from aqueous solution.
- ✦ Best single predictor of volatility under typical environmental conditions.
- ✦ However, because  $H_{pc}$  is a ratio, an absolute vapour pressure cutoff is also necessary.

# BCELQAAC Proposed Volatile Definition: Part 2 – Vapour Pressure Cutoff

Reqm't #2: Vapour Pressure > 0.05 Torr @ 25°C

- ✦ VP at 25°C is the best measure of absolute volatility under typical environmental conditions.
  - M.Wt. and B.Pt. have been suggested as alternatives.
  - Both correlate only loosely with ambient vapour pressure.
- ✦ MOE could lower the 0.05 Torr cutoff if desired:
  - 0.1 Torr ~ the limit for the TO-15 method.
  - 0.05 Torr includes naphthalene + methyl-naphthalenes, but excludes heavier PAHs.
  - 0.05 Torr ~ VP of nC13.
  - Anecdotally, the least volatile substances found in air samples have VP ~ equal to nC16 (0.0014 Torr @ 25°C).

# Physical Constants for Example Substances

<b>SUBSTANCE</b>	B.Pt. ( C)	VP, 25 C (Torr)	M.Wt. (g/mol)	Henry's Law (atm-m <sup>3</sup> /mol)	Volatile by Proposed Def'n?
<u>High Molecular Weight Volatiles:</u>					
dibromochloromethane (DBCM)	120	15.6	208.3	7.8E-04	yes
bromoform (tribromomethane)	149	5.4	252.7	5.4E-04	yes
1,2-dibromo-3-chloropropane (DBCP)	196	0.58	236.3	1.5E-04	yes
1,3-hexachlorobutadiene	215	0.22	260.8	1.0E-02	yes
hexachloroethane	154	0.21	236.7	3.9E-03	yes
hexachlorocyclopentadiene	239	0.06	272.8	2.7E-02	yes
<u>Hydrocarbons:</u>					
nC10	174	1.3	142.3	4.7E+00	yes
nC11	196	0.41	156.3	1.9E+00	yes
nC12	216	0.14	170.3	8.2E+00	yes
nC13	235	0.056	184.4	2.9E+00	yes
nC14	254	0.012	198.4	9.2E+00	no - VP
nC15	271	0.0034	212.4	1.3E+01	no - VP
nC16	287	0.0014	226.5	4.7E-01	no - VP



# Physical Constants for Example Substances

SUBSTANCE	B.Pt. ( C )	VP, 25 C (Torr)	M.Wt. (g/mol)	Henry's Law (atm-m <sup>3</sup> /mol)	Volatile by Proposed Def'n?
<u>PAHs:</u>					
naphthalene	218	0.085	128.2	4.4E-04	yes
2-methylnaphthalene	241	0.055	142.2	5.2E-04	yes
acenaphthylene	280	0.0067	152.2	1.3E-04	no - VP
acenaphthene	279	0.0025	154.2	1.8E-04	no - VP
fluorene	295	0.0084	166.2	9.6E-05	no - VP
pyrene	404	4.5E-06	202.5	1.2E-05	no - VP
<u>Water Soluble Substances:</u>					
formaldehyde	-19	3890	30.03	3.4E-07	no - H
acetone	56	231	58.08	4.0E-05	yes
methanol	65	127	32.04	4.6E-06	no - H

# BCELQAAC Recommended Analytical Methods for Vapour Testing

- ◆ EPA TO-15 – Canister Sampling method
- ◆ EPA TO-17 – Thermal Desorption method
- ◆ Solvent Desorbable Media & Misc methods
  - Based on listed NIOSH / OSHA / Misc methods, eg:
    - Charcoal / Carbon Disulfide methods
    - XAD tube methods
    - Silica gel tube methods
    - Impinger / Bubbler methods
- ◆ Other presenters will summarize these techniques

# Hydrocarbon Vapour Methods

- ✦ Hydrocarbon vapour methods will align with "volatile substance" definition. If VP cutoff of 0.05 Torr is adopted:
  - VPHv method will likely encompass nC6 – nC13.
  - No EPH method will be developed or needed for Sched 11.
- ✦ Details of VPHv method still to be worked out, eg:
  - Permissible collection / analysis techniques.
  - VHv to be measured by GC-FID and/or GCMS?
  - VPHv = VHv minus BTEX, nC6, nC10?
  - Optional subtraction of other Sched 11 substances?

# Format & Timing of Methods Guidance

- ✦ **BCELQAAC is writing BC Lab Manual vapour methods.**
  - Drafts done for TO-15 and TO-17.
  - Solvent desorbable media / misc method IP.
  - Hydrocarbon method(s) still under discussion.
  - Methods will be Performance Based, will refer to published EPA / NIOSH / OSHA & other methods for detailed guidance.
  - Suitable methods will be listed for each Sched 11 substance.
- ✦ **We will issue Interim Guidance to BC MOE by July 18.**
  - By letter to Glyn Fox, prior to final draft of Sched 11.
  - Table of suitable reference methods will be included.

# Detection Limit Issues for Select Schedule 11 Substances

- ✦ For 21 substances, the lowest Sched 11 stds are below practically achievable DLs.
- ✦ BCELQAAC recommends higher stds for these substances.
  - Labs established 1 ug/m<sup>3</sup> as a reasonable minimum achievable DL for most compounds by TO15 or TO17.
  - In all but 2 cases, recommended increases are  $\leq 100x$ . Due to safety factors in their derivation, most stds should remain sufficiently protective.
  - Use original toxicity-based standards if attenuation factors are to be applied.
- ✦ For a few compounds, no methods have been tested by any BC labs; some uncertainties remain.
- ✦ Site-specific matrix or interference issues may also cause higher DLs.

# BCELQAAC Recommended Minimum Sched 11 Stds

Parameter	Lowest Draft Schedule 11 Standard (ug/m <sup>3</sup> )	Recommended Minimum Standard ug/m <sup>3</sup>	Most Sensitive Method
1,1,2,2-tetrachloroethane	0.15	1	TO15 or TO17
1,1-dichloroethene (1,1-dichloroethylene)	0.2	1	TO15 or TO17
1,3-hexachlorobutadiene	0.5	2	TO15 or TO17
1,4-dichloro-2-butene (trans + cis)	0.004	0.4	TO15 or TO17 (SIM if required)
a,a,a-trichlorotoluene (benzotrchloride)	0.002	0.2	TO15 or TO17 (SIM if required)
acrolein (2-propenal)	0.02	2	TO15 or TO17
acrylonitrile (2-propenenitrile)	0.15	1.5	TO15 or TO17
bis(2-chloroethyl)ether	0.03	2	TO17
bis(chloromethyl) ether	0.0002	1	OSHA 10 (GC-ECD, 50L)
bromodichloromethane	0.7	1	TO15 or TO17
bromoethene (vinyl bromide)	0.3	1	TO15 or TO17
chlorine	0.2	20	OSHA ID101 / NIOSH 6011
chloroform (trichloromethane)	0.45	1	TO15 or TO17
crotonaldehyde	0.015	1.5	TO17
dimethylamine	0.015	200	TO17
ethylene dibromide (1,2 dibromoethane)	0.015	1	TO15 or TO17
ethylene oxide	0.1	10	TO15 or TO17
hexachlorocyclopentadiene	0.2	2	TO15 or TO17
methacrylonitrile (2-methylprop-enenitrile)	0.7	10	TO15 or TO17
phosphine	0.3	10	NIOSH 6002
trichloroethylene (TCE)	0.1	0.5	TO15 or TO17 (SIM if required)

Questions?