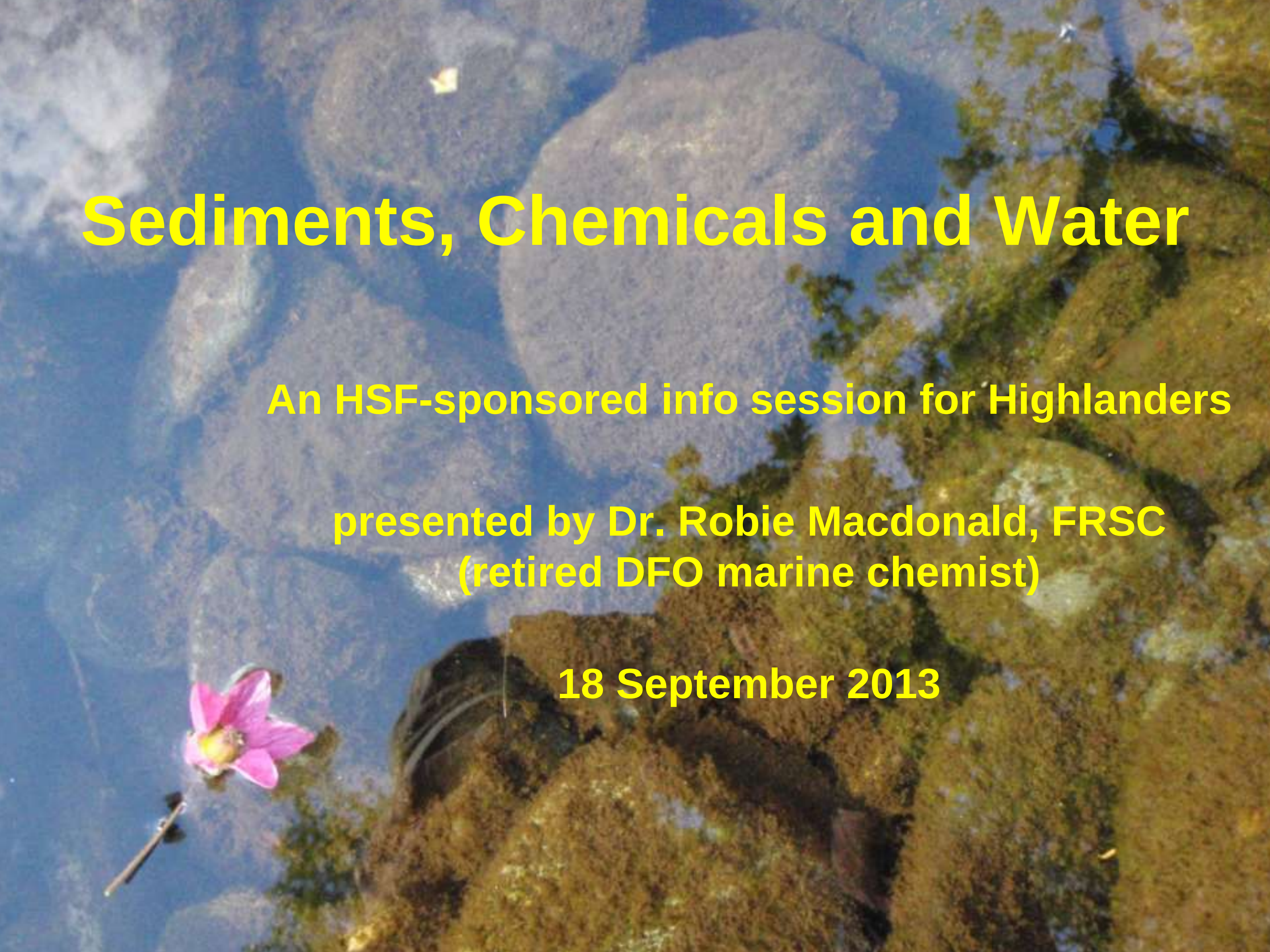


Sediments, Chemicals and Water

An HSF-sponsored info session for Highlanders

presented by Dr. Robie Macdonald, FRSC
(retired DFO marine chemist)

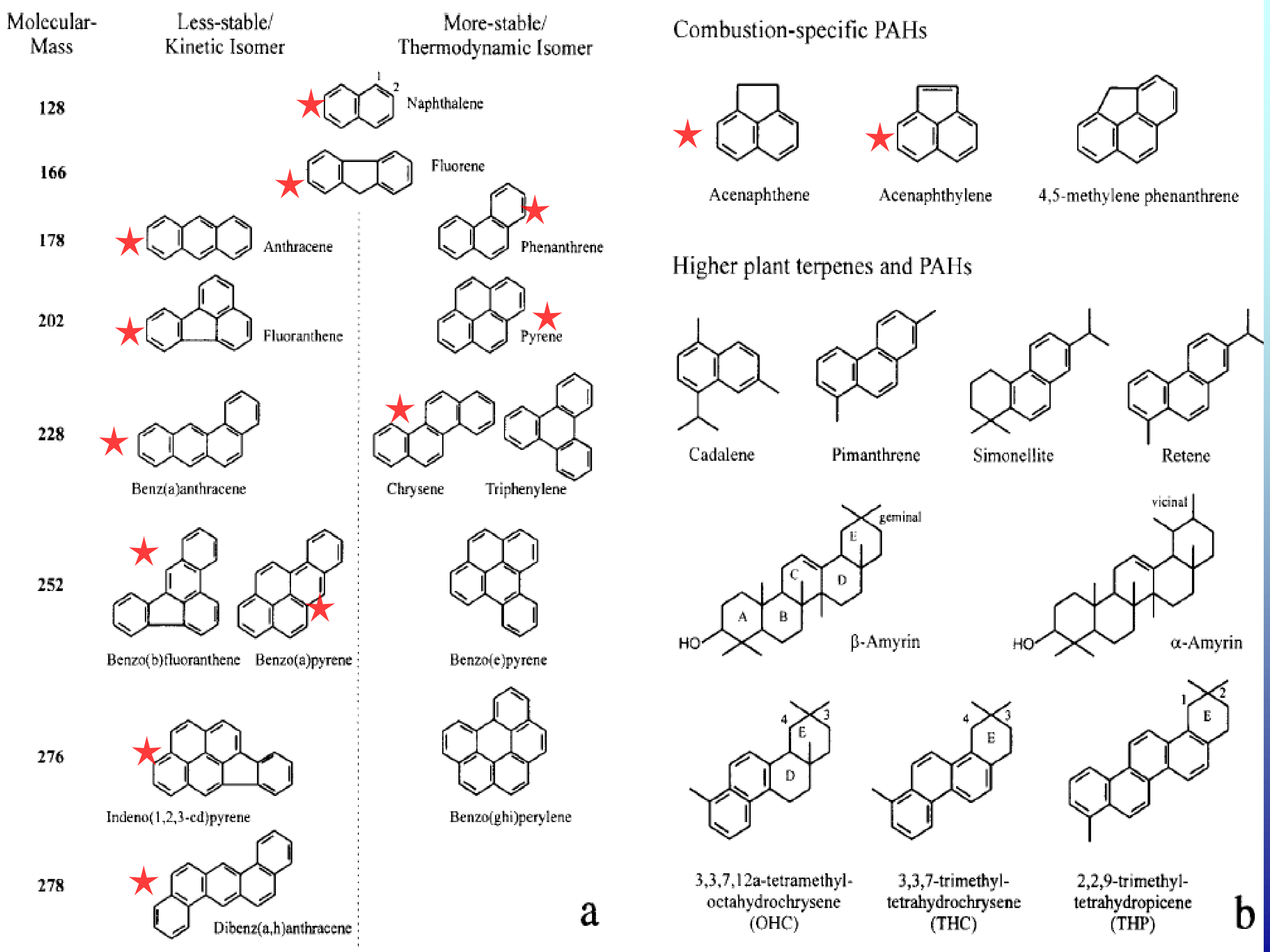
18 September 2013

Some Basic Facts

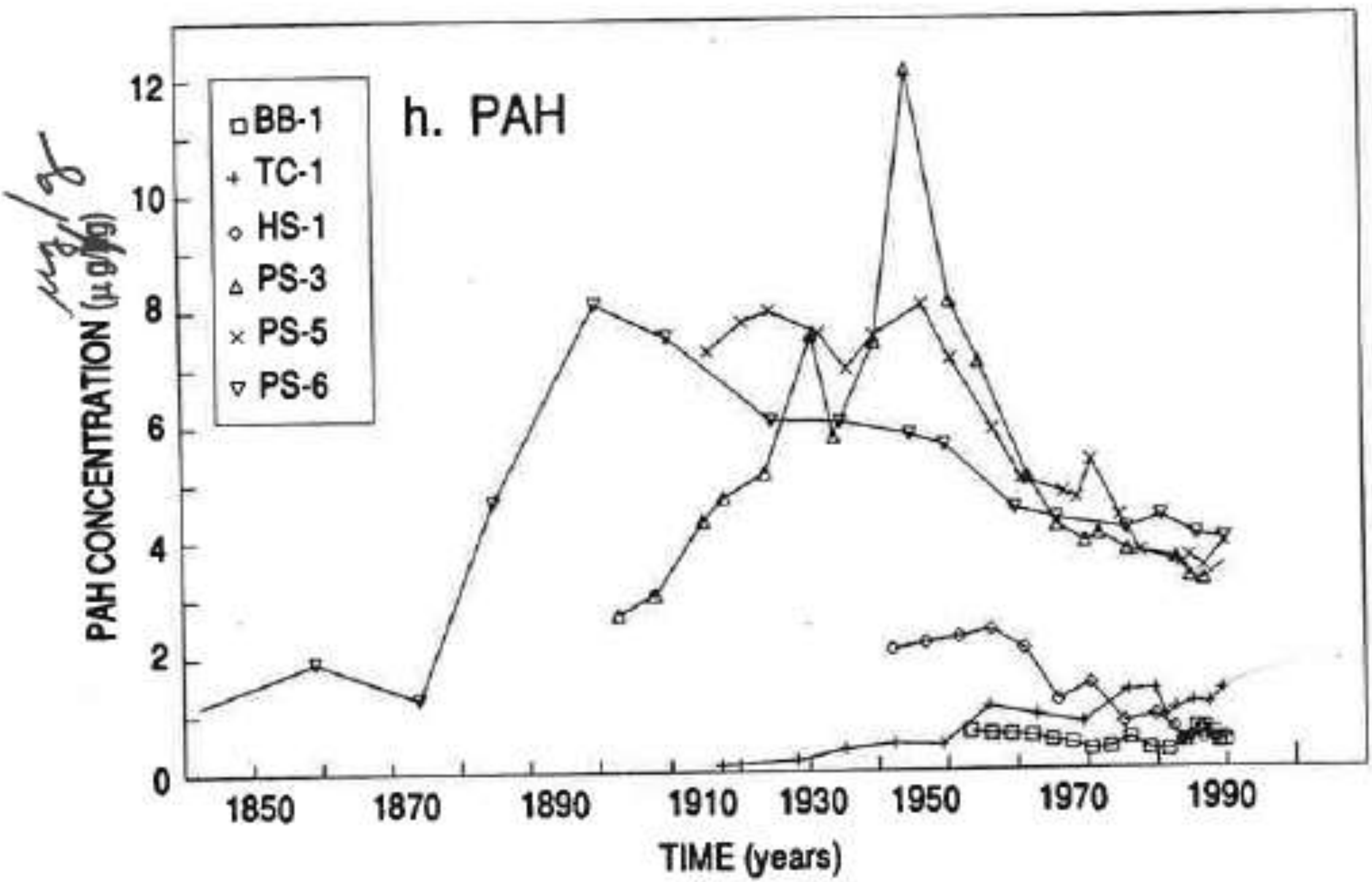
Highwest Facility	
Area of site	2280000 m^2
Capacity of site	658000 m^3
Average depth of spoil (if spread evenly over the site)	0.3 m
Input rate allowed	24000 t yr^{-1}
Esquimalt Graving Dock	150000 m^3 (~200000 tons)
EGD spread over land (if spread evenly over the site)	0.065 m

Esquimalt Graving Dock Sediments

	mean	max	unit	Total kg
Sum PAH	9.8	237	ug/g	1900
Extr PetH	804	4920	ug/g	157,000


Molecular-Mass
Less-stable/ Kinetic Isomer
More-stable/ Thermodynamic Isomer
128
Naphthalene
166
Fluorene
178
Anthracene
Phenanthrene
202
Fluoranthene
Pyrene
228
Benz(a)anthracene
Chrysene
Triphenylene
252
Benzo(b)fluoranthene
Benzo(a)pyrene
Benzo(e)pyrene
276
Indeno(1,2,3-cd)pyrene
Benzo(ghi)perylene
278
Dibenz(a,h)anthracene
a
Combustion-specific PAHs
Acenaphthene
Acenaphthylene
4,5-methylene phenanthrene
Higher plant terpenes and PAHs
Cadalene
Pimanthrene
Simonellite
Retene
geminal
β-Amyrin
vicinal
α-Amyrin
3,3,7,12a-tetramethyl-octahydrochrysene (OHC)
3,3,7-trimethyl-tetrahydrochrysene (THC)
2,2,9-trimethyl-tetrahydropicene (THP)
b

Total PAH (SofG/Puget Sound Sediments)



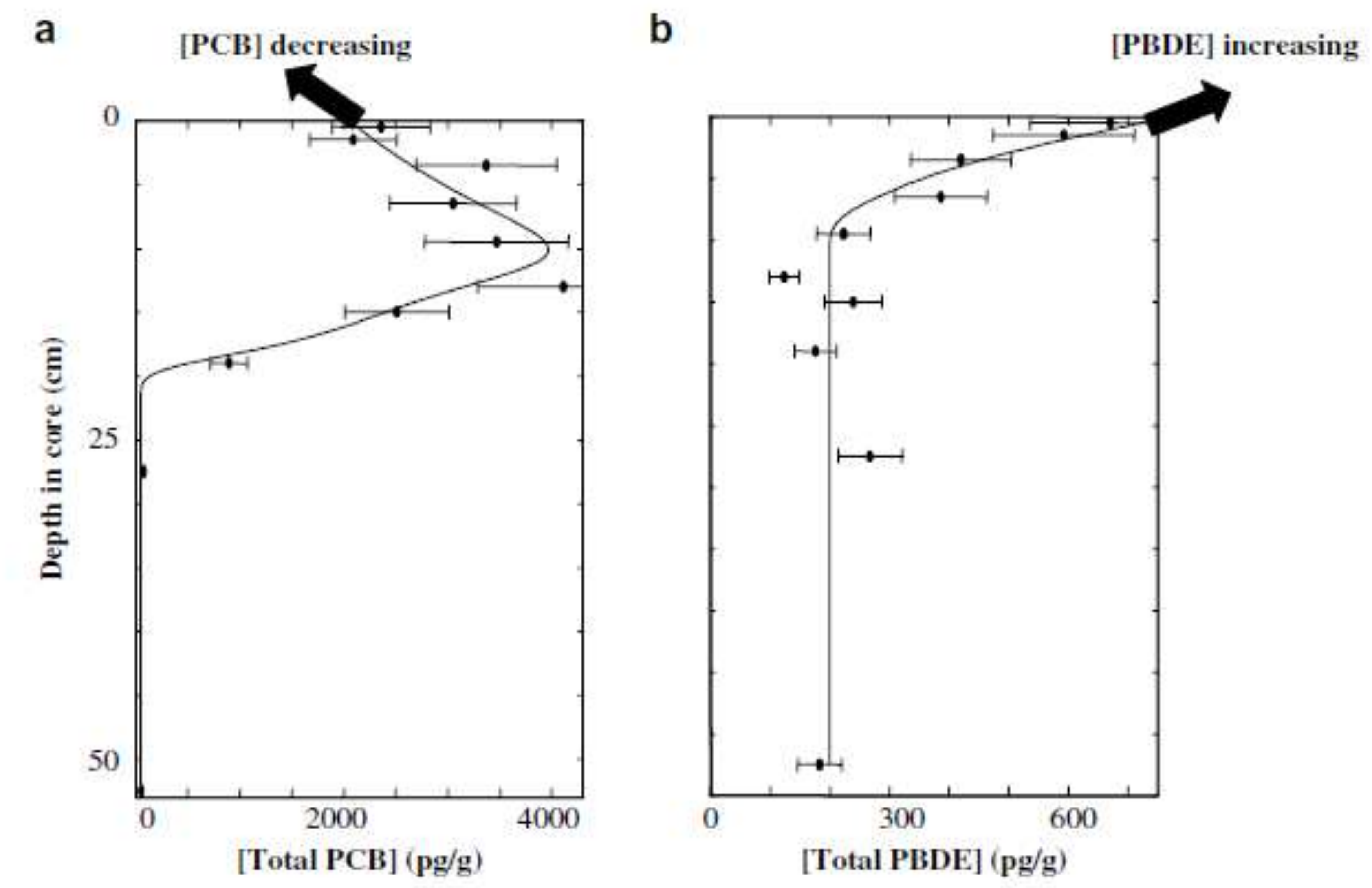
Some PAH Data from the Fraser/Strait of Georgia Sediments

Location units	No. of samples	Lower alkanes (ng/g)	Higher alkanes (ng/g)	UCM (μg/g)	C_{29} OEP	Σ 178–278 PAH (ng/g)	Petroleum PAH (ng/g)	Combustion PAH (ng/g)
Fraser R. particulate	6	35 000 ± 18 000 1100–48 000	45 000 ± 31 000 4800–83 000	320 ± 150 30–430	3.7 ± 2.5 1.7–7.9	670 ± 400 190–1100	960 ± 570 140–1620	550 ± 290 150–920
Fraser estuary[c]	6	1260 ± 820 400–2600	5900 ± 3600 2800–13 000	70 ± 25 38–105	3.4 ± 1.5 1.8–5.9	410 ± 220 220–720	420 ± 170 220–660	360 ± 190 180–620
Burrard inlet[d]	9–52	1100 ± 520 460–1700	3340 ± 1010 2000–5030	59 ± 29 28–110	3.9 ± 0.73 2.8–5.2	13 000 ± 19 000 500–104 000	4980 ± 8000 70–39 500	11 310 ± 16 700 430–91 800
Station A	13	820 ± 320 250–1100	3900 ± 610 2900–4600	26 ± 7.9 8.2–36	5.7 ± 2.4 2.9–9.5	640 ± 110 490–840	760 ± 160 620–1300	540 ± 100 410–730
Station 17	13	620 ± 180 330–920	2800 ± 890 1500–3700	19 ± 6.3 3.3–27	6.9 ± 2.3 3.2–9.3	1790 ± 3400 530–13 000	1060 ± 1000 580–4300	1300 ± 2170 430–8470
Station 21	13	990 ± 150 730–1200	2400 ± 410 1700–3100	17 ± 1.6 14–19	6.7 ± 1.9 4.7–9.4	550 ± 400 370–1900	740 ± 140 560–1100	440 ± 310 300–1460
Station 31	13	760 ± 220 410–1100	2400 ± 610 1600–3400	27 ± 11 13–52	5.3 ± 0.64 4.3–6.2	1060 ± 610 570–2500	900 ± 300 630–1800	860 ± 520 440–2080

Organochlorine Compounds

	mean	max	unit	Total kg
TBT	0.2	3.5	ug/g	39
PCDD/F	6.8	24	pg/g	.001
Total DDT	0.1	0.8	ug/g	20
Total PCB	0.3	8.5	ug/g	60

Note: Some DDT looks fresh?



Avg Total PCB 0.3 ug/g (300,000 pg/g)

Organochlorines in Sediments from BC Lakes

Table 4. Summary of maximum concentrations for organochlorine compounds in sediment cores.

COMPOUND ng/g	MOOSE	STUART	CHILKO	KAMLOOPS	NICOLA	HARRISON
# of samples	18	5	5	8	11	12
HCB	0.2	0.44	0.4	0.17	1.5	0.06
Total HCH	0.14	0.09	0.13	0.29	6.1	0.06
Heptachlor	<0.02–<0.1[1]	<0.06–<0.17	<0.04–<0.43	<0.03–<0.73	<0.003–<0.38	<0.003–<0.07
Aldrin	<0.002–<0.01	<0.002–<0.01	<0.007–<0.09	<0.007–<0.09	0.14	<0.002–<0.02
Chlordane	0.01	0.07	0.02	<0.006–<0.33	3.1	0.06
Total DDT	1.73	1.25	0.32	1.95	323	8.7
Total Nonachlor	0.04	0.06	0.06	<0.006–<0.37	1.4	0.05
Mirex	0.007	0.008	0.01	<0.001–<0.08	0.25	0.06
Dieldrin	0.06	<0.06–<0.22	<0.05–<0.47	0.92	<0.06–<0.62	<0.02–<0.22
Endrin	<0.09–<1.3	<0.22–<0.8	<0.08–<2.1	2.6	<0.15–<1.2	<0.04–<0.53
Methoxychlor	<0.14–<1.7	<0.32–<1.0	<0.2–<4.2	<0.18–<7.9	<0.21–<2.6	<0.2–<0.94
Toxaphene	<0.12–<0.57	<0.46–<1.8	<0.04–<1.1	<0.2–<4.3	<0.13–<2.2	<0.08–<1.2
Total PCB	0.86	0.68	0.94	7.7	1.49	1.5

1. The range of sample detection limits given when compounds were not detected

Total PCB 300 ng/g: Total DDT 100 ng/g

Element	Crustal	mean	max	unit	Total kg
As	2.1	51	3970	ug/g	9950
Cd	0.15	1.5	6.2	ug/g	293
Cr	140	42	234	ug/g	8190
Cu	68	168	232	ug/g	32800
Pb	9.9	140	4910	ug/g	27000
Hg	0.07	2	24.6	ug/g	390
Sn	2.2	16	302	ug/g	3120
Zn	78	293	10700	ug/g	57000
Na		5220			1020000
Cl		9400			1830000

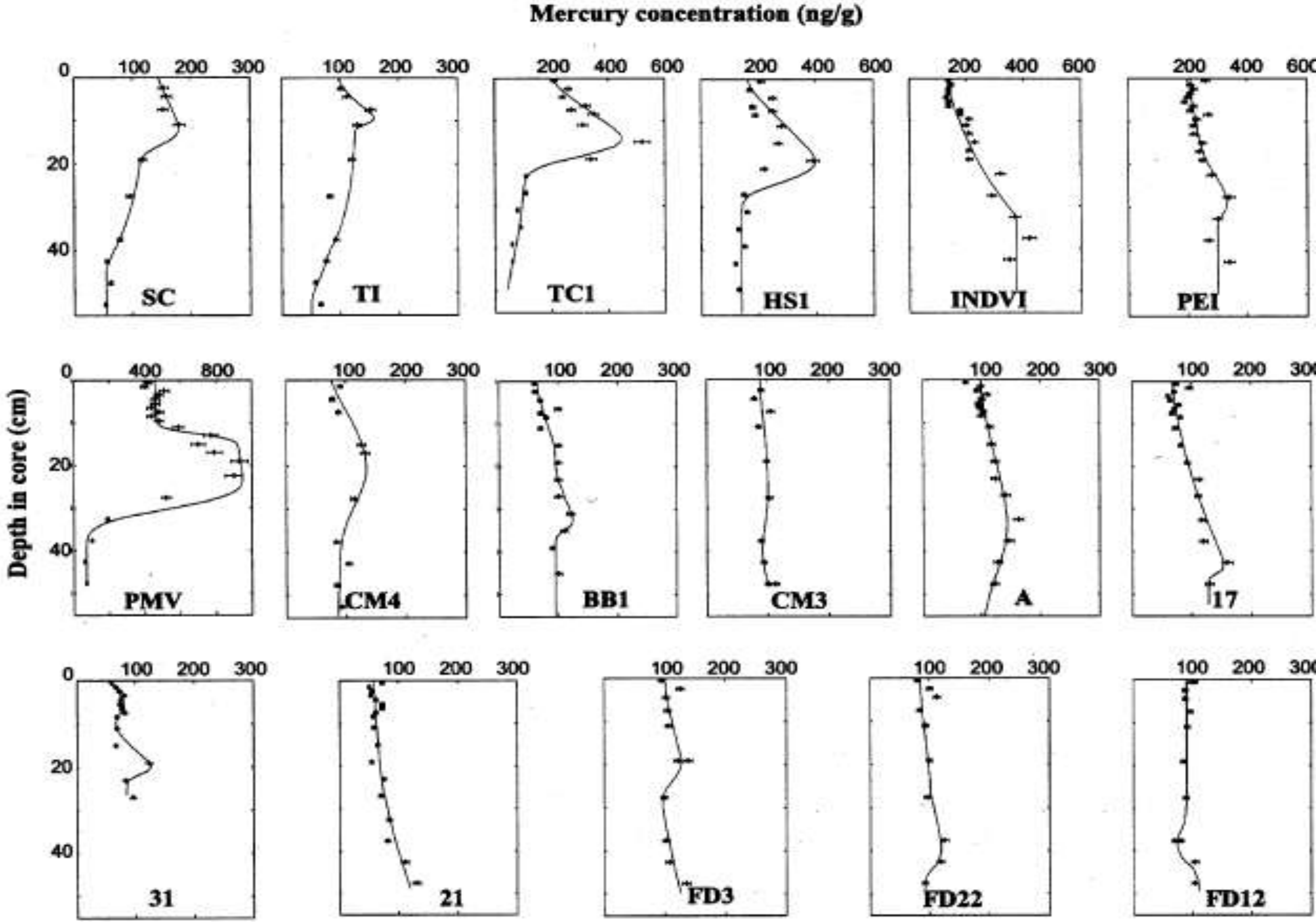
Table 3. Summary of metal data for sediment cores.

METAL µg/g	MOOSE	STUART	CHILKO	KAMLOOPS	NICOLA	HARRISON
Pb (background)[1]	31.0 ± 2.1	15.5 ± 0.86	13.2 ± 2.8	26.3 ± 2.6	8.4 ± 0.6	17.1±1.2(8)
Pb (maximum)[2]	**38.1**	**22.3**	20	**37.5**	**11.3**	**26.5**
Zn (background)	86.7 ± 6.4	119 ± 9	164 ± 15	147 ± 13	87.0 ± 6.6	182 ± 10
Zn (maximum)	**130**	136	188	173	103	**213**
Cu (background)	35.0 ± 1.9	47.6 ± 4.7	83.8 ± 8.5	62.3 ± 5.1	77.4 ± 6.9	105 ± 6
Cu (maximum)	**50.3**	**65.9**	92.6	69.9	89.8	**124**
Ni (background)	41.8 ± 4.6	91 ±8	46.0 ± 11.7	79.6 ± 8.5	45.8 ± 4.3	42.5 ± 1.2
Ni (maximum)	**134**	**117**	63	89.9	52.9	**59.5**
Co (background)	17.9 ± 1.2	17.0 ± 0.7	27.7 ± 3.5	30.0 ± 2.5	19.3 ± 1.7	28.2 ± 1.4
Co (maximum)	**32.2**	**22.3**	32.3	35	22.5	29.5
Cr (background)	113 ± 4	78.5 ± 8.5	84.0 ± 7.5	151 ± 10	106 ± 4	79.4 ± 4.2
Cr (maximum)	**140**	102	102	169	**132**	**110**
Hg (background)[4]	12.5 ± 1.3	19.4 ± 3.3	29.6 ± 7.5	20 ± 3	–[3]	–
Hg (maximum)[4]	**24**	**158**	42	**52**	–	–

Hg – ng/g

Pb 140: Zn 293: Cu 168: Ni 27: Co 10: Cr 42: Hg 2000

Hg in Strait of Georgia Sediments

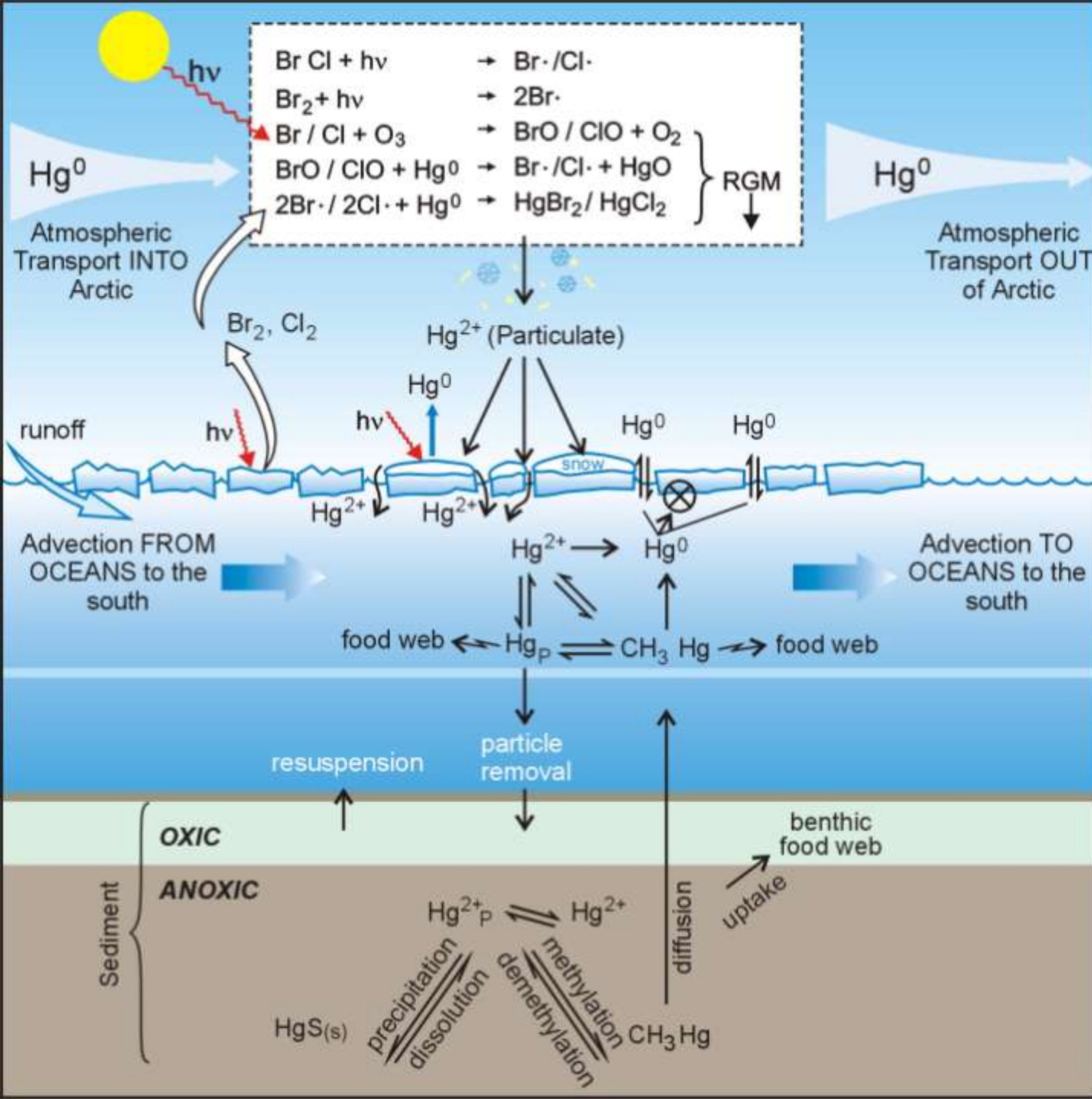


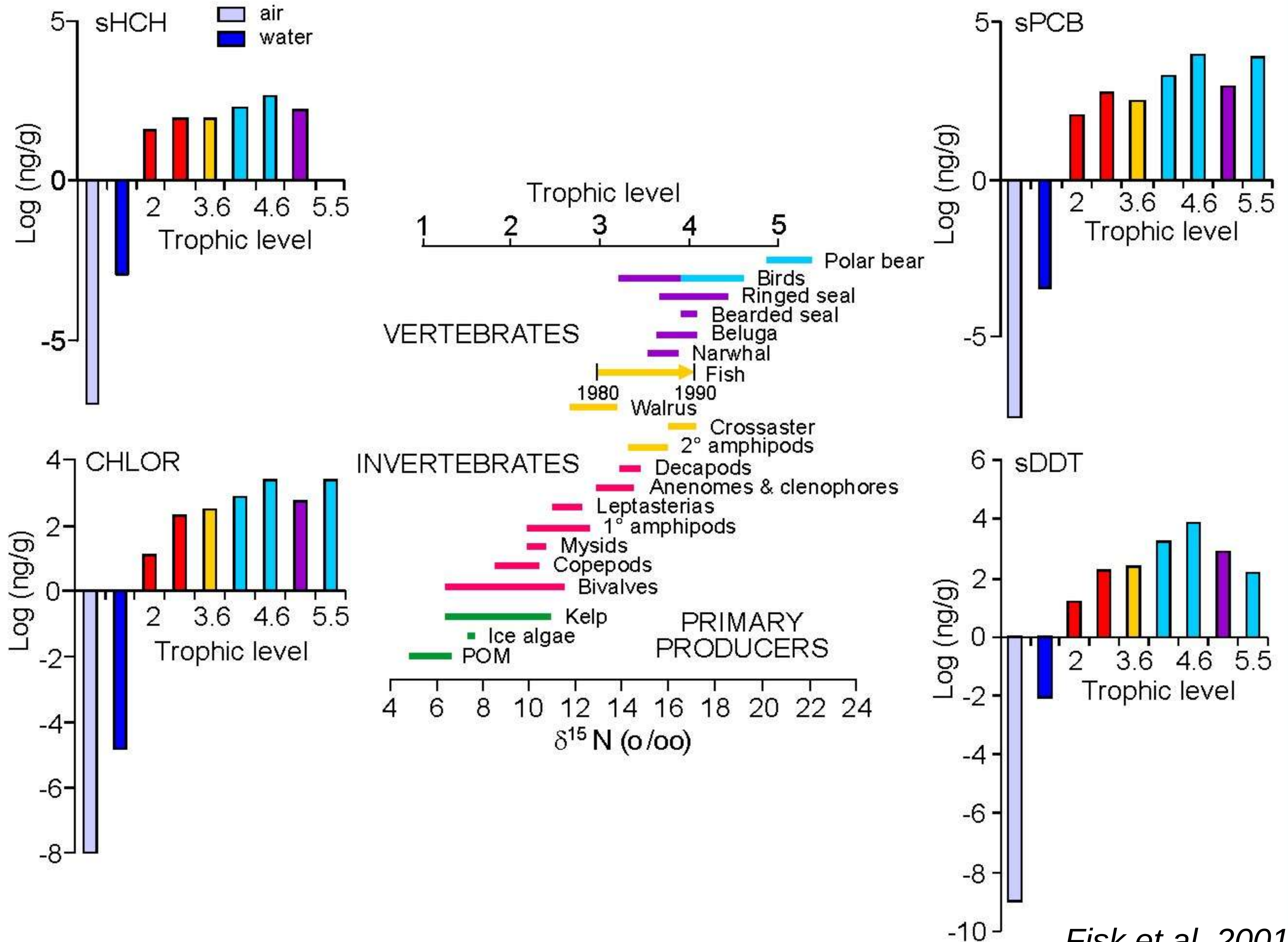
Some Comments

- Containment – physical and chemical
- Chemical containment is best if the compound/element is ‘sticky’
- Most of these contaminants are sticky
- All of these contaminants have had a chance to dissolve and diffuse into water (in the ocean at Esquimalt)

Other Factors

- Compounds like PCB/PBDE/DDT tend to produce high exposure through the foodweb not the water. With burial, you remove the foodweb connection
- Hg can form methyl mercury under the right conditions (much more toxic, biomagnifies). But this form of Hg is also sticky and there is probably not much chance of it going anywhere


hν
Br Cl + hν → Br·/Cl·
Br2+ hν → 2Br·
Br / Cl + O3 → BrO / ClO + O2
BrO / ClO + Hg0 → Br·/Cl· + HgO
2Br·/ 2Cl· + Hg0 → HgBr2/ HgCl2
RGM
Hg0
Atmospheric Transport INTO Arctic
Hg0
Atmospheric Transport OUT of Arctic
Br2, Cl2
Hg2+ (Particulate)
Hg0
runoff
hν
hν
Hg0
Hg0
snow
Hg2+
Hg2+
Advection FROM OCEANS to the south
Hg2+
Hg0
Advection TO OCEANS to the south
food web
HgP
CH3 Hg
food web
resuspension
particle removal
OXIC
ANOXIC
Sediment
benthic food web
uptake
diffusion
Hg2+P
Hg2+
HgS(s)
precipitation
dissolution
demethylation
methylation
CH3Hg



Fisk et al. 2001

Some Metals are Special

- Metals tend to move into the water when their thermodynamic conditions are changed (in this case marine sediment is moved to landfill)
- The problem here is one of taking metal happy in a reducing environment and exposing it to oxygen (acid mine drainage is an example).

7th Edition

Chemical Periodic Table

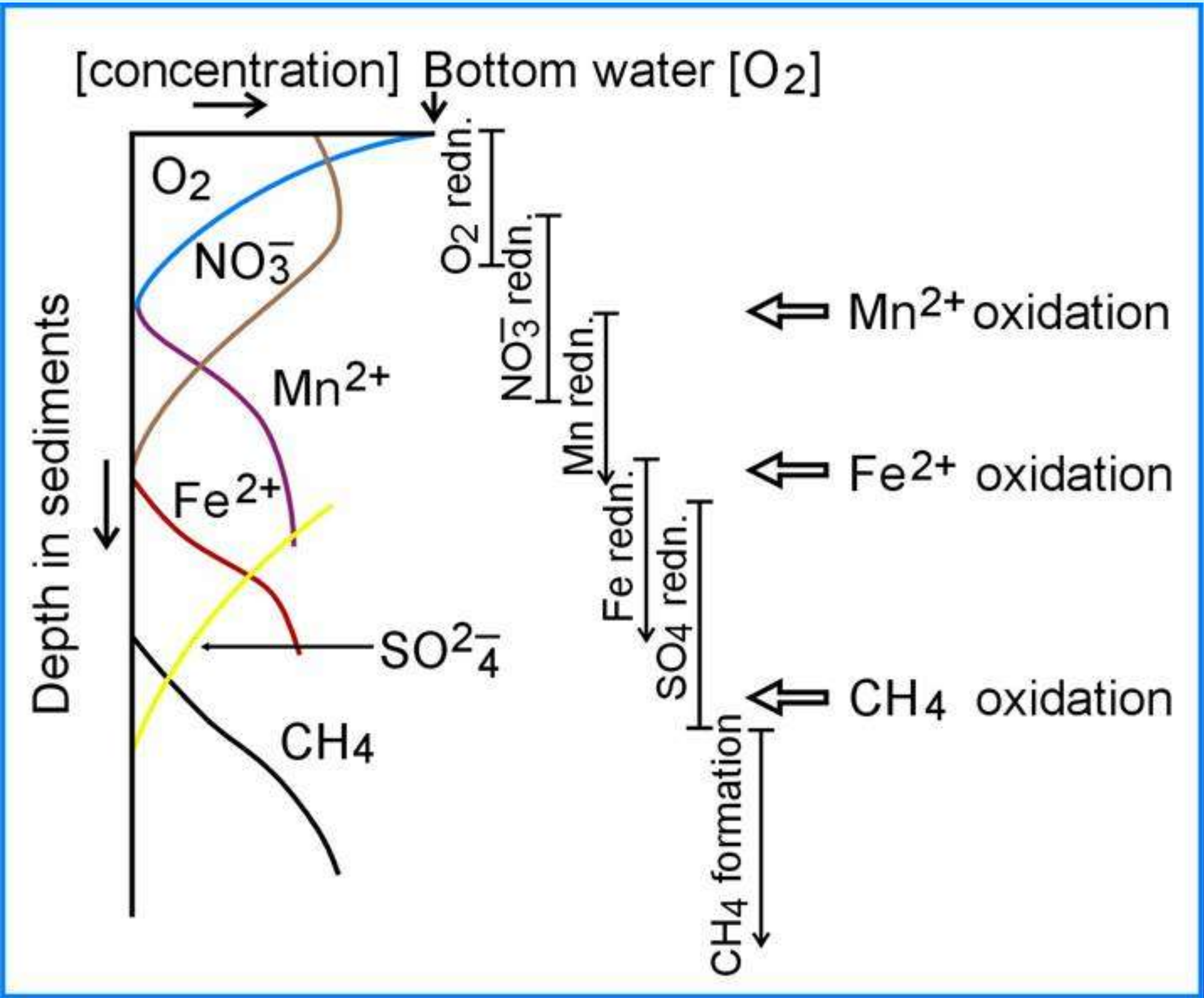
Atomic Weight ( ) indicates longest-lived isotope	8 VIIIA VIII	Group Classifications
Acidity/Basicity & Crystal Structure	26	Atomic Number
Melting Point, °C		Oxidation States (bold indicates most stable state)
Boiling Point, °C	Fe	Symbol
Density (300 K), g/cm³ (for gases: g/L, 273.15 K, 1 atm)		Electronic Configuration
Electronegativity	Iron	Name

1 IA IA	2 IIA IIA	3 IIIA IIIB	4 IVA IVB	5 VA VB	6 VIA VIB	7 VIIA VIIB	8 VIIIA VIII	9 VIIIA VIII	10 VIIIA VIII	11 IB IB	12 IIB IIB	13 IIIB IIIA	14 IVB IVA	15 VB VA	16 VIB VIA	17 VIIB VIIA	18 VIII 0
1 H Hydrogen																	2 He Helium
3 Li Lithium	4 Be Beryllium											5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium											13 Al Aluminum	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon
55 Cs Cesium	56 Ba Barium	57 La Lanthanum *	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
87 Fr Francium	88 Ra Radium	89 Ac Actinium **	104 Rf Rutherfordium*	105 Db Dubnium*	106 Sg Seaborgium*	107 Bh Bohrium*	108 Hs Hassium*	109 Mt Meitnerium*	110 Uun Ununnilium	111 Uuu Unununium	112 Uub Ununbium						

* Unnilquadium, Unnilpentium, Unnilhexium, Unnilseptium, Unniloctium, and Unnilennium are the previous names for elements 104-109, respectively

*	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium
**	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Sediment Metabolism and Early Diagenesis



ΔG

-518

-508

-502

-281

-143

-34

Emerson and Hedges, 2006

Mn and the redox engine

- $CH_2O + 4H^+ + H_2O + 2MnO_2 \rightarrow$

  $2Mn^{++} + CO_2 + 4H_2O$ ($\Delta G = -500\ kJ\ mol^{-1}$)

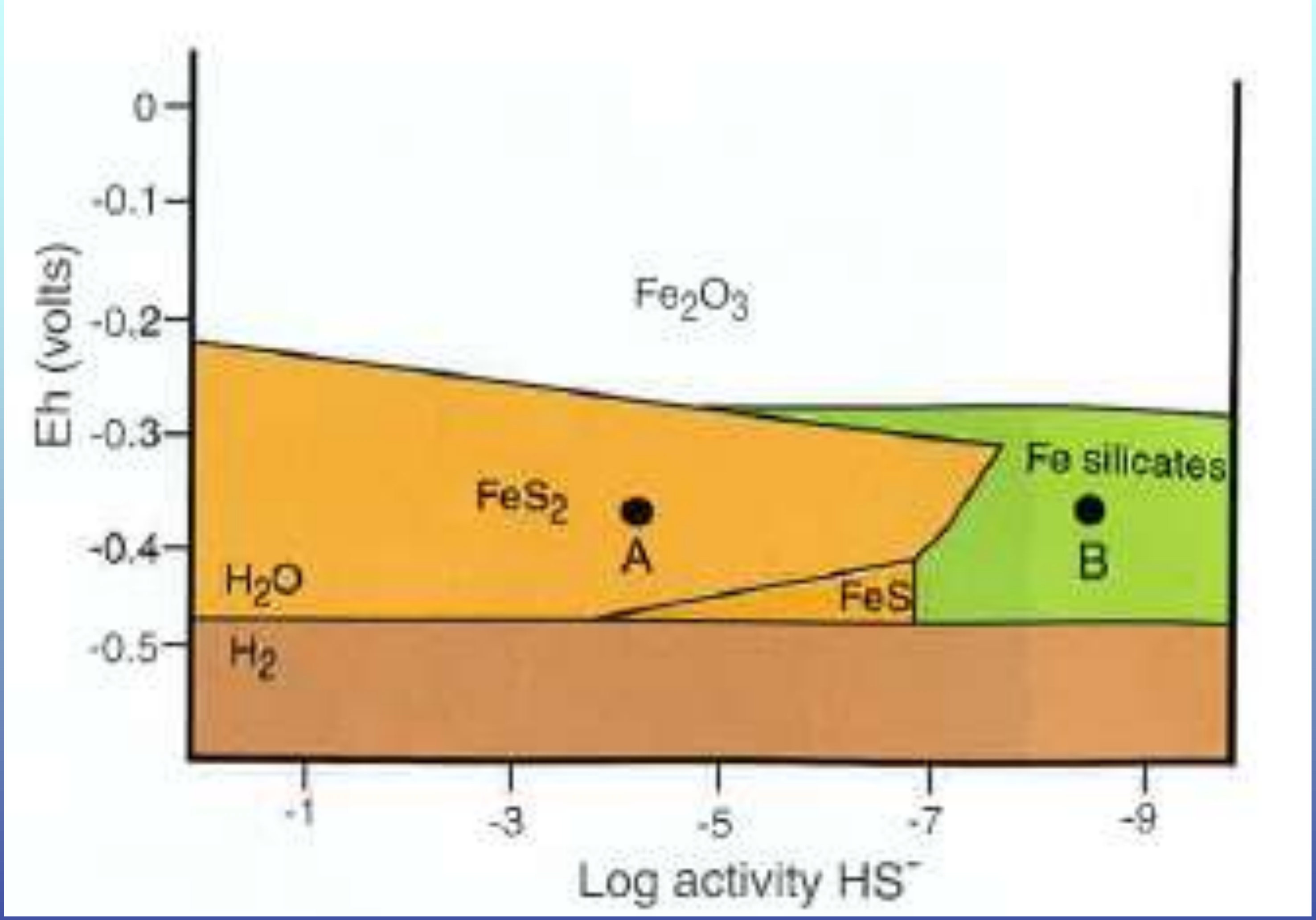
  (O_2 as electron acceptor $\Delta G = -518\ kJ\ mol^{-1}$)

Mn in oxic environments precipitates; organic metabolism has the potential to convert it to soluble Mn^{++})

$$CH_2O + 8H^+ + 2Fe_2O_3(s) \rightarrow$$

$$4Fe^{2+} + CO_2 + 5H_2O \ (\Delta G = -281 \text{ kJ mol}^{-1})$$

The Problem with Fe

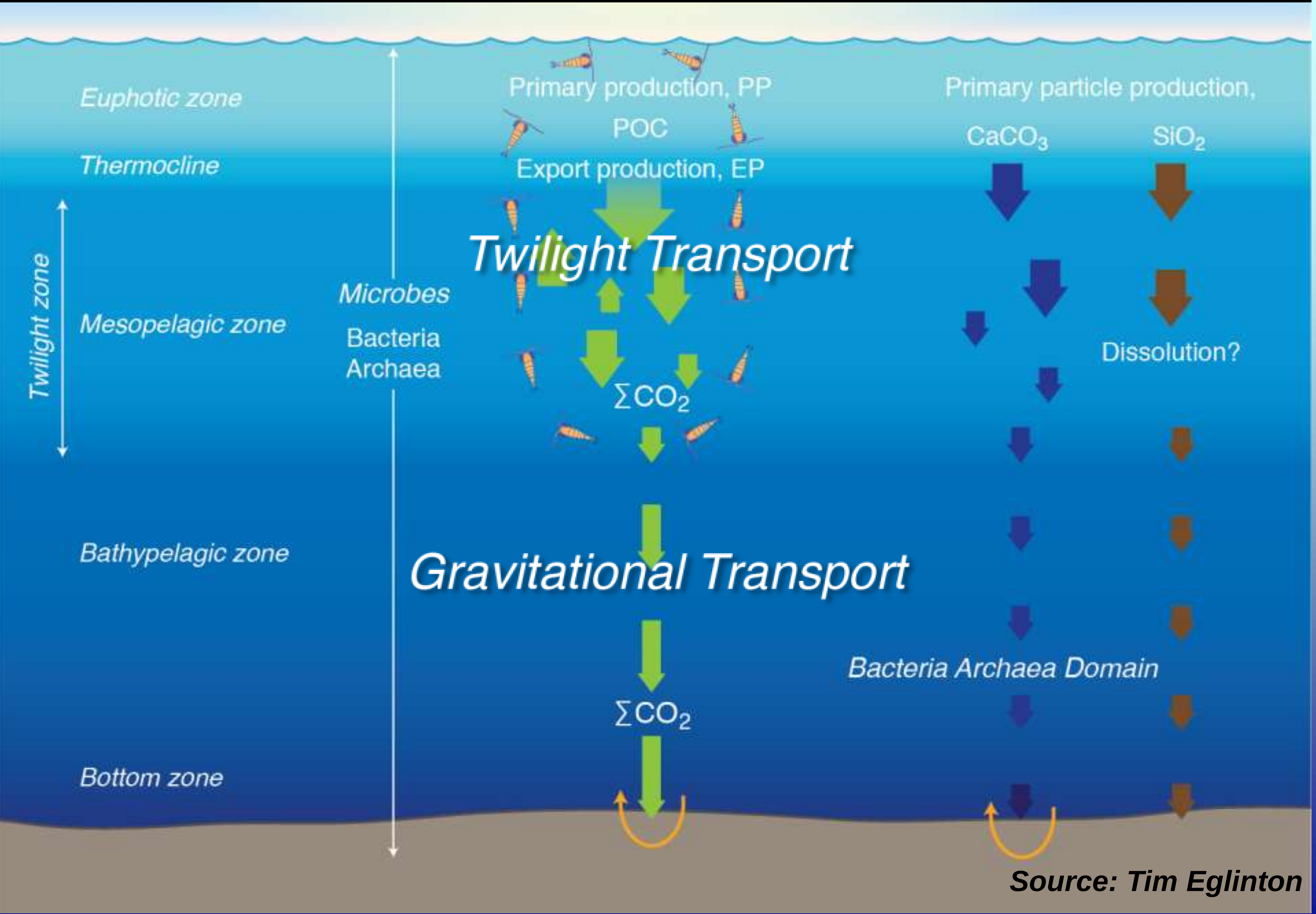


Taylor & Macquaker (2011)

Mn and Fe solid phases can act to scavenge the other elements and organics

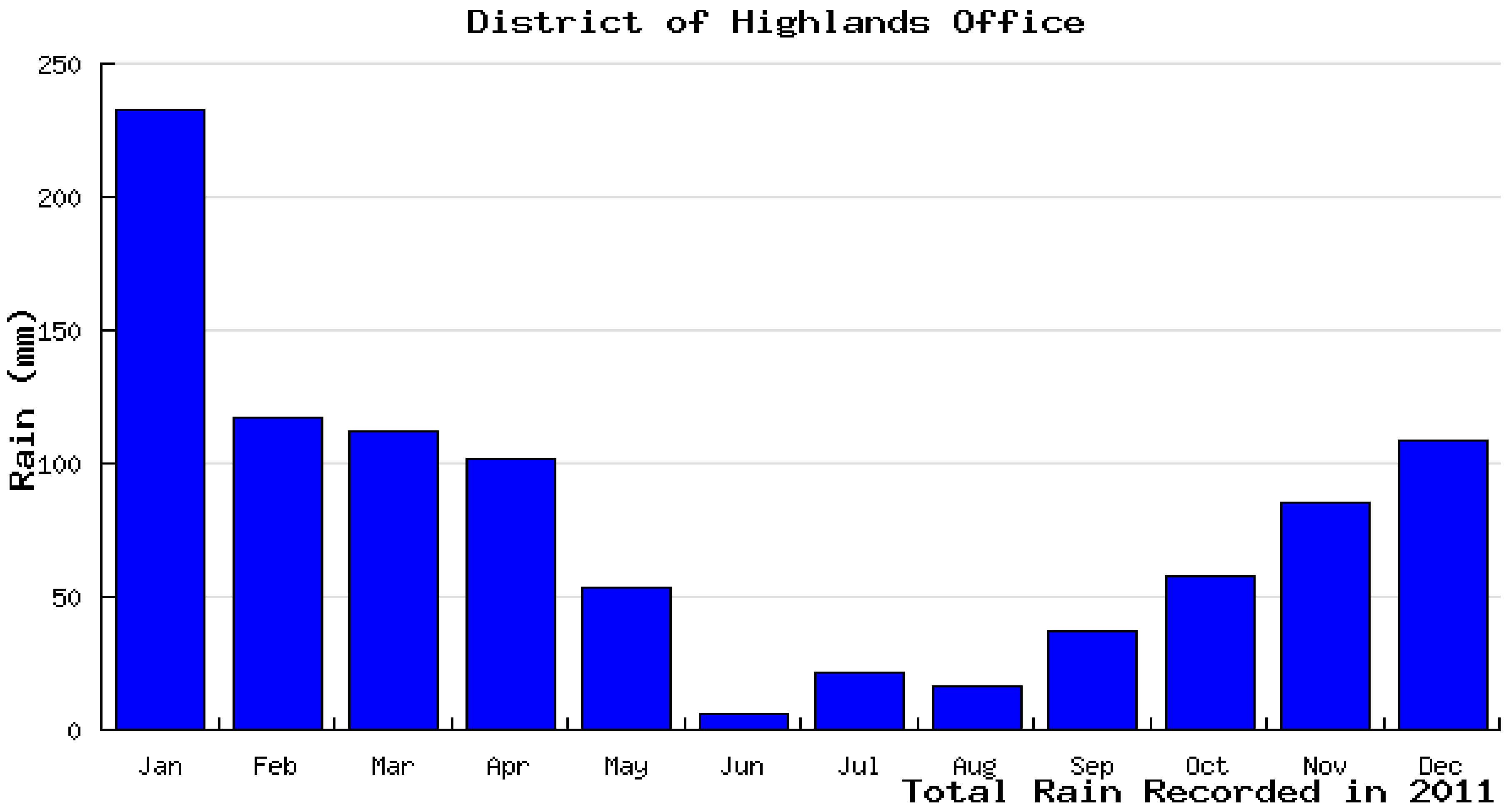
$$4FeS_2(s) + 15O_2 + 2H_2O \rightarrow 4Fe^{3+} + 4H^+ + 8\,SO_4^{2-}$$

Traditional Schematic of the Ocean's Biological Pump



Source: Tim Eglinton

In a landfill site, the organic carbon supplied in the ocean setting stops, to be replaced by O_2 which can diffuse (very slow) or be carried by water (12 mg/L ~ 0.75 mol m^{-3})



Rainfall at Highlands Office

Year	mm	$m^3 \times 10^6$
2012	588	1.3
2011	952	2.2
2010	493	1.1
2009	501	1.1
2008	584	1.6
2007	494	1.1

1to 2 million m^3/yr

A few conclusions

- There are significant contaminant loads in the material
- The compounds of concern tend to be ‘sticky’ and not prone to partition into water; also the major environmental pathway for many of the compounds/elements tends to be foodweb, not water
- The ‘thermodynamic’ conditions of the sediment may shift from reducing in the marine setting (due to organic loadings) toward oxic depending on whether O_2 can get into the buried matter (most likely through water percolation

- With sufficient O_2, some elements may become mobilized, and the absorption characteristics of the solid may alter leading to a re-establishment of equilibria between water and solids
- Most important would be to monitor the water properties, and understand the water pathways within the site and out of the site
- The sediments contain ~ 3000 t of NaCl – should be monitored in groundwater and runoff