The Processes of Ni Partitioning in the Water Column of a Recovering Seasonally Sub-Oxic Lake in Sudbury, Ontario, Canada

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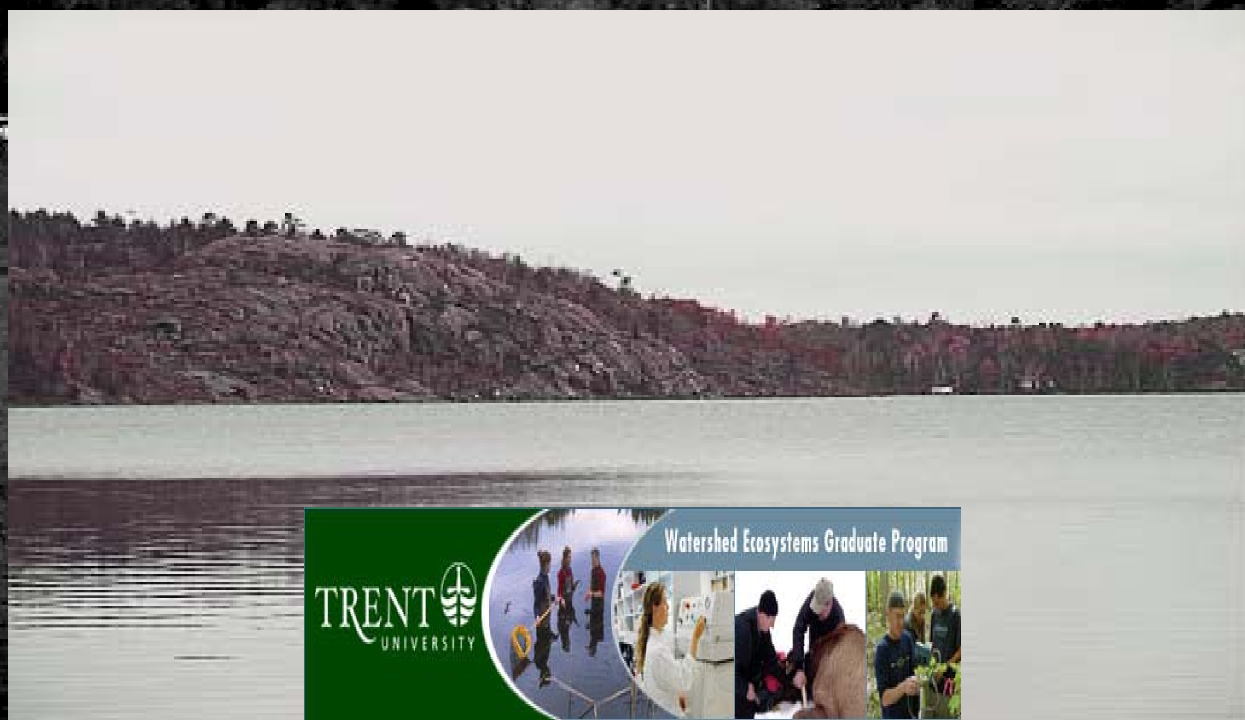
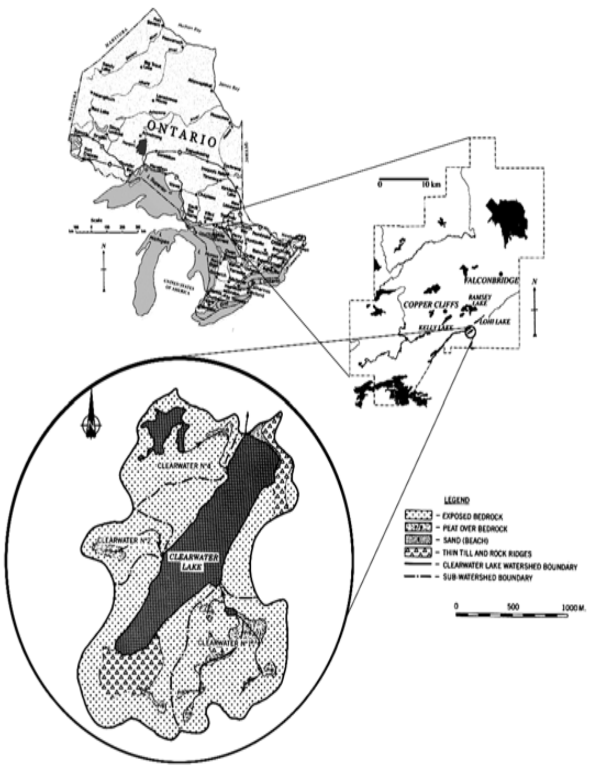


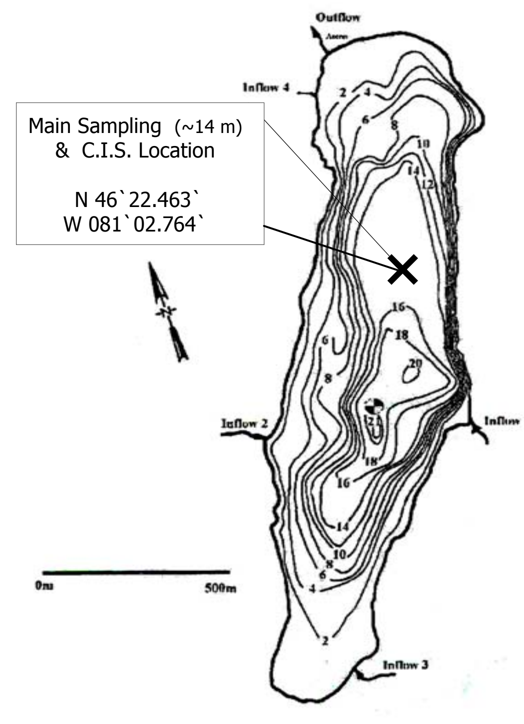
Goals of this Presentation

- **Provide background on research topic and the questions.**
- **Provide a glimpse of the data set :**
  - **Depth profiles (water column [Me] and physicochemical parameters).**
  - **Time series**
  - **K_{P-W} and C_p relationships.**
  - **SEM / EDS results**
  - **Equilibrium modeling.**
  - **Diffusive flux calculations.**
- **Propose a mechanism for the accumulation and particulate Ni formation.**
- **Provide an outlook: direction and focus.**

Clearwater Lake



Lake Volume ($10^5 m^3$)	64.2
Watershed Area (ha)	419
Lake Area (ha)	76.5
Perimeter (km)	4.97
Max. Depth (m)	21.5
Mean Depth (m)	8.39
Elevation (m above s.l.)	285
τ (H_2O replenishment, yrs)	4.4
Longitude/Latitude	46°22'/81°03'



RECOVERY OF THE SUDBURY LAKES

		pH	Alk. mg/L	Ca mg/L	SO_4^{2-} mg/L	Al ug/L	Co ug/L	Ni ug/L	Cu ug/L	Fe ug/L	Mn ug/L	TKN ug/L	DOC mg/L	Cp Mg/L
CLEAR-WATER L. - Unlimed	1990	4.88	-.85	6.10	16.74	130	3-5 (?)	160	35	<60	250	140	0.5	3
	2003	6.33	1.19	4.30	10.70	16 *(18000 μg/g)	1.0 *(80 μg/g)	70 *(2300 μg/g)	10 *(1800 μg/g)	15 *(23000 ug/g)	26 *(140 ug/g)	233	2.9	7
LOHI L. - Limed	1990	4.92	-0.69	6.18	19.57	130		200	50	130	230	170	1.1	N/A
	2003	6.28	2.57	4.34	10.39	22	<=1.5	59	12	106	41	300	3.4	N/A

* Sediment Concentration (Data: Keller et al., 2004)

PWQO:

0.6μg/L (Co)

25μg/L (Ni)

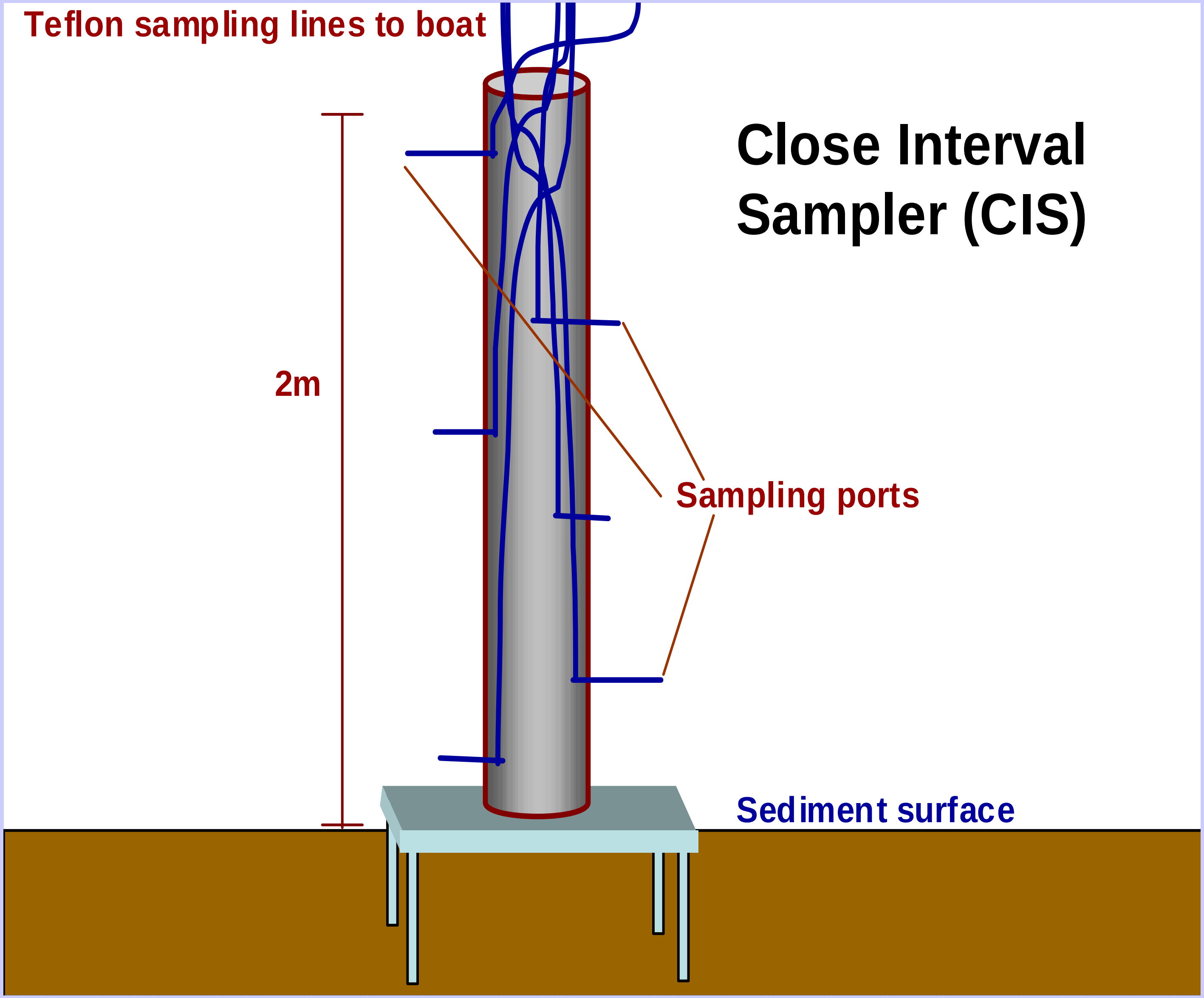
5.0μg/L (Cu)

- **Geochemical and Limnological Recovery.**
- **Significant but Partial Biological Recovery (Lake and Watershed).**
- **Catchment Sources of Ni, Mn, Cu. Lake is sink for Ni, Cu (log Kp-w Cu>Ni) Log Ks-w : Fe>Al>Cu>Co>Ni>Mn**
- **<u>Theories</u>: Decreased atmospheric fall out +**
  - **Alkalinity generation, nutrient replenishments & fish introduction/unusual predation, watershed recovery.**
- **Micromolar quantities of Ni Toxic to:**
  - **Algae, invertebrates, & fish (Stokes, 1988; Mandal et al., 2002).**
  - **Aquatic effects: tissue damage, genotoxicity, growth reduction.**
  - **Humans effects: skin, lungs, nasal, reproductive; anticipated carcinogen.**

Research Questions

- What is the mechanism (processes) of Ni partitioning and solubility in the context of recovery?
- What are the major factors (drivers) of nickel accumulation and particle formation (OM, pH, ORP or Proxy, S) ?
- How is the Ni partitioning to particles affected by other metals (e.g. Fe, Cu, Mn at Sudbury levels)?

We Don't Know Much About the Processes in the Hypolimnion Area, How (in What Form) the Metals Accumulate Before Possible Removal to The Sediments.


Teflon sampling lines to boat
Close Interval
Sampler (CIS)
2m
Sampling ports
Sediment surface

Method Summary

- Conventional water column sampling (P.E. Tubing + Probes).

- Close Interval Sampling (C.I.S.) in the hypolimnion
  - (5, 10, 20, 40, 80 cm);
  - 5, 40, 10, 80, 20 staggered sampling / limited volume.

- 5 main sample types (& triplicates):

  1.) unfiltered / pH 2 acidified, 2.) inline 0.45 μm filtered / pH 2 acidified,
  3.) 0. 0.20 μm cartridge filtered / acidified, 4.) SPM on 0.45 μm filters (2.5 L),
  5.) Nutrients, TOC, H_2S.

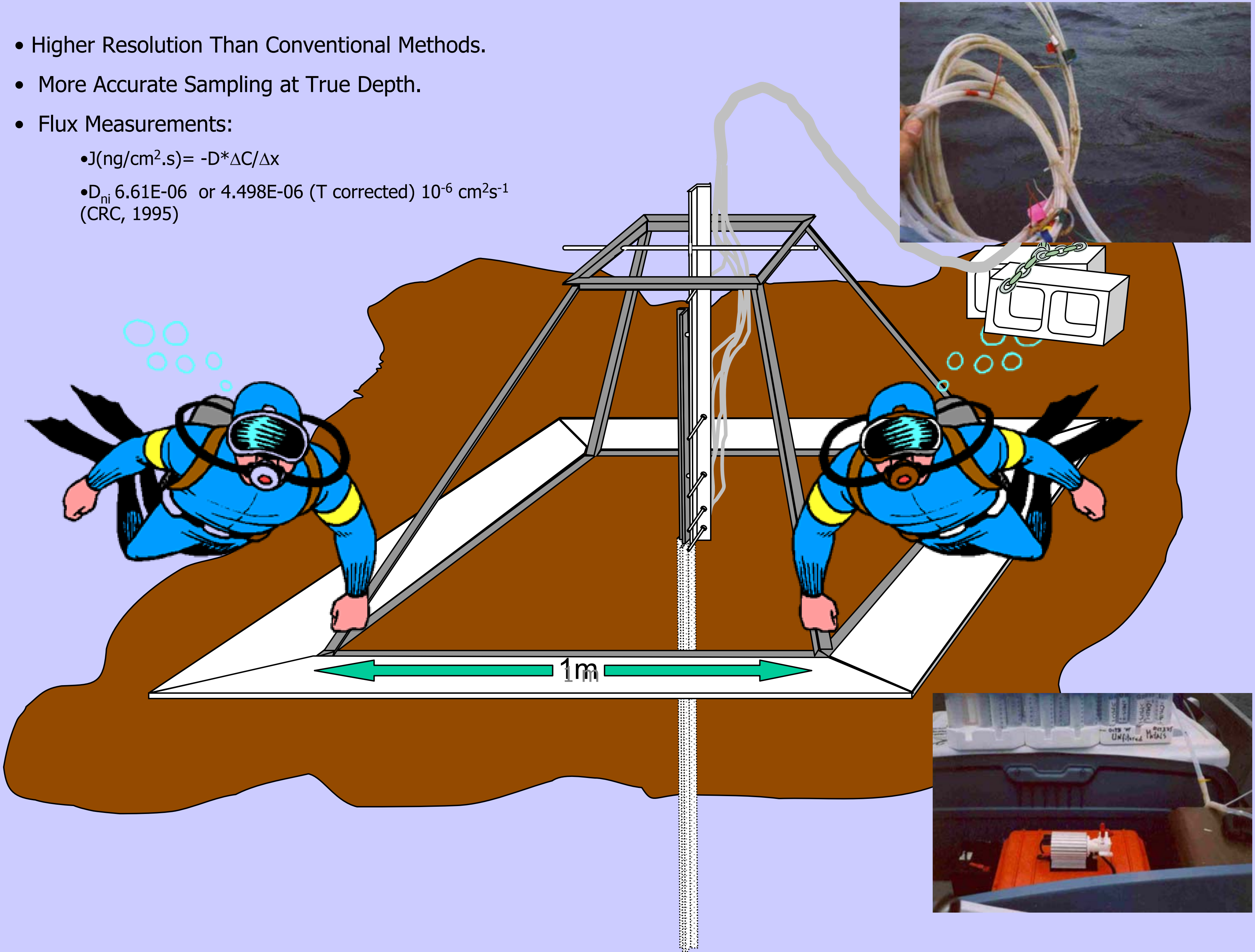
- Total acid soluble metal (MeT) - acid soluble filterable metal (MeD) = particulate metal (MeP).

- TOC, IC, *H_2S*, major cations / anions, pH, and ANC(Gran 2 on unfiltered), using conventional methods.

- Oxidation-Reduction Potential measured in-situ using Ag-AgCl Pt probe.

- ICP-MS metal analysis (Ni, Cu, Fe, Mn, Al, Co)
  - medium resolution, Rh internal standard, SLRS-4, other CRM

- Higher Resolution Than Conventional Methods.
- More Accurate Sampling at True Depth.
- Flux Measurements:
  - $J(ng/cm^2.s) = -D^*\Delta C/\Delta x$
  - D_{ni} 6.61E-06 or 4.498E-06 (T corrected) 10^{-6} cm^2s^{-1} (CRC, 1995)



Stoke's Law

$$v = gd^2 \frac{(\rho_1 - \rho_2)}{18\eta}$$

Where:

v= velocity of settling particle,

g= gravitational acceleration,

d= diameter of particle,

ρ_1 - ρ_2 = density of particle - density of solution,

η= viscocity

"The arbitrary limit of a pore size of 0.2-0.5 µm… has besides all disadvantages – some advantages: particles not retained by such filters do not settle down in natural waters within days and 'move' with the solutes… (Stumm & Morgan, 1996)

OPERATIONALLY-DEFINED PARTITIONING

-Inline 0.45 μm Polycarbonate Filtration.
-Syringe/Cartridge .20 μm Filtration.
-Supplementary MeP> 0.45 μm Hot Aqua-Regia Particle Extraction

Dissolved Fe
(Fe^{2+})
Redox Indicator

MeT (HNO_3 tp pH2), **MeD** ***(<0.20 μm***), **MeD** ***(<O.45 μm),***

MeP *(>0.20 μm)*

Fe Oxyhydroxides Included
(0.20 μm - 0.45 μm
Buffle, 1987)

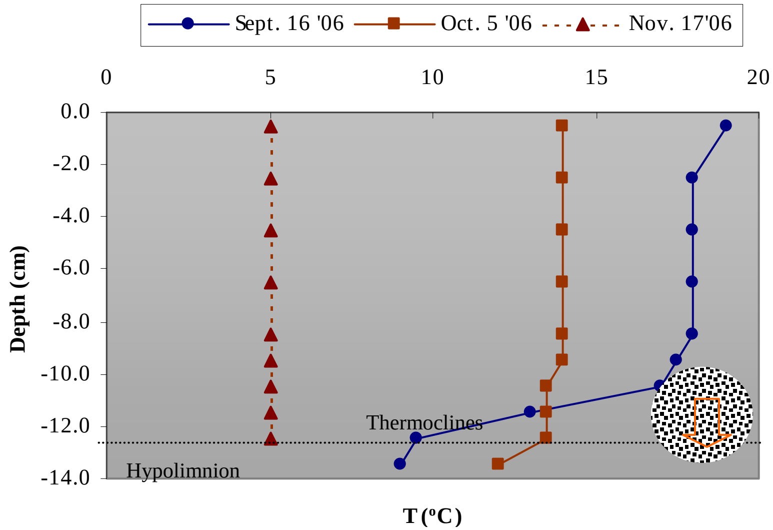
MeP *(> O.45 μm)*

Partitioning Coefficients (K_D Based on 0.45 ***μm cutoff***)

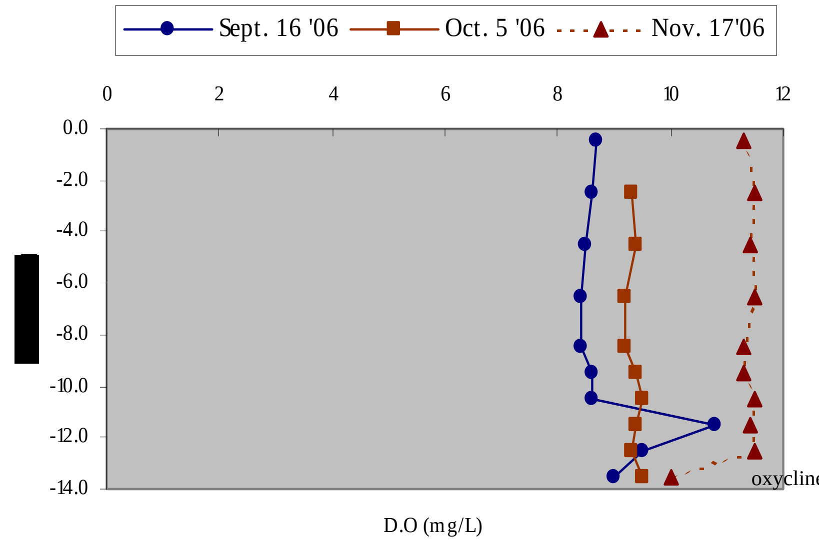
L/Kg

$$K_{S-W} = \frac{C_{WS}}{C_{WD}}$$

$$K_{P-W} = \frac{C_{WP}}{C_{WD}} \times \frac{1}{C_P}$$



Sept. 16 '06
Oct. 5 '06
Nov. 17'06
Depth (cm)
Thermoclines
Hypolimnion
T (°C)



Sept. 16 '06
Oct. 5 '06
Nov. 17'06
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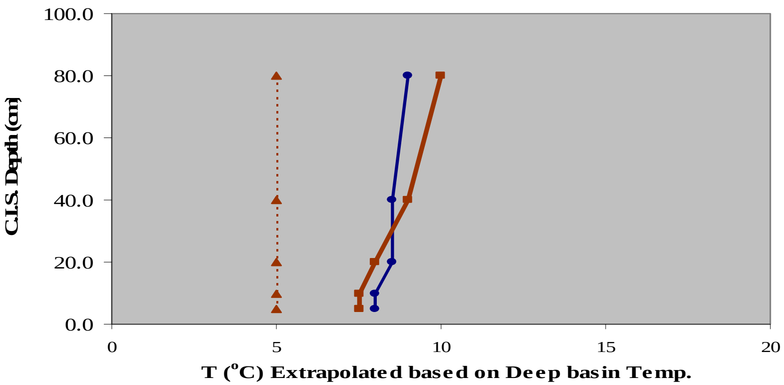
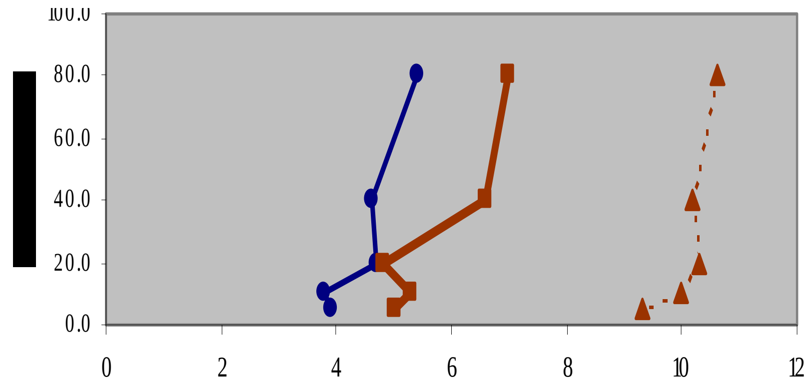
oxycline
D.O (mg/L)



C.I.S. Depth (cm)
T (°C) Extrapolated based on Deep basin Temp.



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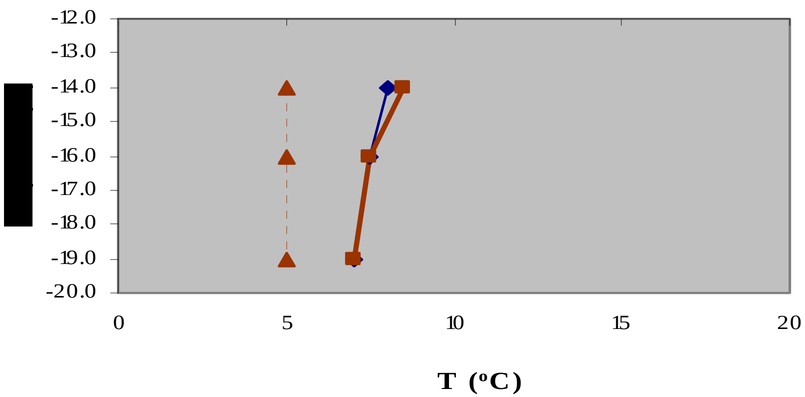

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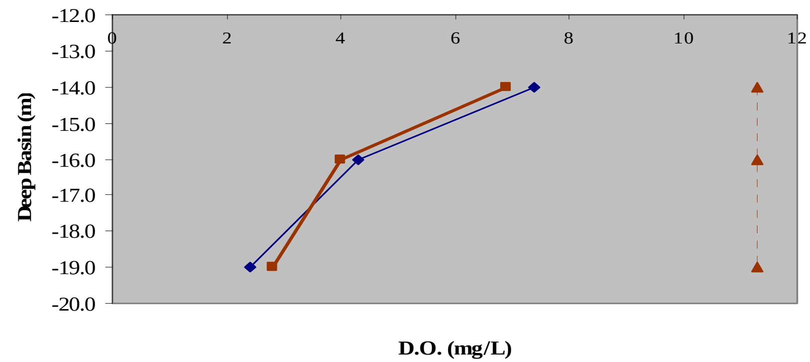
T (°C)



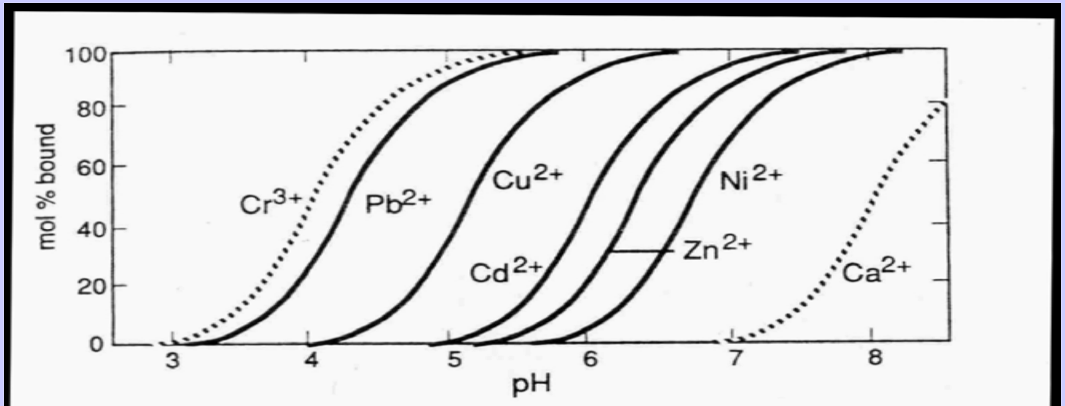
Deep Basin (m)
D.O. (mg/L)

Point of Zero Charge (pzc or PH_0) & Colloid Behaviour:

Table Colloid pH_0 values and electrostatic affinity in lake waters of different pH collected using a Close Interval Sampler in hypolimnion of Clearwater Lake (, Sudbury Ontario (pH_0 values: VanLoon & Duffy, 2005).

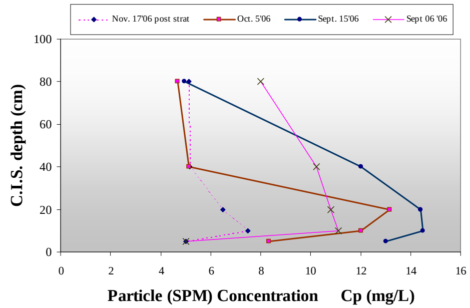
Colloid (interactive particle)	PH_0	Lower pH Areas (5.8) Hypolimnion (BNL)	Higher pH areas (6.4) Metalimnion
SiO_2	2.0	-	-
MnO_2	2-4.5	-	-
Fe_2O_3 hydrated	6.5-9	+	0
goethite	6.5-9	+	0
hematite	8.5	+	+
*Al_2O_3 hydrated	5-9	0	0
Humic material	4-5	-	-
Bacteria	2-3	-	-

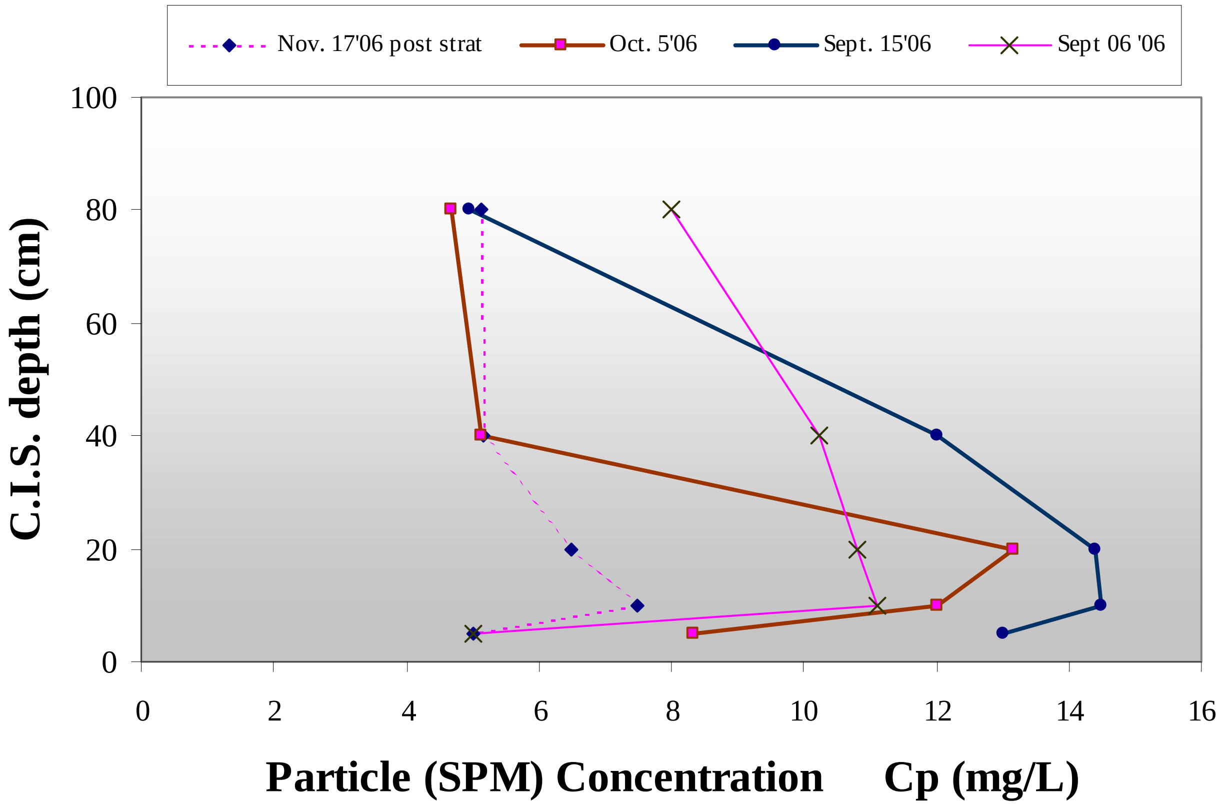
*May form a hydroxide flock at pH 5.8 (Hickie, 2007 personal communication). Actual H_0 values depend on origin, mode of formation, and age of precipitate.



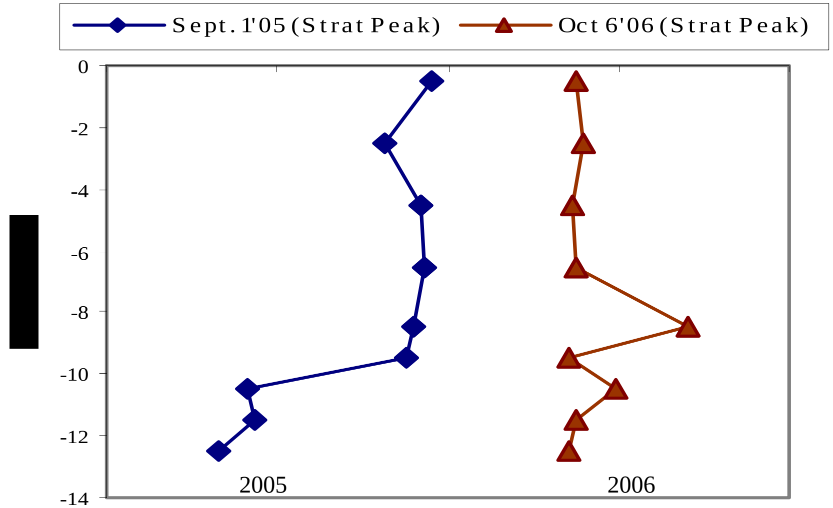
(b)

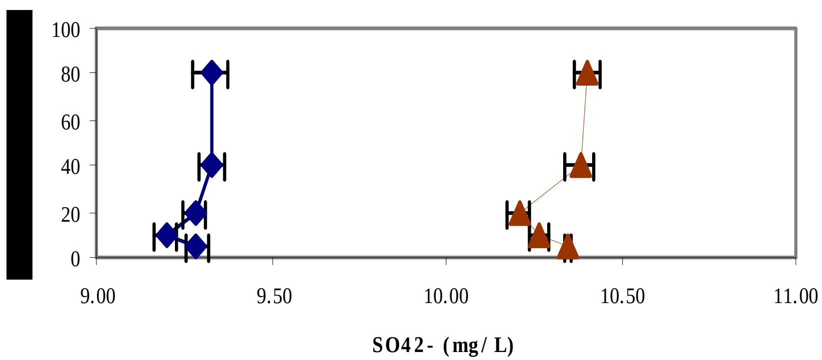
			2005			NiT (ppb)		2006		
		Aug 09'05	Sept 01'05	Oct03 '05	Nov07'05		Sept 6'06	Sept 15'06	Oct 5'06	Nov13'06
Formal	Trips #	1 (Pre CIS)	2	3	4	....	10	11	12	13
Water Column (m)										
	0.5	62.62	60.29	53.17	58.81		44.43	57.44	62.03	61.66
	2.5	61.39	59.40	52.03	59.15		44.48	55.30	62.37	62.00
	4.5	60.28	60.58	52.32	58.02		44.65	57.56	60.79	60.87
	6.5	61.55	60.07	52.99	58.15		45.70	56.53	61.23	61.00
	8.5	63.53	60.27	55.24	59.46		44.74	57.26	63.48	62.31
	9.5	62.54	59.55	54.41	59.27		45.16	56.68	62.79	62.12
	10.5	60.16	**63.46**	54.20	60.39		46.62	57.75	63.14	63.24
	11.5	63.55	**67.69**	55.54	60.16		46.83	**62.26**	62.75	63.01
	12.5	62.95	**65.40**	53.15	59.21		**50.30**	**62.11**	62.86	62.06
	*13.5				-2.85					
C.I.S. (cm)	80	N/A	**65.58**	58.55	59.34		48.74	**61.32**	63.51	62.19
Hypolim. last 1m	40	N/A	**64.56**	58.86	59.61		48.38	59.40	63.27	62.46
	20	N/A	**66.35**	57.40	60.49		47.33	60.34	**67.40**	63.34
	10	N/A	63.88	60.13	60.18		45.77	57.73	**67.08**	63.03
	5	N/A	63.69	58.90	60.20		45.35	59.72	63.23	63.05
Deep Basin	14m	N/A	N/A	N/A	N/A		47.54	59.74	**68.07**	62.70
	16m	N/A	N/A	N/A	N/A		45.74	58.06	62.42	62.30
	19m	N/A	N/A	N/A	N/A		45.33	55.46	58.95	61.91
		s.d range					s.d. range			
		0.8 - 3.0					0.15-1.44			





Nov. 17'06 post strat
Oct. 5'06
Sept. 15'06
Sept 06 '06
100
80
60
40
20
0
0
2
4
6
8
10
12
14
16
C.I.S. depth (cm)
Particle (SPM) Concentration Cp (mg/L)





- No H_2S (HS^-) Detected L.O.D. = 0.05µM or ~1.5 µg/L.

-**No "free" sulphide, assumed to be consumed by all the metals.**

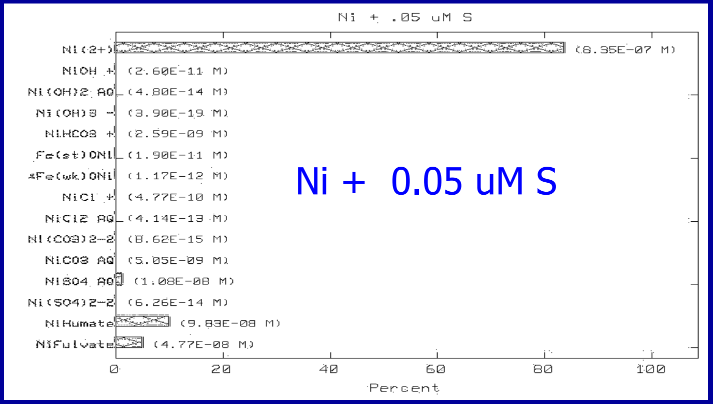
-**Cu > Fe > Ni, Co >Mn.**

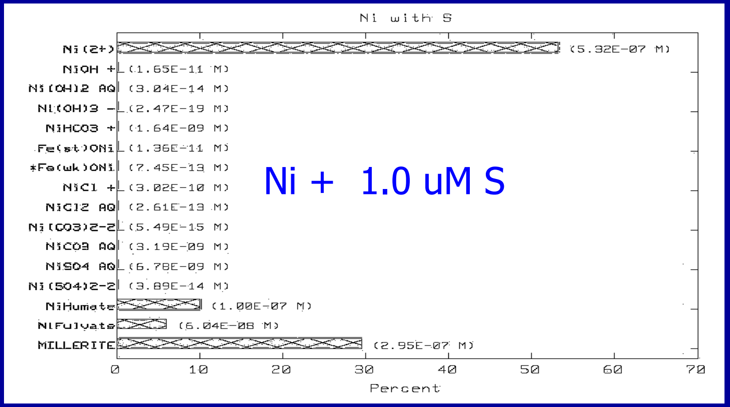
-**Likely reason why Ni remains mostly labile and is Fe-redox dependant.**

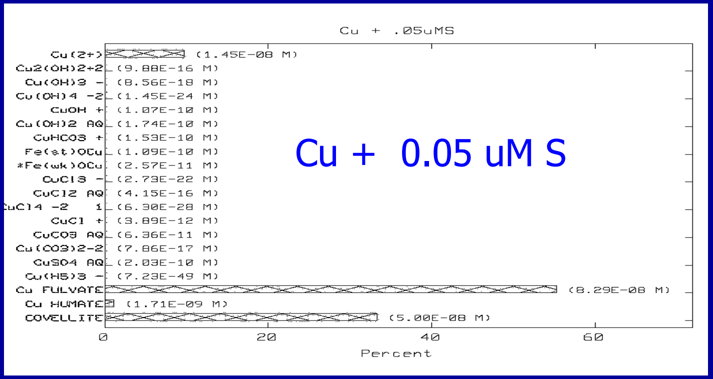
-**CuP will remain closer to the SO_4^{2-} reduction zone (below Fe-reduction zone)**

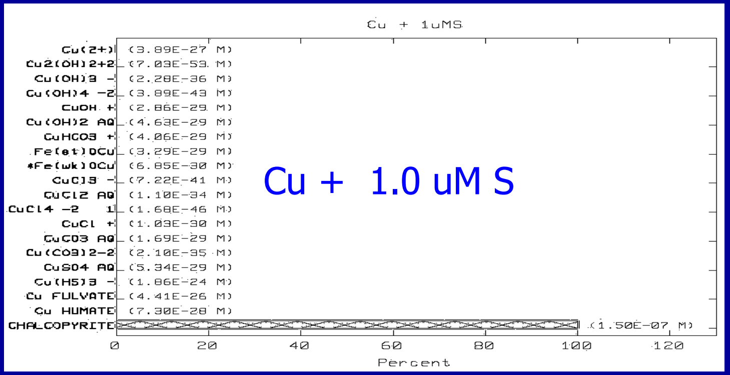
-**The sediments will have more available sulphide. For Ni, if Ni reaches there.**

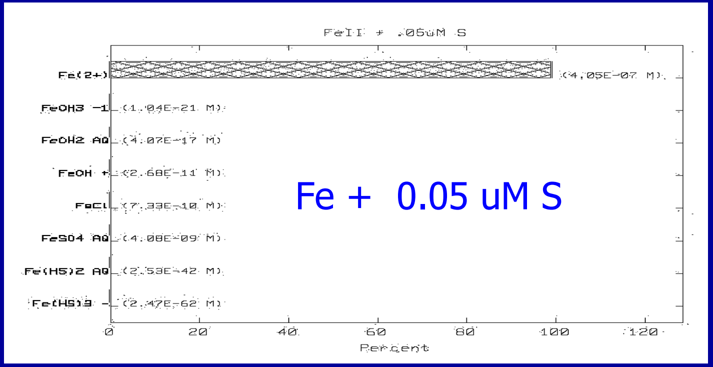
Speciation & Sulphide Availability (MINEQL+)

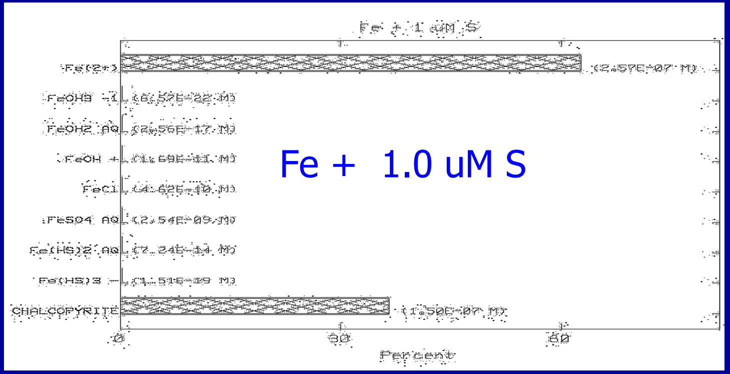


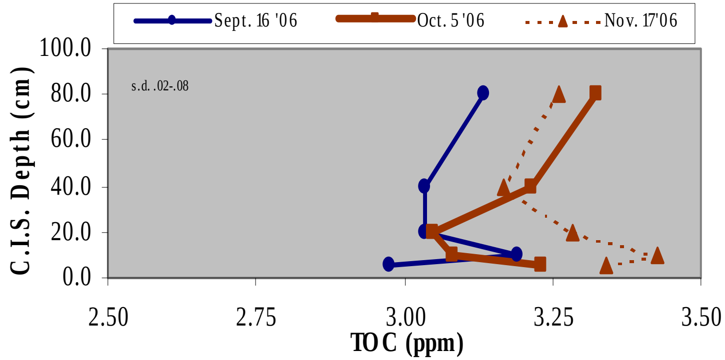


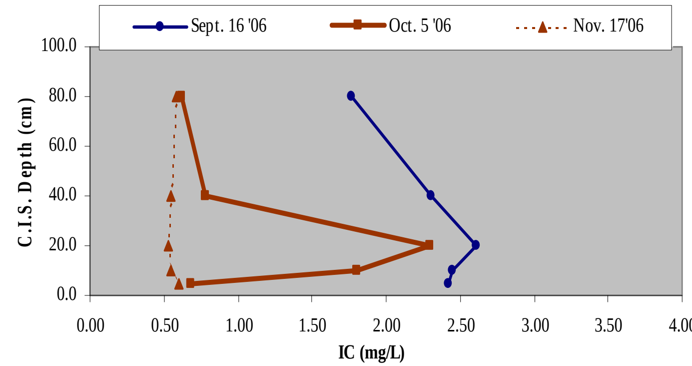


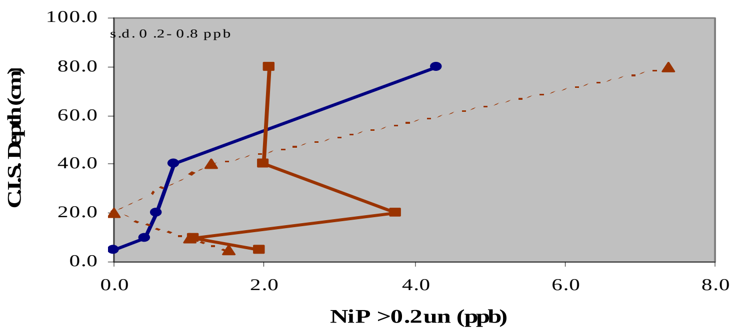


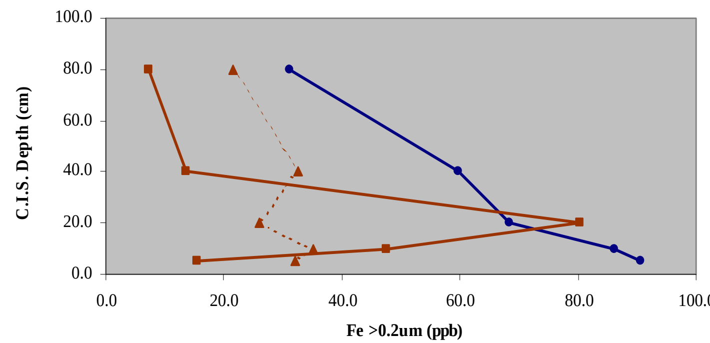


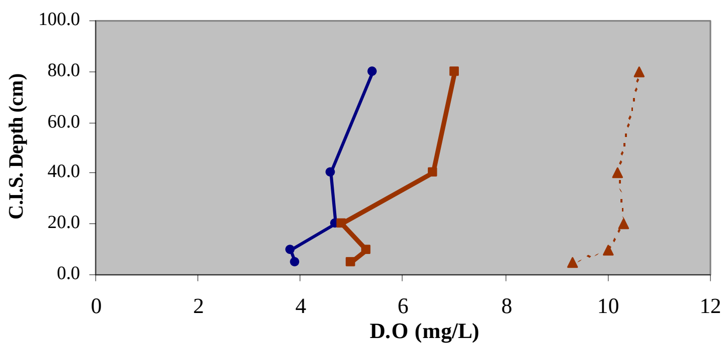


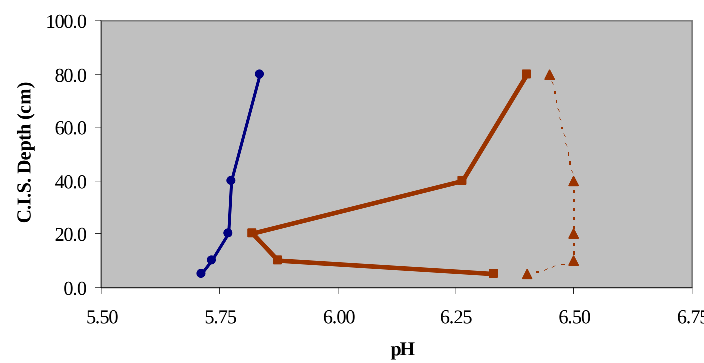

Sept. 16 '06
Oct. 5 '06
Nov. 17'06
s.d. .02-.08
C.I.S. Depth (cm)
100.0
80.0
60.0
40.0
20.0
0.0
2.50
2.75
3.00
3.25
3.50
TOC (ppm)


Sept. 16 '06
Oct. 5 '06
Nov. 17'06
C.I.S. Depth (cm)
100.0
80.0
60.0
40.0
20.0
0.0
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
IC (mg/L)


s.d. 0.2-0.8 ppb
C.I.S Depth (cm)
100.0
80.0
60.0
40.0
20.0
0.0
0.0
2.0
4.0
6.0
8.0
NiP >0.2un (ppb)


C.I.S. Depth (cm)
100.0
80.0
60.0
40.0
20.0
0.0
0.0
20.0
40.0
60.0
80.0
100.0
Fe >0.2um (ppb)


C.I.S. Depth (cm)
100.0
80.0
60.0
40.0
20.0
0.0
0
2
4
6
8
10
12
D.O (mg/L)


C.I.S. Depth (cm)
100.0
80.0
60.0
40.0
20.0
0.0
5.50
5.75
6.00
6.25
6.50
6.75
pH

ppb

Water Column

(onventional sampling)

Depth (m)	NiP (>0.2 *u* m) Sept. 16 '0	Oct. 5 '06	Nov. 17'06	FeP (>0.2 *u* m) Sept. 16 '0	Oct. 5 '06	Nov. 17'06	CuP (>0.2 *u* m) Sept. 16 '0	Oct. 5 '06	Nov. 17'06
-0.5	1.2	0.9	*0.6*	2.5	4.9	8.0	0.6	7.926161	0.5
-2.5	0.7	*0.0*	*0.5*	1.8	4.8	11.5	0.6	1.009039	0.6
-4.5	0.7	*0.0*	*0.0*	3.1	5.8	12.0	0.3	0.91844	0.3
-6.5	0.0	*0.0*	*0.0*	4.2	6.2	11.4	0.3	0.975756	0.3
-8.5	1.5	1.1	*0.8*	4.6	6.9	12.5	0.6	1.05379	0.6
-9.5	*0.0*	0.5	*0.5*	4.0	7.1	11.2	0.5	0.855889	0.5
-10.5	0.4	0.3	*0.0*	5.4	7.4	13.0	0.2	0.901826	0.6
-11.5	0.9	*0.0*	*0.8*	6.7	7.0	18.1	0.0	0.734351	0.5
-12.5	*0.0*	*0.0*	**4.5**	13.8	5.7	19.2	0.2	0.676665	1.0
	s.d. avg 0.6			s.d. avg 1.5			s.d. avg 0.18		

Detailed Hypolimnion

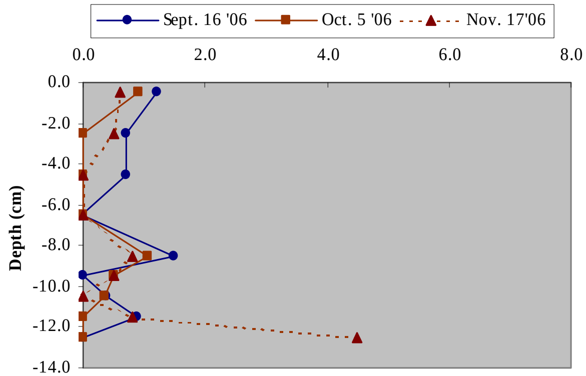
(Close Interval Sampler)

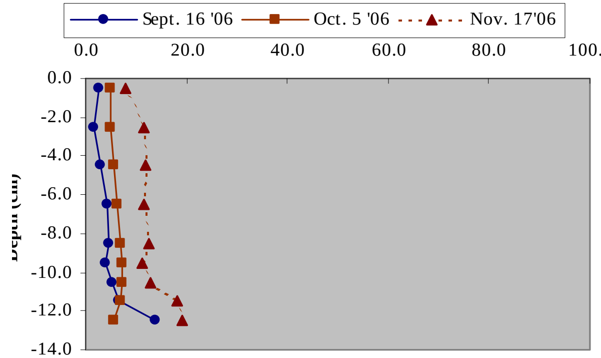
Depth (cm)	NiP (>0.2 *u* m) Sept. 16 '0	Oct. 5 '06	Nov. 17'06	FeP (>0.2 *u* m) Sept. 16 '0	Oct. 5 '06	Nov. 17'06	CuP (>0.2 *u* m) Sept. 16 '0	Oct. 5 '06	Nov. 17'06
80.0	**4.3**	2.1	**7.4**	31.0	7.3	21.53741	1.4	3.994199	0.575076
40.0	0.8	2.0	1.3	59.6	13.7	32.51972	1.5	7.006071	0.660483
20.0	0.6	**3.7**	*0.0*	68.3	80.4	25.9634	1.4	5.260285	*0*
10.0	0.4	1.1	1.0	86.2	47.5	35.09338	2.0	0.670117	0.449577
5.0	*0.0*	1.9	1.5	90.6	15.5	32.19077	1.1	2.435362	1.02066
0.0									

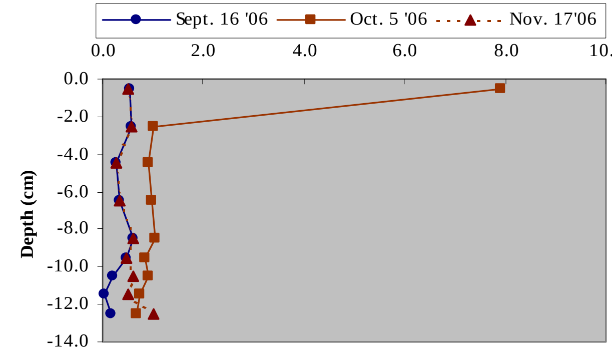
Deep Basin

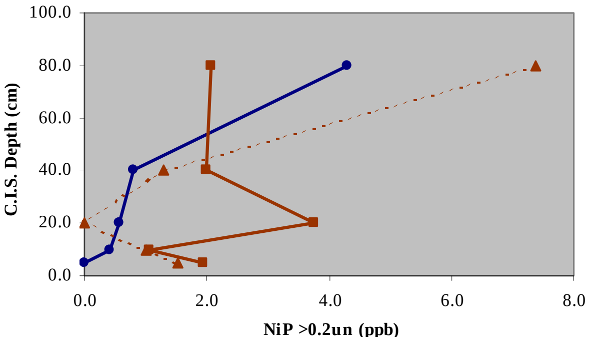
(conventional)

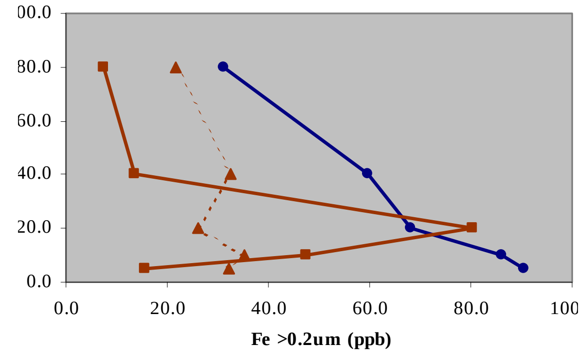
DB Depth (m)	NiP (>0.2 *u* m)			FeP (>0.2 *u* m)			CuP (>0.2 *u* m)		
-14.0	0.0	1.9	**7.9**	21.1	26.0	31.93954	0.6	5.090407	1.506812
-16.0	0.3	2.3	0.9	80.7	**222.8**	26.94322	0.8	5.47234	0.309617
-19.0	0.6	2.0	1.4	161.4	**555.0**	42.39909	1.0	7.018353	0.027285

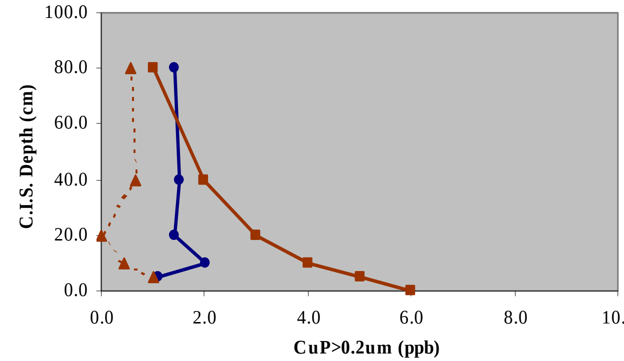


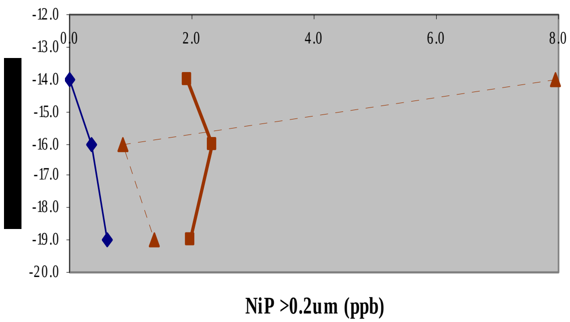


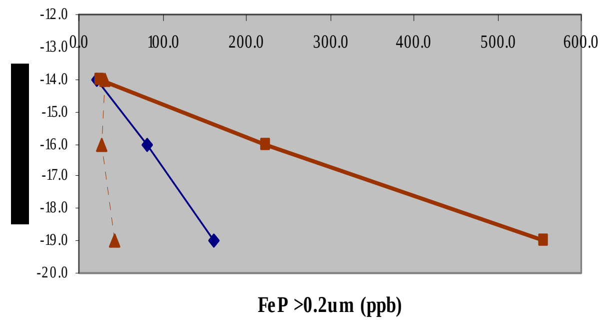


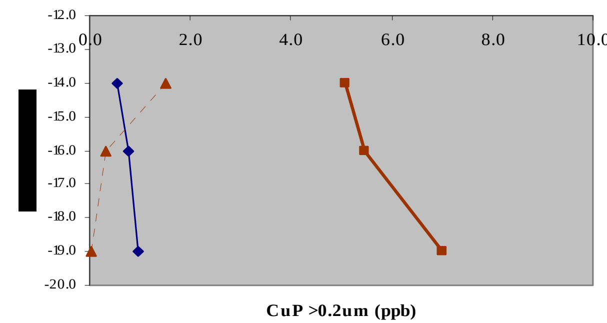












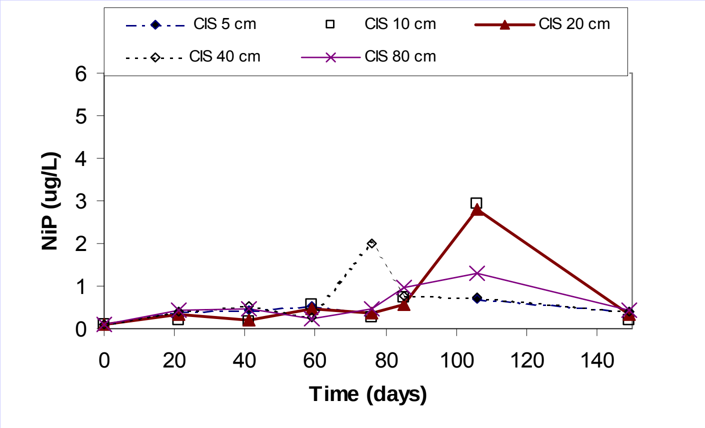
Oct'06 (Peak Strat.)	% NiP of NiT	%FeP of FeT	%CuP of CuT	%MnP
C.I.S. 20 cm	5.5	45.2	24.3	10.8
Deep Basin	3.7	58.5	30.9	9.2

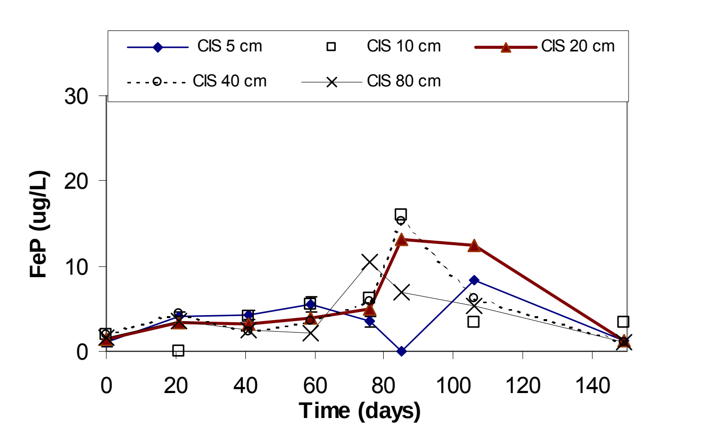
> 2% is significant: Based on the range of calculated precision from field triplicate samples.

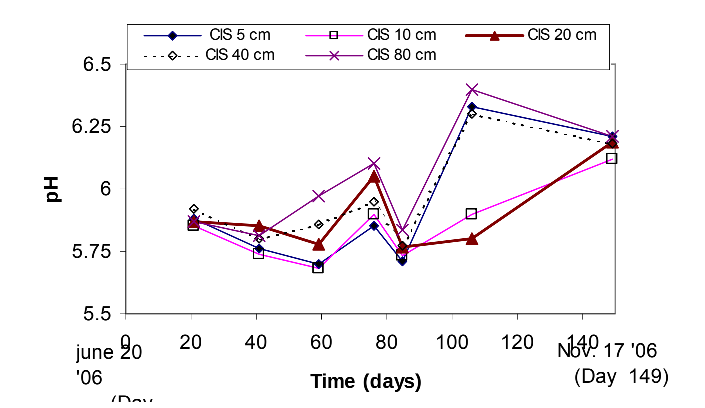
Aqua regia digested metals (MeP>0.45 µm):

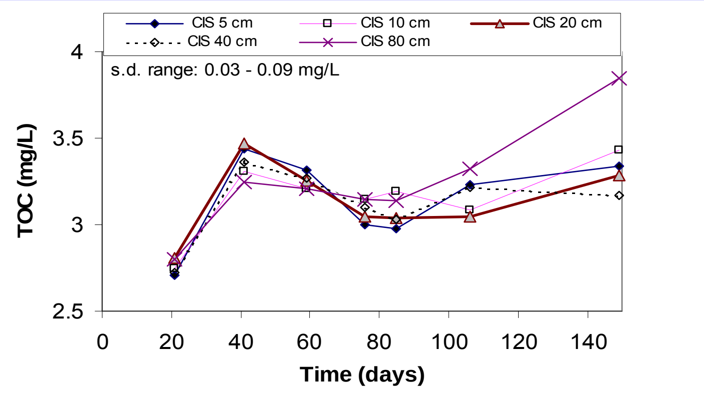
-includes NiP (>0.2 µm – 0.45 µm) Floccs/Aggregates-

Trip	2006	Time (days from start)
6	20-Jun	0
7	11-Jul	21
8	1-Aug	41
9	20-Aug	59
10	6-Sep	76
11	15-Sep	85
12	5-Oct	106
13	17-Nov	149







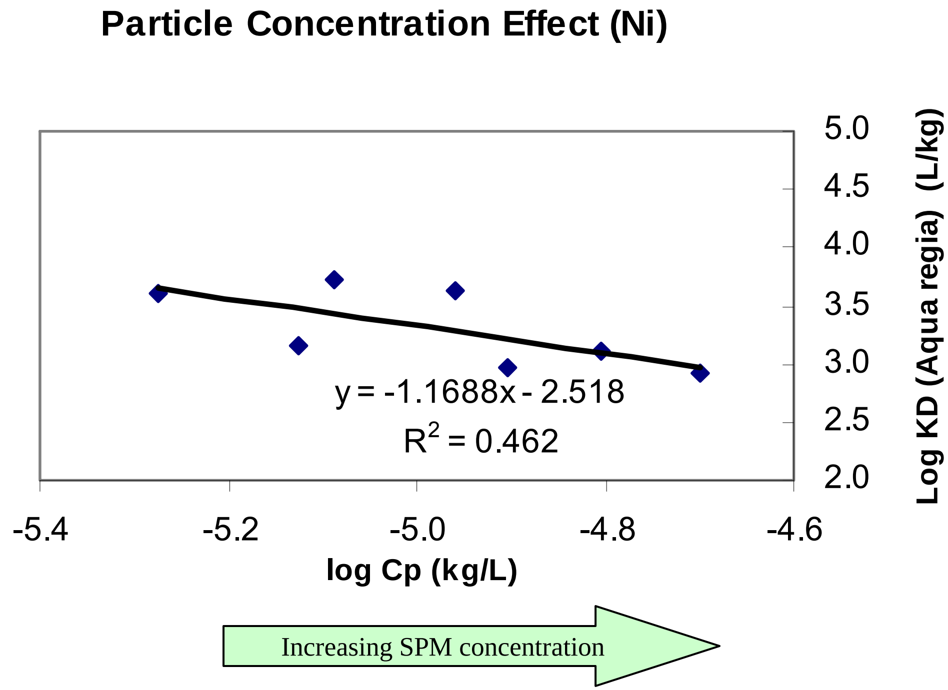


-Decreasing Overall partition coefficients with increasing particle concentration.

-**Particle concentration effect** on K_D - colloids inclusion in the “dissolved” (<.45цm) – *artifact ?*

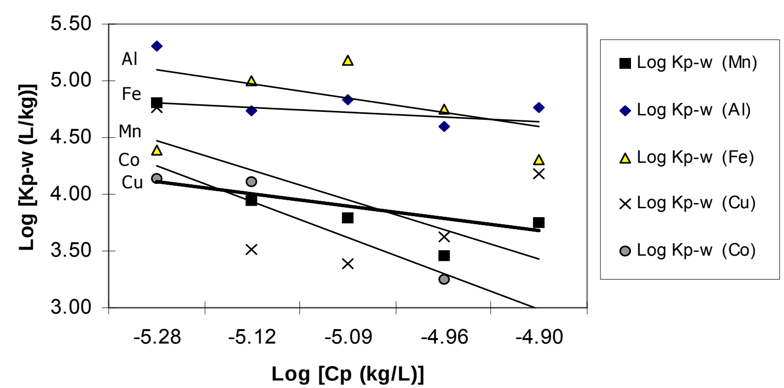
Trace element scavenging is enhanced in low [SPM] conditions.

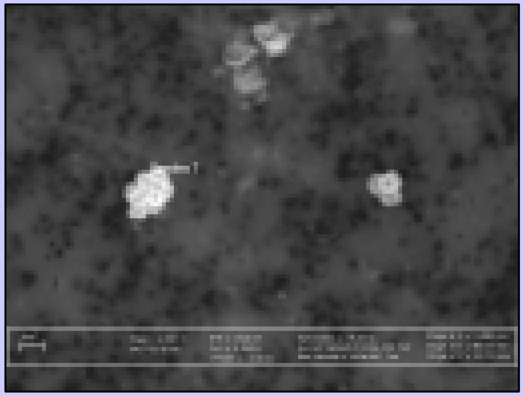
Availability of trapped trace metals governed by steric constraints in colloidal aggregates.

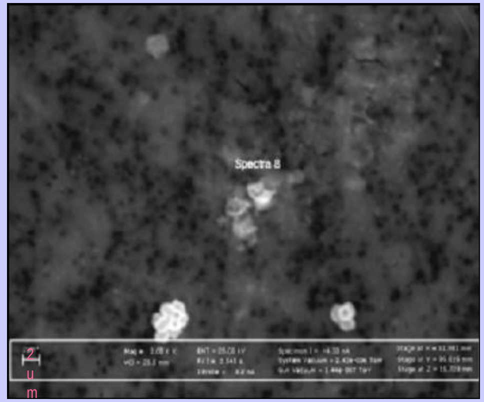


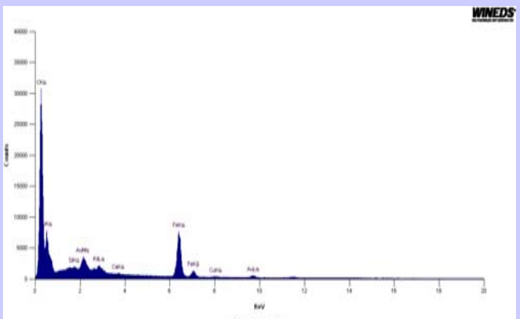
Brownian pumping (suggested):
1. Metal-colloid S-complexation (fast), 2. Colloid to particle coagulation (slower).

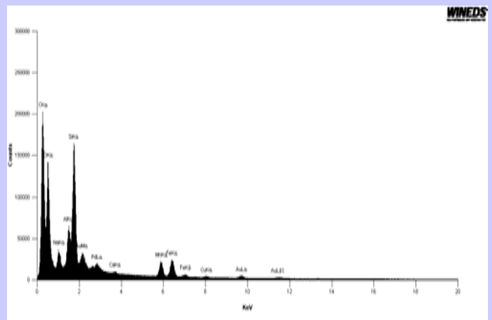
[Santschi et al. (’97), Balistrieri et al (’94), Honeyman & Santschi (’89)].

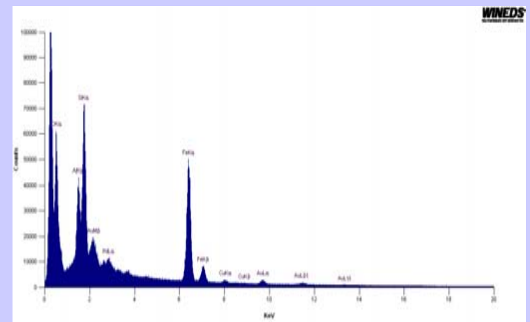












Spectra 7: Well formed layered crystal; Mostly alpha FeOOH (lepidocrosite

Element	Atoms%	Compound	Weight%	Error(±)	Norm%
O	41		-85.62	0	0
C	57.55	CO2	177.7	0.54	95.74
Fe	1.32	Fe2O3	7.39	0.05	3.98
Cu	0.03	Cu2O	0.14	0.02	0.08
Si	0.04	SiO2	0.18	0.02	0.1
Al	0.06	Al2O3	0.21	0.02	0.11
Ni	N.D.	N.D.	N.D.	N.D.	N.D.
<Total>	100		185.62		100

Table 1: Elemental Composition at Site 6 (Spectra 8) of Deep Basin Sample (19r

Element	Atoms%	Compoun	Weight%	Error(±)	Norm%
O	44.98		-67.18	0	0
C	49.82	CO2	148.63	0.16	88.9
Fe	0.34	Fe2O3	1.82	0.01	1.09
Cu	0.04	Cu2O	0.18	0.01	0.11
Si	2.11	SiO2	8.59	0.01	5.14
Al	1.02	Al2O3	3.51	0.01	2.1
Ni	0.01	NiO	0.06	0.01	0.04
Mn	0.29	MnO	1.39	0.01	0.83
Co	0.01	CoO	0.08	0.01	0.05
Na	1.39	Na2O	2.92	0.01	1.75
<Total>	100		167.18		100
Significant Elemental Values > 0.01 %					

Table 2: Site 2 spectra 1 . Luminous Backscatter build-up on edge of partially degr

Element	Atoms%	Compour	Weight%	Error(±)	Norm%
O	43.35		-73.03	0	0
C	51.82	CO2	152.25	0.21	87.99
Fe	1.64	Fe2O3	8.75	0.02	5.05
Cu	0.06	Cu2O	0.27	0.01	0.15
Si	1.79	SiO2	7.18	0.02	4.15
Al	1.34	Al2O3	4.55	0.01	2.63
Ni	0.01	NiO	0.03	0.01	0.02
<Total>	100		173.03		100

Me: C normalization in EDS data

	Fe:C (ato	Mn:C	Ni:C	Cu:C	Al:C	Co:C	C (% atom)
Spectra 7, site 6 (white well-formed lepidocrocite)	0.0229	0.0000	0.0000	0.0005	0.0455	0.0000	57.5500
Spectra 8 site 6 (white area/backscatter on cloudy organic + inorganic matter)	0.0068	0.0058	0.0002	0.0008	0.0205	0.0002	49.8200
Site 1 Spectra 1 (OM fistula) the bright Back scatter left edge	0.0316	0.0000	0.0002	0.0012	0.0259	0.0000	51.8200
Site 1 Spectra 2 (more transluscent part of OM fragment)	0.0052	0.0000	0.0000	0.0007	0.0046	0.0007	58.1100
Blank	0.0002	0.0000	0.0000	0.0017	0.0509	0.0000	60.5300
Site 2 Spectra 3 (organic ground mass - bkgd matrix - not Blank)	0.0052	0.0000	0.0000	0.0007	0.0046	0.0000	58.1100
Site 8 Spectra 10: **1 um grey to white cluster** within organic film (less backscatt	0.0037	0.0000	0.0000	0.0005	0.0002	0.0000	60.03

Works well for Ni, Fe, Co, Mn with C-normalization

Problematic for Cu, Al ...

Molecular Diffusion

Table X: Net diffusive flux (J) of in water column up to the bottom of metalimnion (12.5 m). Sediment porewater data from August 2005. Diffusion Coefficients (Temp. Corrected): D_{Ni} 4.49E-06, D_{Cu} 4.86E-06, D_{Mn} 4.84E-06, D_{Al} 3.68E-06 $_{l}$, D_{Fe} 4.89E-06, D_{Co} 4.98E-06 $cm^2 s^{-1}$

$J\,(ng\,cm^{-2}s^{-1}) = -D\,(\Delta C/\Delta X)$	Ni	Cu	Mn	Al	Fe	Co
Sediment - Hypolimnion	2.49E-05	-1.24E-05	-1.62E-04	-6.54E-05	-2.93E-04	-2.53E-07
***Water Column** (bottom 1m)*	-7.40E-07	1.99E-07	-4.96E-06	-4.69E-07	-1.43E-05	-1.41E-07

Legend: = E-04 = E-05 = E-06 = E-07

Summary of Findings

- There is a progressive accumulation of all metals studies, moving downwards (MeT) as accumulation develops and then peaks (maximum NiP captured by CIS at 10, 20 cm above sediment).

- Ni is limited to modes of occurrence as:
  - with Fe Oxy-hydroxide s with/on organic matter flocks (+ Mn, Co, Al,Cu).
  - With OM fragments (e.g. diatoms)+ coatings
  - Diffusion (Unique for Ni).
- Ni scavenging by settling particles (Fe/TOC), diffusion,

- Ni persists(resuspended) as 0.2-0.45 um (particle size associated with Fe-OOH) after mixing higher up in the hypolimnion.

- SEM/EDS Indicated ~10% pure Lepidocrocite 3 (α-Goethite)FeOOH coated OM fragment with Ni, Co, Al, Mn enriched coating (matter coat. Rest of ground mass some Fe-enriched but no other elements.

- KD values are realistic within EPA range for Ni
- Log KD vs. Log Cp relationships imply a particle concentration effect.

- Sulphidisation ruled out for now as a mode of Ni-particulate partitioning in this type of water column, but not Cu.

– Cu more stable particulates and less suspended than Ni During strat to mixing
  - (Both metals were subject to the Fe effect - start similarly but end differently).

Ni Particle Partitioning Mechanism:

Conditions:

- **Settling / accumulation.**
- **Directly tied to Fe particulates in hypolimnion in a stable (during early)"suspension" zone (BNL).**
- **Fe cycle (Fe has a photoreductive Fe2+ contrib. from Epilimnion)**
- **Competing metals (Co, Mn, Cu?), Cooperative: Fe, Cu?(S-removed)**
- **Favourable connditions: TOC consumed, $Fe3^{+}$ "poised" redox conditions, lower pH (5.8 favourable for FeP, CuP, not necessarily for Ni)),**

–1. Downward movement and diffusion during the progress of stratification.

–2. Brownian pumping (suggested):
1. Metal-colloid S-complexation (fast), 2. Colloid to particle coagulation (slower).
-3 . Remain sediment (further reduced) or Re-suspended with Fe-oxides

-*Downward Molecular Diffusion near the S-W interface may be more significant than other metals.*

Outlook

Ni partitioning in the water column may change with time as lakes recover: Sulphides, Mn-oxides.

Tackle some uncertainties:

-Redox patterns (usefulness of ORP vs. other proxies).

-More SEM/EDS work.

-Fluorescence data…

-Other metals focus.

-Finish-up the Ph.D !

Suggestions for Future Researchers:

-Sulphide involvement and detection in the water column.

-more work on OM involvement.

-more kinetic modeling.

-Improve particle collection and filtration artifacts.

Acknowledgements

Trent Watershed Ecosystems G P & Worsfold Water Q Centre:

Dr. Holger Hintelmann Dr. Peter Dillon

Brian Dimock, Heather Broadbent.

Dr. Olivier Clarise, Dr. Delphine Foucher.

Dr. Celine Gueguen, Dr. Dirk Wallschlager, Dr. Nelson Belzille.

Dr. Nouri Hassan, Dr. Qin Lee.

The Cooperative Freshwater Ecology Unit:

(Dr.) Bill Keller , Dr. John Gunn, Jocelynne Henneberry.

Cottagers:

Nicole and Dennis Chartrand.

Others:

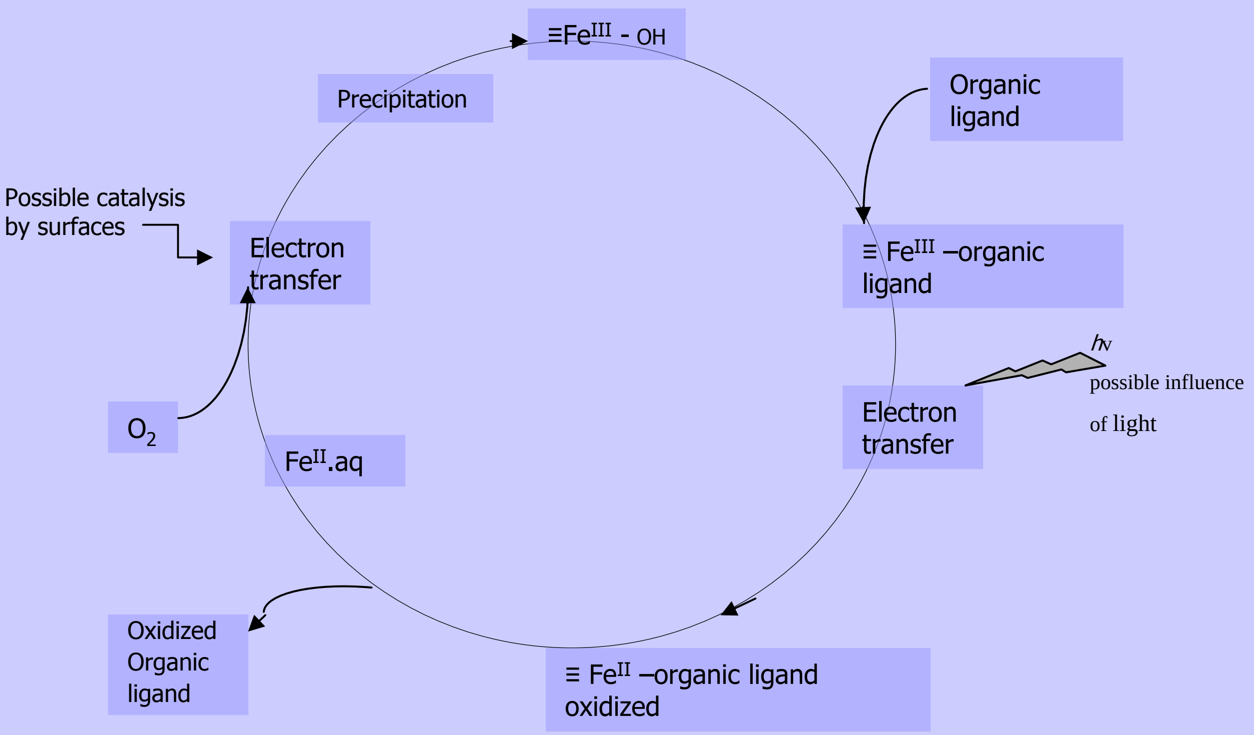
Wang Zheng, Mark Dzurko, Colin Hibbert, Jeff Chambers,

Mr. Wayne Wilson (Biology), Miles Ecclestone (Geography),

Friends/Colleagues at Trent: (Dr.) Ralph Bona, Nagmedine El-Waer,

Questions ?

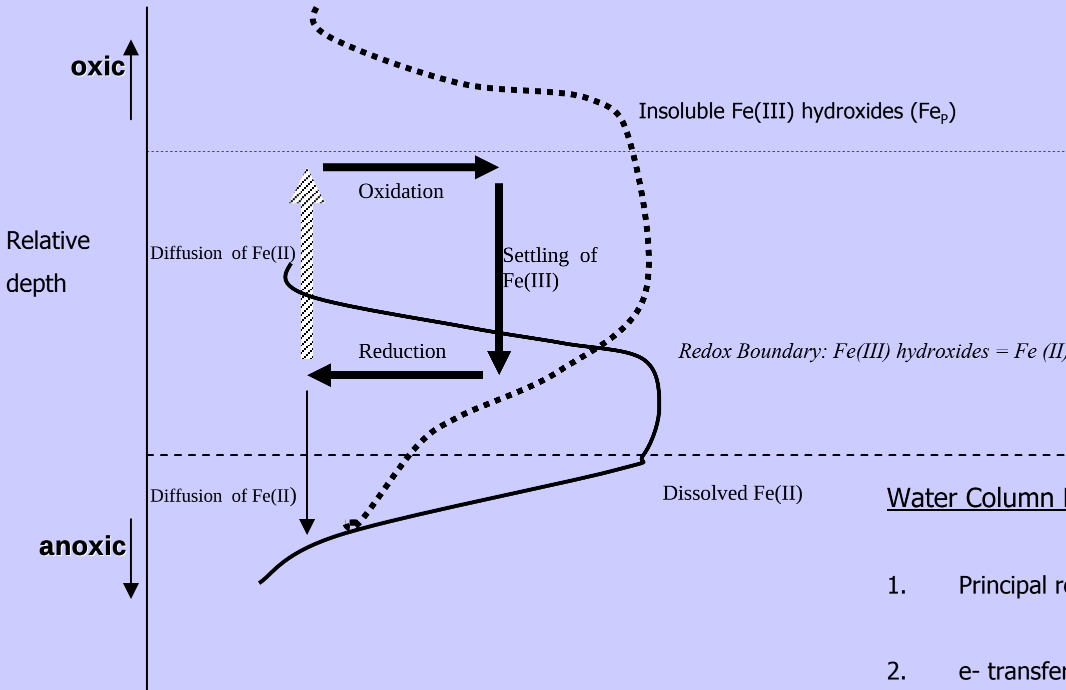
(Photoredox) Cycle of Iron (Fe) (Stumm & Morgan, 1996)



≡ denotes lattice surface of Fe(III) hydroxide.

- A mediation by the Fe of oxidation of organic matter by oxygen. Oxidation is important in degradation & polymerization OM.
- Interdependence of Fe with other redox cycles: Fe(II) reduces Mn(III,IV)oxides & HS^-
- Microorganism mediated production of organic acids involved in ligand-promoted Fe(III) dissolution.
- Mn oxides involved in oxidation of organic matter to low molecular weight fulvic acid (Stumm & Morgan, '96)

Transformation of Fe (II, III) at oxic-anoxic boundary of water or sediment column (Stumm & Morgan, 1996)



Fe Dissol.: ¼ CH_2O + FeOOH(s) + $2H^+$ = ¼ CO_2 + 7/4 H_2O + Fe^{2+}

Water Column Redox Transformation (focus, Stumm & Morgan):

1. Principal reductant: settling bio/photo-degradable biogenic material.

2. e- transfer more feasible with fermentation processes (0.22 to –0.22V) – formation of reactive hydroxy/carboxylic functional group molecules.

3. Fe(III) overly Fe(II) concentration peaks within depth-dependant redox gradient.

4. Fe(II) forming complexes (w. OH, COOH ligands), in their upward diffusion, encounter more Fe(III) hydroxides and reduce them.

reduction occurs at higher ORP than reduction.

6. Mn oxygenation is usually slower than Fe(II) oxygenation.

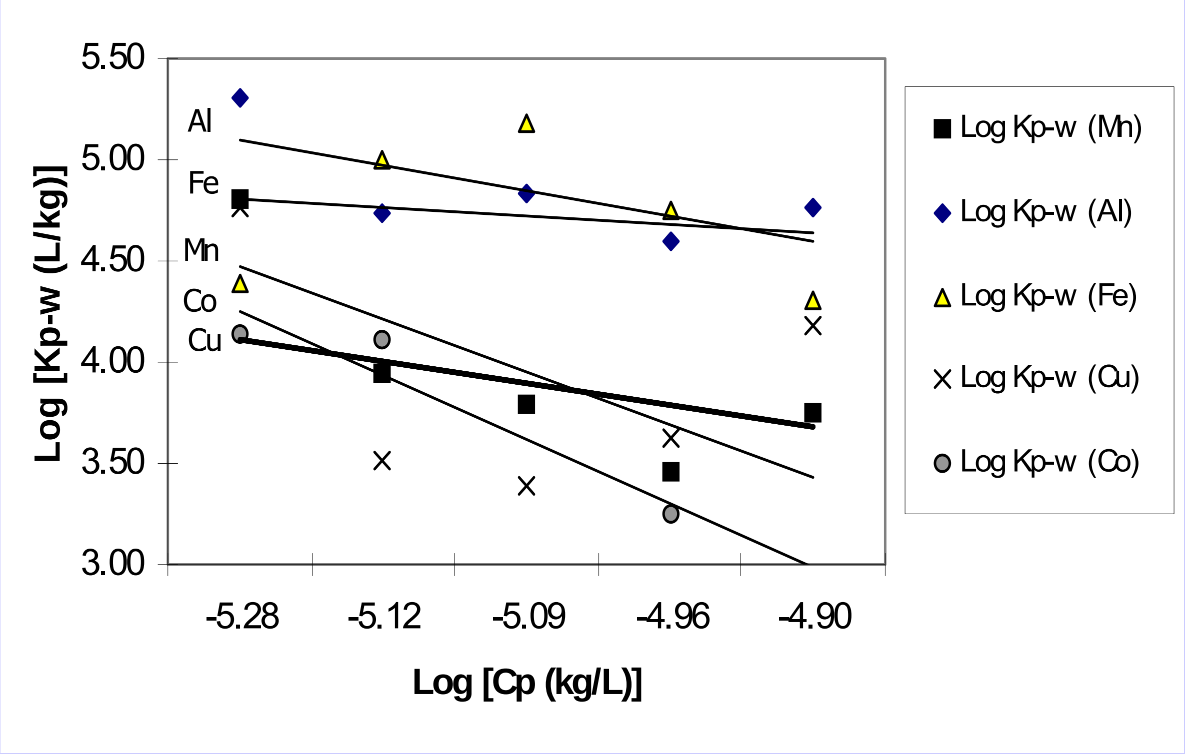
Particle concentration effect on K_D - colloids in the “dissolved” (<.45μm) -artifact

Brownian pumping (suggested):

1. Metal-colloid S-complexation (fast), 2. Colloid to particle coagulation (slower).

availibility of trapped trace metals governed by steric constraints in colloidal aggregates.

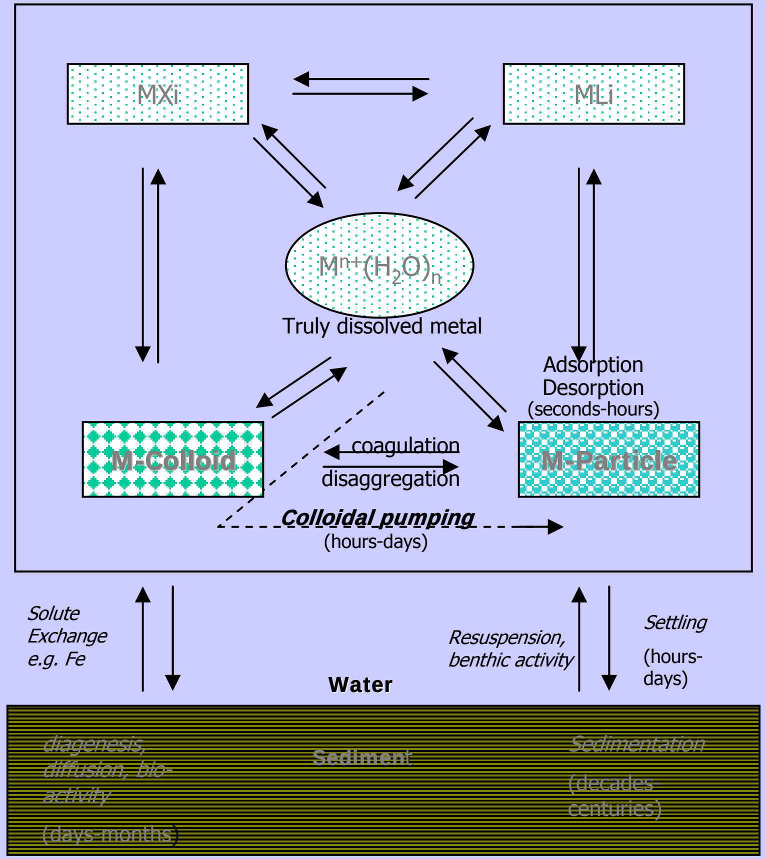
[Santschi et al. (’97), Balistrieri et al (’94), Honeyman & Santschi (’89)].



Average Slope:

-0.25

Figure x: Log of particle concentration (Log [Cp (kg/L)]) versus log of particle-water partitioning coefficient (Log Kp-w (L/kg)), for selected heavy metal in Clearwater L., Sudbury, Ontario. Ni is absent due to zero acid-soluble $[Ni]_P$.



Labile: "metal readily releases ligand"
(Stumm & Morgan, 1996)

Fig x: Schematic of trace metal speciation as it relates to processes regulating trace metal interchanges between water & sedimenting particles (Colloidal pumping, Santschi et al., '97).

Models of trace metal complexation by organic and inorganic ligands:

1. Metals distributed between high few actual metal—binding affinity ligands of bio-origin; kinetic effects due to slow attainment of equilibrium (conventional).

2. Colloidal Pumping + Model: metal availability governed by steric constraints due to trapping of metals within colloidal aggregates, leading to particle formation (onion model: trace metal glue holds aggregate together with slow diffusion into solution, Mackey & Zirino, '94).

- Lability governed by mass transport limitations.
- Composition of the bulk of colloidal organic matter becomes of greater importance

Hypolimnetic alkalinity generation during summer stratification (Dillon et al., ’97)

- In-lake alkalinity generation in dilute oligotrophic (to mesotrophic?) lakes.
- Redox reactions (reduction) prevail in the hypolimnion.
- Dissimilatory Fe(III) to Fe(II) reduction temporary (reversible reaction).
- SO_4^{2-} to HS^- reduction (products in sediments) (or NO_3^- to N_20/N_2) is permanent.
- Stratification isolates hypolimnion: only diffusion and settling.

- Alkalinity generated (change) = Increase in [TBC] + Decrease in [SO_4^{2-}]
  = increase in [Fe] + increase in [Mn]
  = decrease in [NO3-] + decrease in [A-]
  = increase in [NH4+].