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Uptake Characteristics and Speciation of Heavy Metals on the Chemcatcher Passive Sampler

Master's Thesis in the International Master's Programme Applied Environmental Measurement Techniques

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CHALMERS UNIVERSITY OF TECHNOLOGY

Göteborg, Sweden 2006

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Cover: Lake Horsickan in October 2004; Mölndal, Sweden.

Chalmers Reproservice / Department of Civil and Environmental Engineering
Göteborg, Sweden 2006

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ABSTRACT

Abstract The recently developed passive sampling device (passive sampler) has shown its advantages and increasing importance in research of environmental science. The samplers had been applied in different laboratory conditions. The data obtained from the experiments shows that the device effects differentially with different experimental setup, ligands, concentration of ligands, the number of filter membrane and the materials of them. The experiment data shows that the filter made from polysulphone (supor-450) make the ions diffuse more easily than that of CA-ME filter which is made from cellulose acetate mixed with esters. A 7 days exposure would be enough for the passive sampler with single layer filter. In additional, the labile fractions of metal ions from experiments show very good consistency with theoretical calculations.

Key words: passive sampler, Supor-450, CA-ME ligands, ICP-MS

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1. Introduction

According to various estimates, sampling and sample preparation typically account for 70–90% of analysis time (Gorecki, Namiesnik et al. 2002). Therefore, undoubtedly, sampling is the most important steps of any analytical procedure. Any errors taken place in this period will not be able to be corrected and thus irreversibly affect the analysis eventually. For water sampling, there are plenty of methods. In the most common scenario, a water sample is analyzed directly on site or in the laboratory, following the correction of a discrete grab, spot or bottle sampler of water at a given time. There are drawbacks of this approach. Large volume of water sample is needed when the pollutants exist only at trace level. In the environment where pollutants vary over time, the frequency of sampling should be raised or the automatic sampling system should be installed in order to obtain more reliable analysis data. However, this is costly and impractical in many cases. Another approach depends on using biota. The pollutants extracted from which are passively bioaccumulated in the tissues or lipid of organism(s) are analyzed. These biological relevant concentrations show an indication of the equilibrium level of waterborne contamination. However, a number of factors---metabolism, depuration rates, excretion, stress, viability and condition of test organism---can influence the results. Besides, extraction of analytes from animal tissues for the instrumental analysis is complicated. (Vrana et al. 2005)

Thus, a great effort is going into the development of reliable sampling methods characterized by the simplicity of both the operations and the devices involved in the process. Recently developed passive sampling method is one of the efforts made among them. Passive sampling techniques overcome many of the drawbacks listed above. They usually combine sampling, analytes isolation and preconcentration into a single step. Moreover, passive sampling methods usually simplify sample pretreatment and very easy to implement. Thus, passive methods have shown much promise as tools for measuring aqueous concentrations of a wide range of priority pollutants. (Gorecki, Namiesnik et al. 2002, Vrana et al. 2005)

2. Aims and Objectives

The aim of this work was to study the uptake characteristics and speciation of heavy metals on chemcatcher passive sampler in artificial water environment. Filters made from different materials were also tested. This was achieved by applying Chemcatcher passive sampler to the solution in beakers with 23 metals and additives of various kinds of synthetic ligands such as ethylenediaminetetraacetic acid (EDTA), sodium dihydrogen phosphate (NaH_2PO_4) and humic acid (HA) and followed by the experiment in simplified simulated fresh water for a period of two weeks time. The water sample and extractions from receiving phase of the passive samplers were analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

3. Passive Sampling System

3.1 Passive Sampler Device

The passive sampler (Figure 1) which was recently named Chemcatcher consists of a receiving membrane (3M Empore chelating extraction disk in this thesis) and a diffusion limiting porous membrane (both CA-ME and supor-450 in the experiment). The sampler can also include a protective mesh for mechanical protection for which was excluded in our laboratory experiments, however.

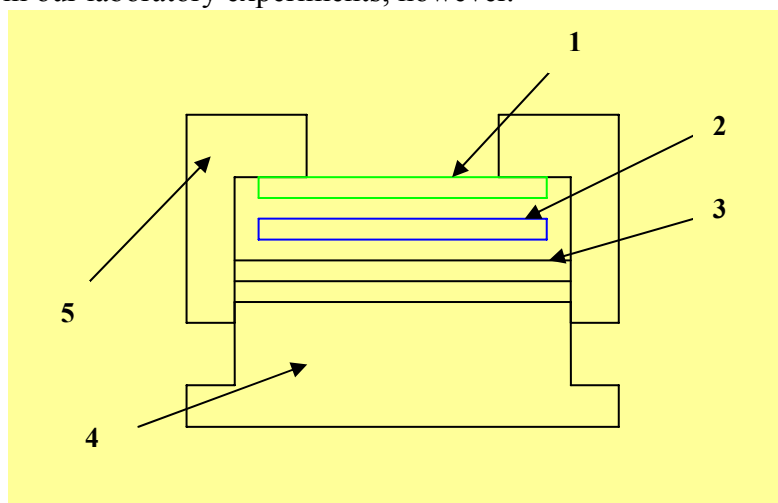


Figure 1 Cross-section of the passive sampler: 1 diffusion limiting porous membrane, 2 receiving membrane, 3 polypropylene supporting disk, 4 polypropylene screw lid, 5 polypropylene body.

3.2 Principle

Passive sampling is based on free flow (according to the Fick's first law of diffusion) of analyte molecules from the sampled medium to a collecting medium. Diffusion driving forces and separation mechanisms depend on the different chemical potentials of trapped and nontrapped (remaining in the sample) analytes. The devices used for passive sampling are usually based on diffusion through a well-defined diffusion barrier or permeation through a membrane, as shown in Figure 2. No extra energy is needed during sampling proceeds rather than the chemical potential difference (Gorecki et al, 2002. Vrana et al, 2005). This chemical potential difference drives analytes from aqueous phase (high in concentration) to receiving membrane (low in concentration). When the analyte concentration is higher in aqueous phase than in the receiving phase, the analyte molecules will be passively transported through the permeable filter and trapped on the surface of suitable medium known as

receiving reference phase or receiving phase. This can be a solvent, chemical reagent or a porous adsorbent (Vrana et al, 2005). In our experiments, porous adsorbent was applied.

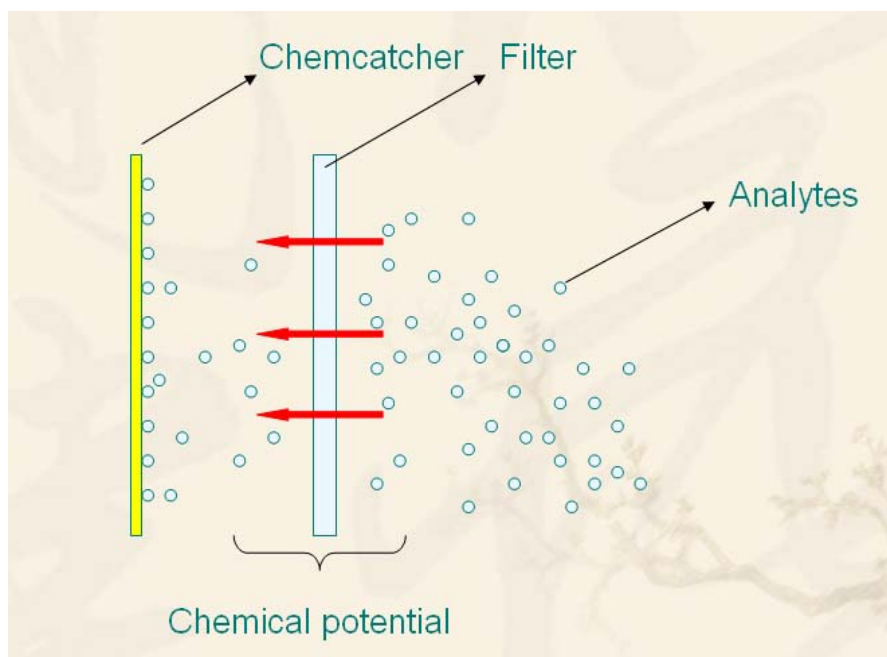


Figure 2 The uptake principle of passive sampler.

Pollutant adsorption or absorption from water into most passive sampling systems generally follows the pattern shown in Figure 3 (Vrana et al, 2005). The exchange kinetics between a passive sampler and water phase can be described by a first-order, one compartment mathematical model:

$$C_s(t) = C_w \frac{K_1}{K_2} (1 - e^{-k_2 t}) \quad (1)$$

where $C_s(t)$ is the concentration of the analyte in the sampler at exposure time t , C_w is the analyte concentration in the aqueous environment, and k_1 and k_2 are the uptake and offload rate constants, respectively. Two main accumulation regimes, either kinetic or equilibrium, can be distinguished in the operation of a sampler during field deployment.

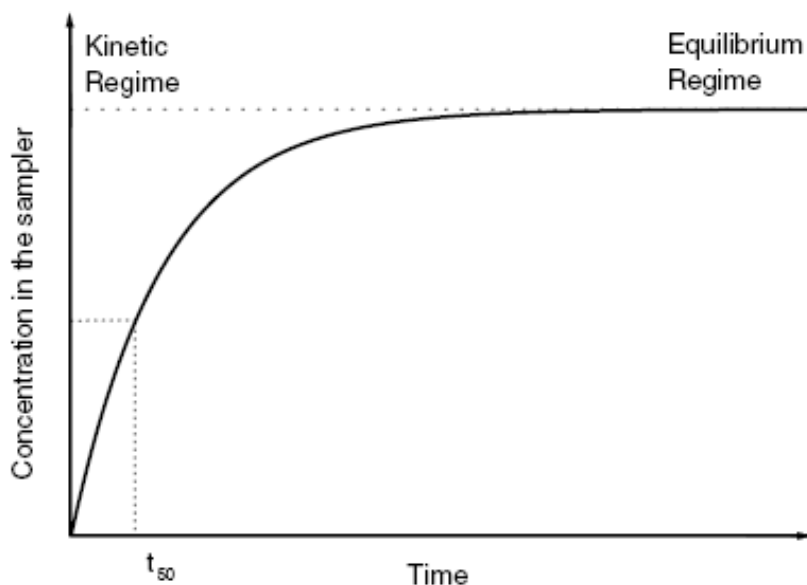


Figure 3 Passive sampling devices operate in two main regimes (kinetic and equilibrium).

3.2.1 Equilibrium-passive samplers

In equilibrium sampling, the exposure time is sufficiently long to permit the establishment of thermodynamic equilibrium between the water and reference phases. In this situation, equation (1) reduces to:

$$C_s = C_w \frac{K_1}{K_2} = C_w K \quad (2)$$

Knowledge of the phase-water partition coefficient (K) allows estimation of dissolved analyte concentration. The basic requirements of the equilibrium-sampling approach are that stable concentrations are reached after a known response time, the sampler capacity is kept well below that of the sample to avoid depletion during extraction and the device response time needs to be shorter than any fluctuations in the environmental medium. Passive diffusion bag samplers (PDBSs) have been used extensively for monitoring volatile organic compounds (VOCs) in water (Vrana et al, 2005).

3.3 Kinetic passive samplers

With kinetic sampling, it is assumed that the rate of mass transfer to the reference/receiving phase is linearly proportional to the difference between the chemical activity of the contaminant in the water phase and that in the reference phase. In the initial phase of sampler exposure, the rate of desorption of analyte from the receiving phase to water is negligible, the sampler works in the linear uptake regime, and equation (1) reduces to:

$$C_s(t) = C_w K_1 t \quad (3)$$

Equation (3) can be rearranged to an equivalent relationship:

$$M_s(t) = C_w R_s t \quad (4)$$

where $M_s(t)$ is the mass of analyte accumulated in the receiving phase after an exposure time (t) and R_s is the proportionality constant (sampling rate), which is the product of the first-order rate constant for uptake of pollutant (k_1) and the volume of water that gives the same chemical activity as the volume of receiving phase. R_s may be interpreted as the volume of water cleared of analyte per unit of exposure time by the device. When R_s is known, C_w [the time-weighted average (TWA) concentration of a pollutant in the water phase] may be calculated from the sampling rate (R_s), exposure time (t) and the amount ($M_s(t)$) of the analyte trapped by the receiving phase. For most devices operating in the kinetic mode, R_s does not vary with C_w , but is often affected by water flow or turbulence, temperature and biofouling. The advantages of kinetic or integrative sampling are that they sequester contaminants from episodic events commonly not detected with spot sampling, and can be used where water concentrations are variable. They permit measurement of ultra-trace, yet toxicologically relevant, contaminant concentrations over extended time periods (Vrana et al, 2005).

3.3 Diffusion Theory

Diffusion in the passive sampler is through an assumed boundary layer (L_1) and a diffusion limiting porous membrane (L_p) before reaching the receiving surface during the analyte collecting progress (Figure 4). A comprehensive description was given in the article about the diffusional behaviour of metals in the passive sampler system by Persson et al.

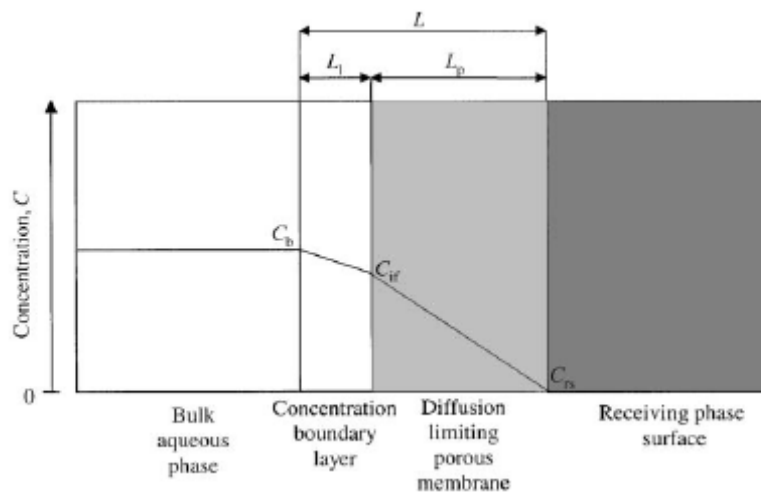


Figure 4 Diagrammatic representation of the diffusion path for analytes from the bulk aqueous phase to the surface of the receiving phase in the passive sampler.

The diffusion in the passive samplers can be described by Fick's first law:

$$F = D \frac{(C_b - C')}{\Delta g} \quad (5)$$

where F is the mass flux of metals through the diffusion layer, D is the diffusion coefficient, C_b is the solute concentration in the bulk phase, C' is the free concentration at the surface of the binding phase and Δg is the thickness of the diffusion layer. If the uptake to the binding phase is effective enough, the equation can be simplified as equation (6):

$$F = D \frac{C_b}{\Delta g} \quad (6)$$

The mass transfer across an area can also be described by equation (7):

$$F = \frac{M}{At} \quad (7)$$

where M is the mass, A is the cross-sectional area of diffusion layer and t is the time.

Combination and rearrangement of equation (6) and (7) will come to

$$M = \frac{DC_b t A}{\Delta g} \quad (8)$$

Alternatively:

$$C_b = \frac{\Delta g M}{DtA} \quad (9)$$

The solute concentration C_b decreases with time in a small volume of water sample.

3.3.1 Bulk removal theory

The first-order rate law for removal of an analyte says that

$$-\frac{dC_b(t)}{dt} = kC_b(t) \quad (10)$$

where t is time (s), C_b is the concentration in bulk solution (g/cm^3), k is the uptake rate constant (s^{-1}).

Equation can be integrated and modified to equation (11) which present the exponential decrease of the analyte with time,

$$C_b(t) = C_{b0} e^{-kt} \quad (11)$$

where C_{b0} is the bulk concentration at time zero and $C_b(t)$ is the bulk concentration at time t.

Take natural logarithm at both side of equation (11) gives

$$\ln\left(\frac{C_b}{C_{b0}}\right) = -kt \quad (12)$$

The physical significance of minus means that bulk concentration is decreasing with the time t (Persson et al, 2001).

3.4 Chelating mechanisms of various ligands

3.4.1 EDTA

EDTA is the abbreviation of chemical compound ethylenediaminetetraacetic acid, EDTA is a chelating agent, forming coordination compounds with most monovalent, divalent, trivalent and tetravalent metal ions. It contains 4 carboxylic acid and 2 tertiary amine groups that can participate in acid-base reactions as shown in the Figure 5 EDTA loses its hydrogen molecules forming carboxylic groups with negative charges which are the major force that bind to positively charged ions covalently. (<http://en.wikipedia.org/wiki/EDTA>)

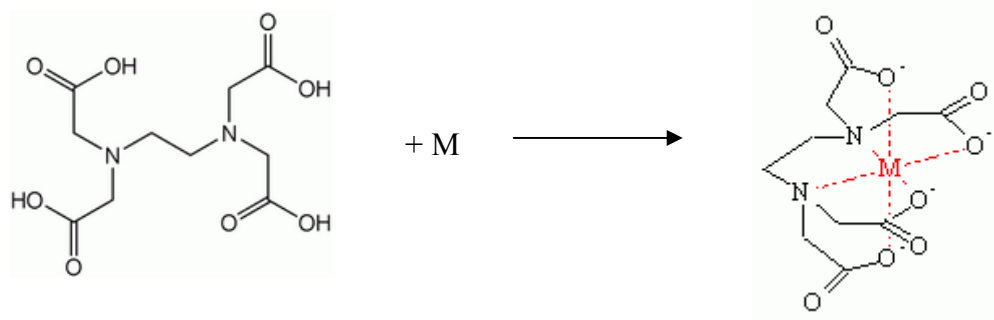
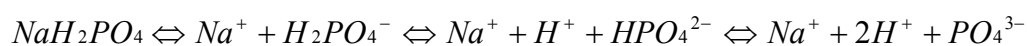


Figure 5 The formation of metal-EDTA complex

3.4.2 NaH_2PO_4

Sodium dihydrogen phosphate, NaH_2PO_4 is easily ionized to H_2PO_4^- and Na^+ in the solution. H_2PO_4^- also can be ionized to HPO_4^{2-} and PO_4^{3-} anions which are capable of chelating with cations. The chemical equilibriums are shown below:



These anions of the phosphates then are capable of reacting with metal ions.

3.4.3 Humic acid

A substantial fraction of the mass of the humic acid is in carboxylic acid functional groups, which endow these molecules with the ability to chelate positively charged multivalent ions. This chelation of ions is probably the most important role of humic acids with respect to living systems (Craig Bingman, 1996 <http://www.thekrib.com/Chemistry/humic.html>).

4. Methodology

4.1 Beaker experiments

4.1.1 Preparation of samplers

All parts of the passive sampler except filter and receiving phase were rinsed in 3M nitric acid solution in order to remove metals attaching on the surface of the sampler body. Receiving membranes were activated follow the product instruction. The membranes were placed on a filter holder of a vacuum and wetted with 20ml MilliQ water, washing with 20ml 3M nitric acid rinsing the samplers before applying 50ml 0.1 ammonium acetate to activate the samplers. The samplers were ready to be assembled after washing several times with MilliQ water. After this disk conditioning and extraction, the membranes were assembled in the passive sampler devices with filters, either one layer or two. Filters are made from two different materials. Supor-450 is made from polysulphone. CA-ME is made from cellulose acetate mixed with esters. They both have a pore size of 0.45 μm .

4.1.2 Experiments

In all beaker experiments, samplers were exposed in PE plastic beakers without metal particles in contact with the solution. Sodium nitrate was used in all experiments to provide an equal strength electrolyte. The final concentration of sodium nitrate is 0.01M. It was selected because none of its ionic species interact with the metal ions of interest. Metal ions were added to the solutions using dilute ICP-MS certified standard solutions and pH was kept close to 7 at all times. PTFE coated metal rods were used to stir the water samples at a speed of 300rpm. The rotation provides a well defined concentration boundary layer outside the diffusion limiting porous membrane. The experiment setups were shown in the Table 1 below:

Table 1 Experiment setups. In all experiments $10 \mu\text{g L}^{-1}$ of 23 elements[#] in 0.01 M NaNO_3 at pH 7.0 and vigorous stirring (300rpm) was used unless otherwise stated.

		Beaker 1	Beaker 2	Beaker 3	Beaker 4
		Single layer filter (Supor-450)	Double layer filter (Supor-450)	Single layer filter (CE-ME)	Double layer filter (CE-ME)
I	Lability test	-	-	-	-
II	Lability test	0.1 μM EDTA	0.1 μM EDTA	0.1 μM EDTA	0.1 μM EDTA

III	Lability test	0.1 M NaH ₂ PO ₄	0.1 M NaH ₂ PO ₄	0.1 M NaH ₂ PO ₄	0.1 M NaH ₂ PO ₄
IV	Lability test	10 ug/l Humic Acid	10 ug/l Humic Acid	10 ug/l Humic Acid	10 ug/l Humic Acid
V	Repeatability	Single DLM (CE-ME)with 5mg/l DOC	Double DLM (CE-ME)with 5mg/l DOC	Single DLM (CE-ME)with 5mg/l DOC	Double DLM (CE-ME)with 5mg/l DOC

[#]: 23 elements are Ag Al Ba Bi Ca Cd Co Cr Cu Fe Ga In K Li Mg Mn Na Ni Pb Sr Tl Zn

Water samples were taken from the beakers at different time intervals and analyzed subsequently by ICP-MS. At the end of each beaker experiment (about 3 exposure days), samplers were extracted with 3M nitric acid overnight and then diluted for further instrumental analysis.

4.2 Simulating experiment of fresh water

The sythetic freshwater medium was made for the simulation experiment. The composition of the artificial freshwater is shown in Table 2. In total, 12 passive samplers were prepared, followed the method described in previous section. In these 12 samplers, half of them were single layer CA-ME filter while the other half were double layers. All samplers with both single and double layers filters were exposed in the synthetic freshwater medium with a sustainably stable ions concentration. The speed of water flow is 120ml/hour. After 7 days exposure, 3 of the single layer and 3 of the double layers samplers were removed. The rest of the samplers were brought out after another 7 days period. The receiving membrane dismantaled from these samplers were then extracted as soon as leaving the aquatic environment. For determination of average concentration of total metals the water samples were taken each working day for ICP-MS analysis.

Table 2 The composition of sythetic freshwater medium

Compounds		S1		S2	S3		Humic acid	23 [#] elements
		MgCl ₂ •6H ₂ O	CaCl ₂	CaCO ₃	NaSO ₄	NaHCO ₃		
Concentration(mg/l)		12.168	8.838	85	16.334	3.356	26.15	10*10 ⁻³
Ion conc. in final solution	C ^{z+} (mg/l)	1.458	3.206	6.814	5.288	0.916	—	—
	A ^{z-} (mg/l)	4.254	5.672	10.201	11.046	2.44	—	—

[#]: 23 elements are Ag Al Ba Bi Ca Cd Co Cr Cu Fe Ga In K Li Mg Mn Na Ni Pb Sr Tl Zn

4.3 ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) analysis

As the state-of-the art technique, ICP-MS is using for bulk elemental and/or isotopic analysis of liquids or soluble organic and inorganic materials. It is a comprehensive technique which is able to analyze most elements from lithium through uranium. It is an extremely sensitive technique with detection limits in the parts per trillion (ppt) range for many elements in aqueous solutions. Its high level of relative accuracy (1 to 2%) coupled with its sensitivity allows the analyst to cover more than nine orders of magnitude in concentration. The advantages of ICPMS include elemental and isotopic analysis for majors, minors, trace and ultra-trace impurities. This has eliminated the need to use several techniques to obtain a complete analysis. (<http://www.northernanalytical.com/tech1.htm>)

During the ICP-MS analysis, the sample is atomized, dissolved, and introduced into an extremely high temperature (6,000 to 10,000 °C) radio frequency induced argon plasma. The plume of the argon plasma is then sampled directly into the entrance orifice of a quadrupole mass spectrometer. Analyte ions produced by the plasma are accelerated, magnetically separated and counted using an electron multiplier, and give the concentration of metallic pollutants.

Due to its properties of multielements analysis and excellent selectivity and sensitivity, ICP-MS was used to analyze the water samples taken from each experiment.

5. Result and Discussion

The data obtained from the ICP-MS analysis of the beaker experiments and simulating freshwater experiment has shown very interesting results. Given that the results are complex, it will be present in several separate sections.

5.1 Water samples of beaker experiments

In the beaker experiments, different ligands were applied and variety behaviors of metals were observed. The concentrations of the selected metals in water samples were plotted with sampling time, as shown in the Figure 6.

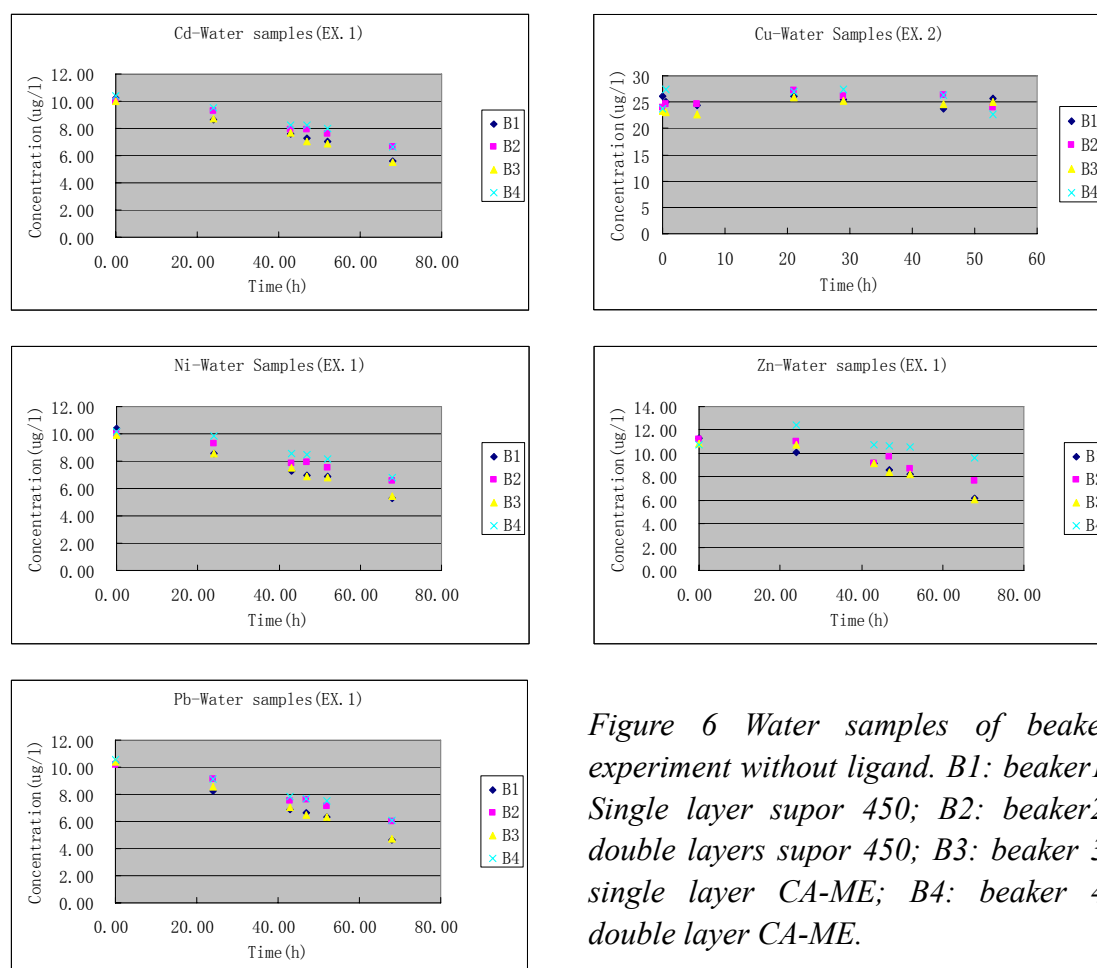
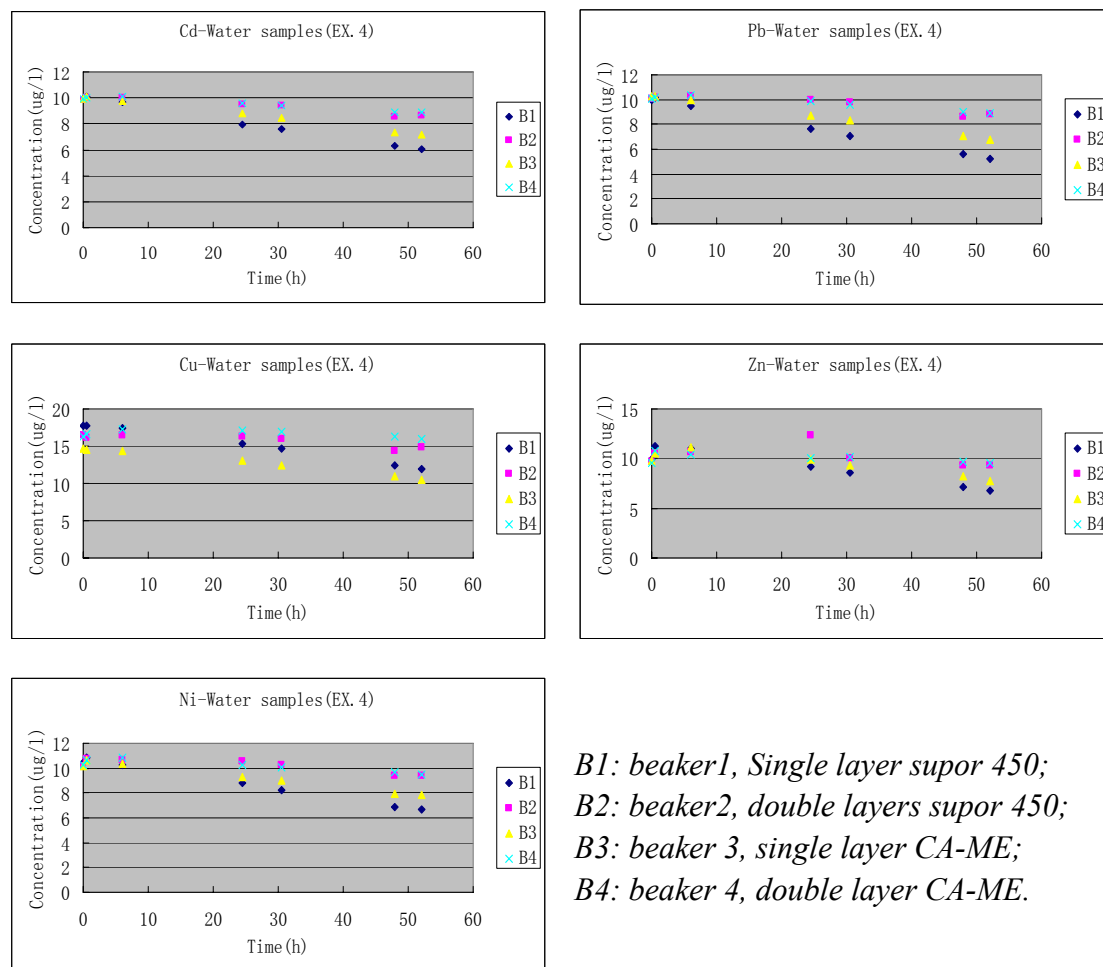


Figure 6 Water samples of beaker experiment without ligand. B1: beaker1, Single layer supor 450; B2: beaker2, double layers supor 450; B3: beaker 3, single layer CA-ME; B4: beaker 4, double layer CA-ME.

It is obviously indicated in the fig.6 that the concentrations of all metals in water samples are decreasing with the passage of time. Both of beaker1 and beaker3 are subjected to a faster decrease than beaker 2 and 4. That is because in beaker 1 and 3, there is only one layer of filter between the water and receiving membrane. In beaker 2 and 4 the layers are two. As the solute concentration is reversely proportional to the thickness of the filter, it takes more time for these metal ions to diffuse through the

filter onto the chemcatchers in beaker 2 and beaker 4.

Different ligands were also applied in the experiments. They are 0.1 μM EDTA, 0.01M NaH_2PO_4 and two different amount of humic acid. Here takes humic acid for example (see Figure 7).



*B1: beaker1, Single layer supor 450;
 B2: beaker2, double layers supor 450;
 B3: beaker 3, single layer CA-ME;
 B4: beaker 4, double layer CA-ME.*

Figure 7 Water samples of beaker experiment with 10 $\mu\text{g/l}$ humic acid as ligand.

Figure 7 is the water samples of beaker experiment with 10 $\mu\text{g/l}$ humic acid as ligand. It explicitly shows the consistent trend with experiment 1 in which no ligand was added in the experiment. The metals concentrations drop faster in beaker 1 and 3 than in 2 and 4. The only difference is that for the single layer of filter of supor 450 dropped faster than single layer CA-Me except copper. The same trend also could be found in the experiment with ligand EDTA. However, the experiment results of Na_2HPO_4 additives were different from others. The concentrations of metal copper, nickel, lead and zinc exhibit different behaviors (see Figure 8). The metal contents in water dropped faster in beaker 2 which has two layers filter than beaker 3 which has only one layer of filter.

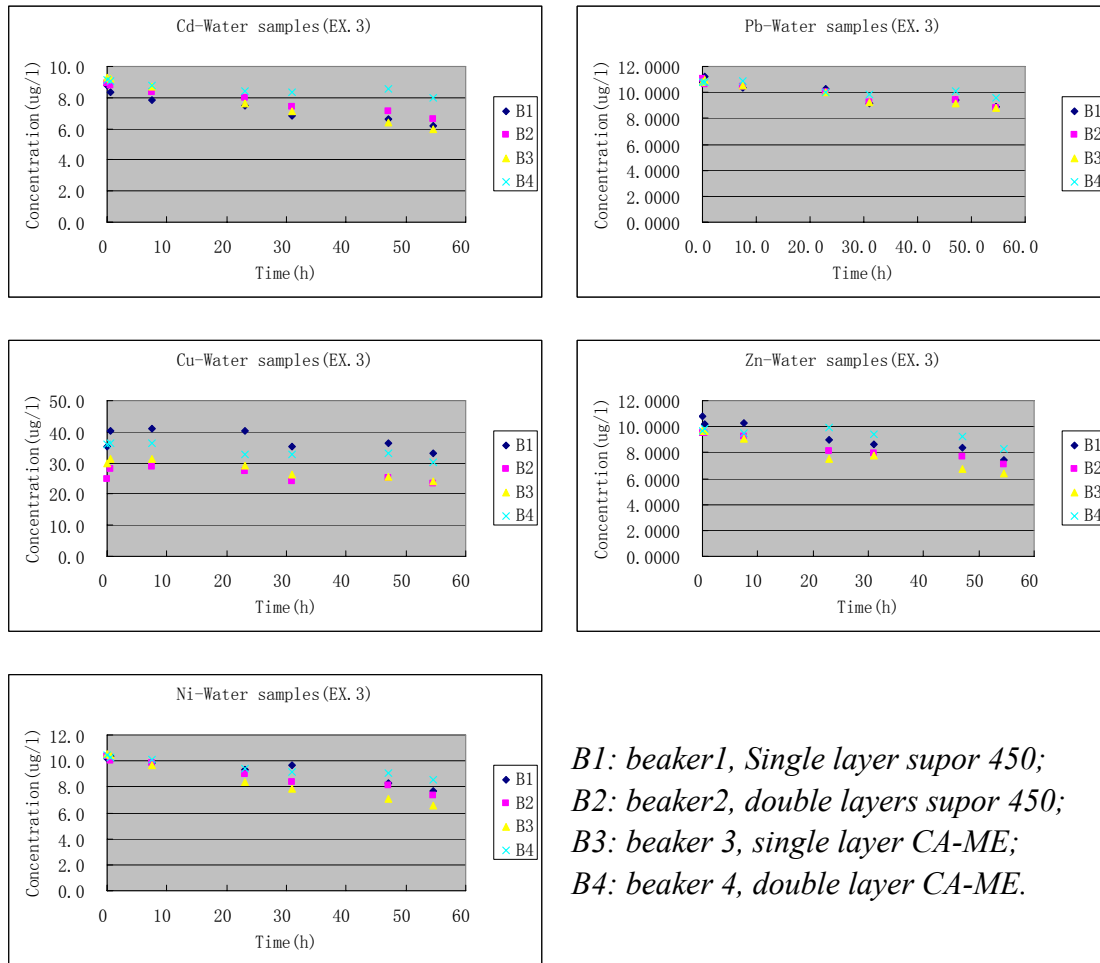


Figure 8 Water samples of beaker experiment with 0.01M NaH₂PO₄ as ligand.

For copper, the differences in final concentrations and original samples, ΔC , in beakers 1, 2, 3 and 4 are 2.0010 $\mu\text{g/l}$, 1.4810 $\mu\text{g/l}$, 5.6010 $\mu\text{g/l}$ and 5.5410 $\mu\text{g/l}$, respectively. The differences are higher in single layer filter compared with double layers with the same material, either supor-450 or CA-ME. But the differences in supo-450 beakers are much higher than the CA-ME beaker. This might suggest diverse diffusive mechanisms under the condition of different filter and need to be further investigated.

For all the plotting figures of beaker experiments, see appendix 1.

5.2 Labile metal ions in the presence of ligands

The bulk removal theory was described in the section 3.3. The first-order rate law finally was given as equation (12)

$$\text{Ln}\left(\frac{C_b}{C_{b0}}\right) = -kt \quad (12)$$

The water samples in the beaker experiments were taken with time intervals which

means the original concentration and bulk concentration of analytes and time were known. The uptake rate constant, k was then calculated (see Figure 9).

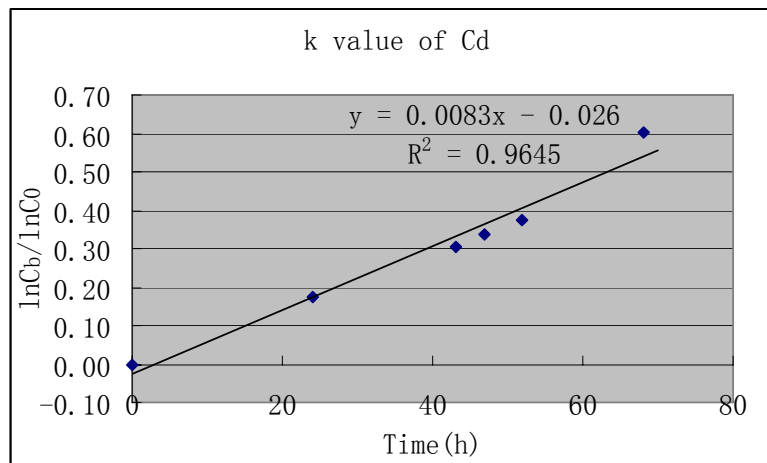


Figure 9 The example of k value calculation

In the experiments, each analyte in all beakers has a fixed k value. The Table 3 shows the k values of experiment 1:

Table 3 k values of experiment 1 (no ligand)

Analytes	Cd	Cu	Ni	Pb	Zn
k(Beaker1)	8.337	9.761	9.316	11.073	8.166
k(Beaker2)	6.057	6.226	6.205	7.709	5.674
k(Beaker3)	8.464	8.621	8.603	11.133	8.099
k(Beaker4)	6.341	4.352	5.639	7.774	1.971

Since there is no extra ligand added in experiment 1, all the metals in beakers were considered as free ions and can be 100% taken by passive samplers without chelating. Therefore, these k values were used to numerically estimate the free fractions of metals in water sample. Assume there are free fraction of metals and fraction which is chelated by ligands that gives equation (13):

$$C_b = C_{bo}\psi_{cc}e^{-kt} + C_{bo}(1 - \psi_{cc}) \quad (13)$$

where C_{bo} , C_b , k and t refer to the same as described previously, ψ_{cc} is the percentage of free fraction of metals in water samples. Notably this is a simplified model. The change of speciation because of metal concentration decrease was not taken into account. The metal fraction chelating with ligands was assumed unchanged with time.

It is a double-step process to make the numerical calculation of k values, first the C_b and then k values. In the beaker experiments with ligands in them the bulk concentrations, C_b were calculated with time from 0 to 60 hours for each postulated ψ_{cc} values, 100%, 95%, 90% until 0 with the k values obtained from experiment 1 (no ligand). The starting concentration of metal ions was 10ug/l. These known postulated parameters were then operated in equation (12). Therefore a set of C_b data for each metal ion in each beaker was obtained. These C_b data was then used to calculate the k values following the method described at the beginning of this section. Eventually, these would lead to achievement of a series of functions of line with percentages as

x-axis and k values as y-axis. For example, beaker 1 of experiment 1 have functions $y=8.282x$, $y=9.674x$, $y=9.240x$, $y=10.946x$ and $y=8.115x$ (shown in Figure 10) for Cd, Cu, Ni, Pb and Zn, respectively.

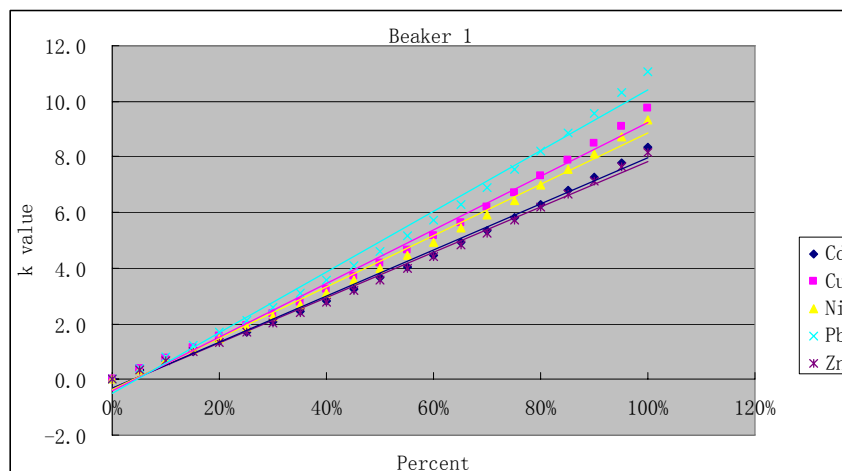


Figure 10 Calculation of k values for beaker 1

These functions were used to calculate the free metal fractions for each of the experiments. Each k value corresponds to a percentage value. This percentage value is the free fraction value of the corresponding metal ion. All details about calculations could be found in the appendix II and appendix III.

5.2.1 Labile metals in the presence of 0.1 uM EDTA

In our beaker experiment, a concentration of 0.1 uM EDTA was added. The free fractions of metals in different beakers were shown Figure 11.

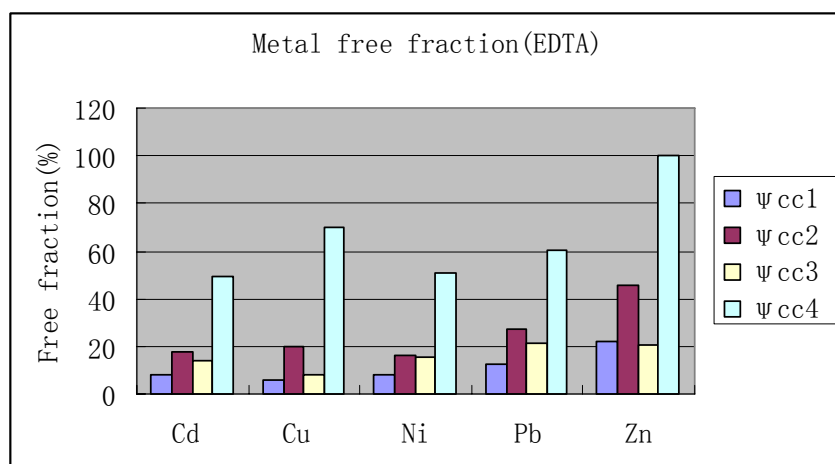


Figure 11 Metal free fractions in EDTA beaker experiment; ψ_{cc1} : ψ_{cc} of beaker 1; ψ_{cc2} : ψ_{cc} of beaker 2; ψ_{cc3} : ψ_{cc} of beaker 3; ψ_{cc4} : ψ_{cc} of beaker 4.

The set up of passive samplers in beakers were single layer supor-450 filter, double layers supor-450 filter, single layer CA-ME filter and double layers CA-ME filter for Beaker 1, 2, 3 and 4, respectively. It is clearly indicated in the figure that the values of

free fractions of metals are much higher in the beaker 4, with double layers of CA-ME filter and higher in beaker 2 with double layers of supor-450 filter for all metals. That is because the molecules take more time to diffuse through the double layers filter than that of single one. The appropriate time of exposure will be discussed in later section. Regarding the different filters, the result indicates that there are more free metals in the beakers with CA-ME as filter than supor-450. This suggests that the interactions between metal ions and filter would impose on the uptake rate and it is different between supor-450 filter and CA-ME. In the presence of ligand EDTA, metal ions are more readily diffuse through supor-450 filter.

5.2.2 Labile metal in the presence of 10mM NaH₂PO₄

The proportions of free ions in the presence of 10 mM Sodium dihydrogen phosphate were shown in the Figure 12.

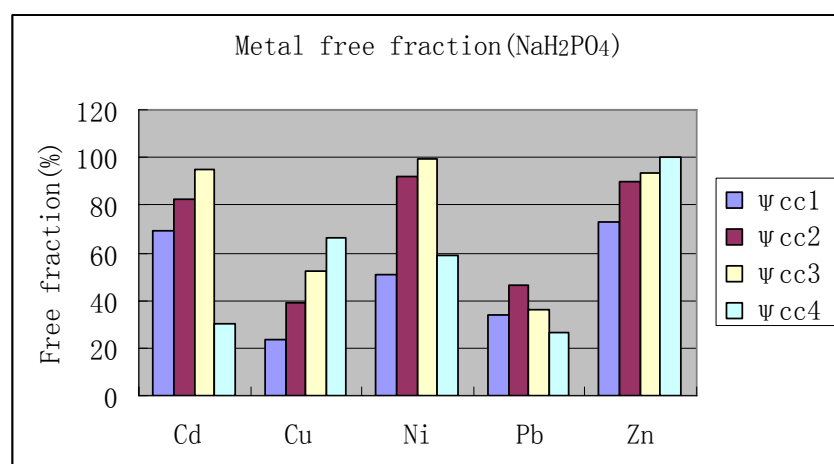


Figure 12 Metal free fractions in NaH₂PO₄ beaker experiment; ψ_{cc1} : ψ_{cc} of beaker 1; ψ_{cc2} : ψ_{cc} of beaker 2; ψ_{cc3} : ψ_{cc} of beaker 3; ψ_{cc4} : ψ_{cc} of beaker 4.

The figure indicates free fractions diverge among diverse metals in the presence of NaH₂PO₄. As a whole, free fraction of cadmium nickel and zinc are high, whereas copper and lead are lower. That is because there are discriminations when phosphate anions bind to metal ions. Some of the bindings for example, bindings with copper and lead are stronger than others. These metal-ligand complexes are stable. Therefore, only a small proportion of these metals are free in the aqueous phase.

Other indication is that beaker 1 and beaker 2 share the same trend except that the free fraction of metal ions in beaker 2 is higher than in beaker 1 for each of the metals. It is quite reasonable because they had different layer number of filter. On average, the metal fractions remain in beaker 3 are much higher than in beaker 1, both of which are single layer samplers. Again, it confirms that metal ions are more readily diffuse through filter supor-450 than CA-ME. One possible explanation is interaction between filter and chelating compounds. The interactions of the compounds are much weaker on the surface of supor-450 filter which is made from polysulphone (beaker 1) than CA-ME. These interactions retard the passive transport of ions from water to

receiving membrane. It takes more time to overcome the force of interaction and get through the filter.

In general, the more filter layers a passive sampler has, the more time it will spend for ions to come through it. Interestingly, labile fraction of cadmium and nickel ions in beaker 3 is much higher than in beaker 4 which has a double layers filter. The abnormal observation needs further experimentation and analysis.

5.2.3 Labile metals in the presence of humic acid

Two beaker experiments were performed with additive of different amount of humic acid. In the first experiment of humic acid, a final concentration of 10ug/l was reached in the water samples. For the other, 13.59mg humic acid was added in 1 l solution. The 13.59mg/l humic acid in water made it a 5mg/l DOC concentration contained in the water sample. The fractions of free ions in the two experiments are shown in Figure 13.

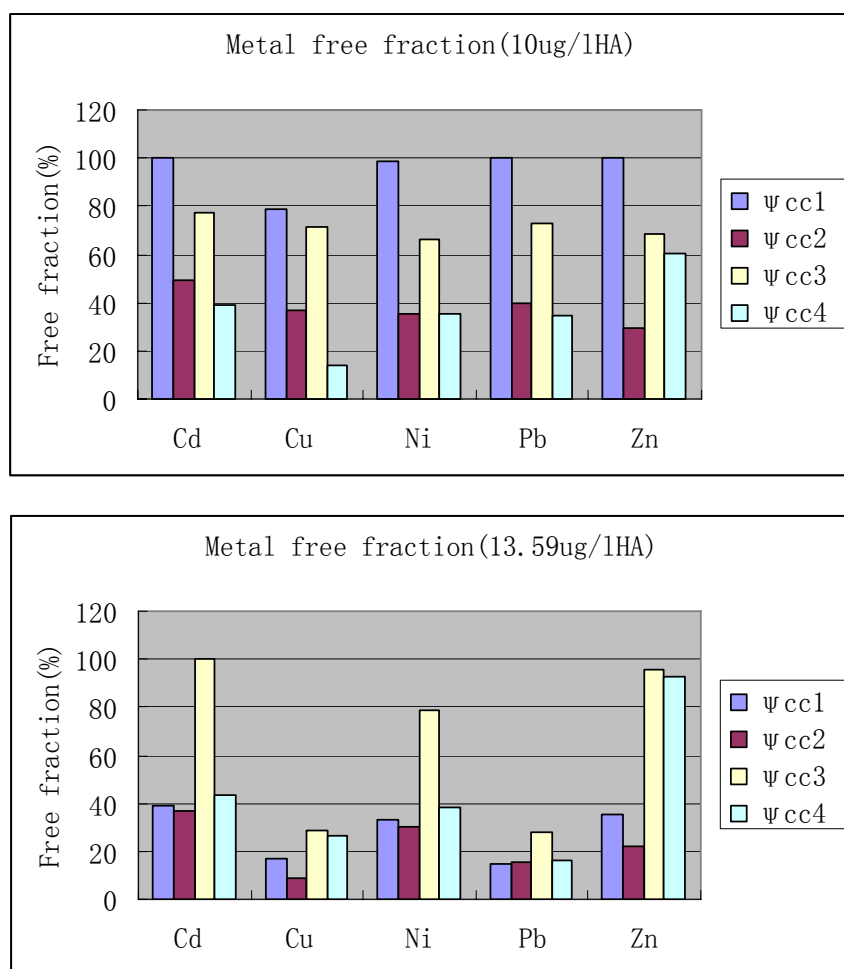


Figure 13 Metal free fractions in humic acid (HA) beaker experiments. The upper panel is 10ug/l humic acid experiment; the panel is 15.59ug/l (5mg/l DOC) humic acid experiment.

In the first experiment of humic acid, metals Cd, Pb and Zn remain intact in beaker 1. They are 100% free. Only a small portion of nickel and copper was

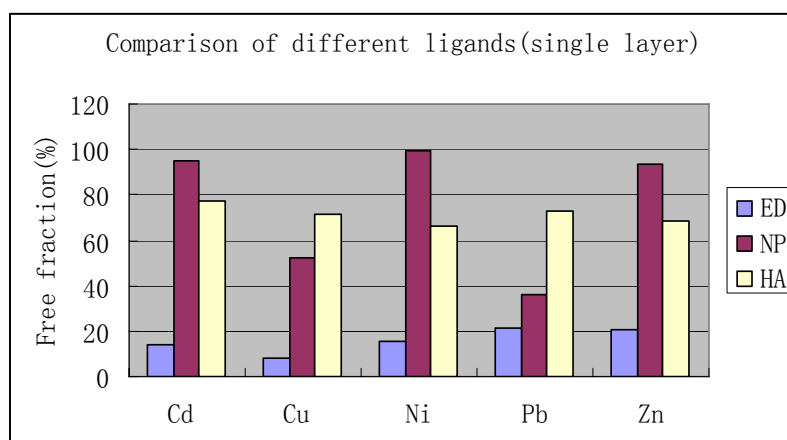
chelating by humic acid and most of them remain unchelated. However, in beaker 2 with double layer supor-450 filter, the concentration of free ions for all metals were decreased dramatically compared with beaker 1. Beaker 3 and beaker 4 have the same tendency with their corresponding coordinates only with a lower value of the free ions. It suggests that the number of layers is the key factor to the availability of the ions in solution.

When the concentration of humic acid was raised to 13.59ug/l in experiment 2, as shown in the lower panel of Fig. 13, large proportions of metal ions were chelated by ligands except for cadmium nickel and zinc in beaker 3 and zinc in beaker 4. The most importance factor is not the layer number of filter but the concentration of the humic acid ligand. Because when much more ligand exists the chelating activities become the dominant factors in determining the labile fraction of metal ions.

Making the comparison, the fraction of free metals dropped remarkably in the second humic acid experiment when raised the ligand concentration although there are some exceptions. This may suggest that there is a transitional ligand concentration between 10-13.59ug/l which makes metal-ligand complexes easily formed. However, the labile fractions of cadmium nickel and zinc in beaker 3 and zinc in beaker 4 actually increased but not decreased. Even surprisingly, 100% of cadmium in beaker 3 is free. To be more surprised the free fractions of metal ions are higher in single layer beakers than in double layers beakers for both of the experiments. These abnormal observations need to be further investigated.

5.2.4 Comparison between different experiments

The data from three experiments are compared. They are EDTA experiment, NaH_2PO_4 experiment and 10mg/l humic acid experiment. The samplers with CA-ME as filters are analyzed because we this kind of filter were utilized for the final stage of the experiments. The comparisons and the orders of metal ions free fraction are shown in the Figure 14 and Table 4.



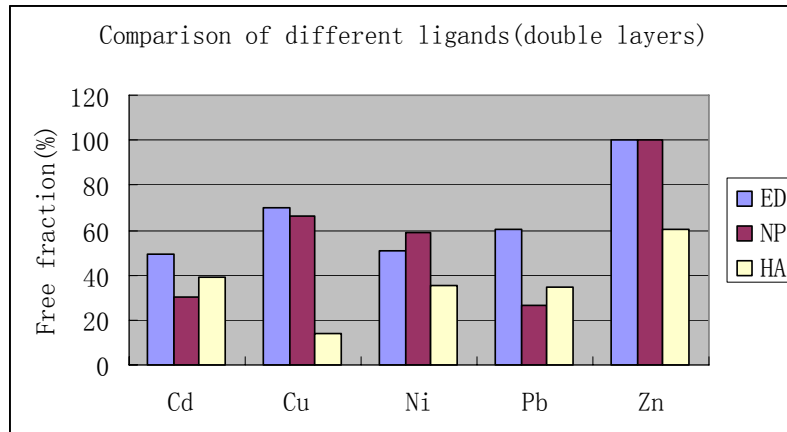


Figure 14 Free fraction comparisons of different beaker experiments. Upper panel single layer comparison; lower panel double layers comparison.

Table 4 Orders of free metal ions fractions

Ψ_{cc}	Cd	Cu	Ni	Pb	Zn
S-layer	NP*>HA*>ED *	HA>NP>E D	NP>HA>E D	HA>NP>E D	NP>HA>E D
D-layer	ED>HA>NP	ED>NP>H A	NP>ED>H A	ED>HA>N P	ED=NP>H A

*: For simplicity, NaH_2PO_4 abbreviates for NP; HA for humic acid; ED for EDTA

In these comparisons the free fractions of all metal ions are least in the beakers with EDTA as ligand for the single layer passive samplers. That means in single layer passive sampler beakers, the fractions of the metals-EDTA complexes are more than other two experiments. It suggests that metals-EDTA complexes are more stable than both of the metals- HPO_4 and metals-HA complexes. But in the experiments with double layer passive sampler, the results are almost reversed. The fractions of metals-EDTA complexes are more for cadmium, copper lead and Zinc than in other two experiments.

According to the equation (8) $M = DC_b t A / \Delta g$, the mass of the metal that diffuse through the filter is proportional to time and reversely proportional to the thickness of the filter. In the left panel of the Figure15 it represents one layer filter. In this circumstance it takes less time for metal ions to diffuse the filter because of the short path of one layer filter. However, when there are two layers of filter more time is needed to pass the way in order to arrive at the receiving membrane as shown in the figure, $t_2 > t_1$. Therefore some other mechanisms take into effects and become significant important factors. One possible explanation is that the exchange of metal ions and metal-ligand complexes. The more time the diffusion takes, the more molecules remain in between the filter. The equilibrium between metal-ligand and metal ions and ligand moves forwards and thus more metal ions get in touch with the receiving membrane. A more detailed description and argumentation could be found in the paper written by Li et al.

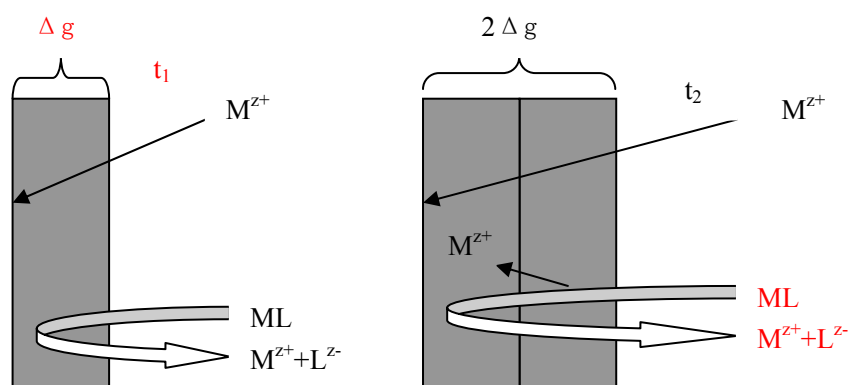


Figure 15 Schematic of diffusive path and exchange of metal-ligand complex and their ions species

5.3 Theoretical calculation of free fractions

The theoretical metal ion fractions with which were not bound by the ligands was calculated using a free of charge software CHEAQS Pro (The software can be downloaded from the website <http://home.tiscali.nl/cheaqs/regdownl.html>), a program for calculating Chemical Equilibrium in Aquatic System. These calculations require a great deal of inputs of known parameters, for instance, concentration of ligands and metal ions, pH of the solution and other ionic species like sodium nitrate. The result is shown in the Table 5, calculating with no ligand, 0.1uM EDTA, 10 mM NaH₂PO₄ and 10mg/l humic acid.

Table 5 Theoretical calculations of labile metals

Free ions	Cd ²⁺ (%)	Cu ²⁺ (%)	Ni ²⁺ (%)	Pb ²⁺ (%)	Zn ²⁺ (%)
No ligand	99.72	96.83	99.68	99.72	96.5
0.1uM EDTA	0.680	0.280	46.550	40.920	1.68
10mM NaH ₂ PO ₄	76.170	15.140	0.930	37.870	63.85
10ug/l Humic acid	95.270	25.600	97.750	98.910	76.82

As clearly shown in Table 5, the labile fractions of all kinds of metal ions in the theoretical calculations are close to 100% free. The consumption of those small proportions of non-free ions may be due to the assumption of absorption by the surface of the experiment devices in the setup of the software. However, in the presence of 0.1uM EDTA most of the metal ions in the water were chelated by the compounds especially for cadmium, copper and zinc. In the presence of 10mM NaH₂PO₄ nickel is the most active ion responding to the phosphate anion and then is the copper and lead. In contrast, cadmium and zinc are now relatively inert. In the

presence of 10ug/l humic acid most of the ions were remaining in water sample except copper ion. About three quarters of the copper ions were chelated. In general, the calculation results indicated that 0.1uM EDTA is the most powerful chelating compound among them following the 10mM NaH₂PO₄ and 10ug/l humic acid in theory.

In order to compare the theoretical results from the calculation and the experimental labile fractions of these ions, both sets of the data were plotted in the diagram as shown in Figure 16. Each dot on the plot is corresponding to a pair of data, one from experiment on x-axes and the other from the CHAEQS Pro outcome on the y-axes.

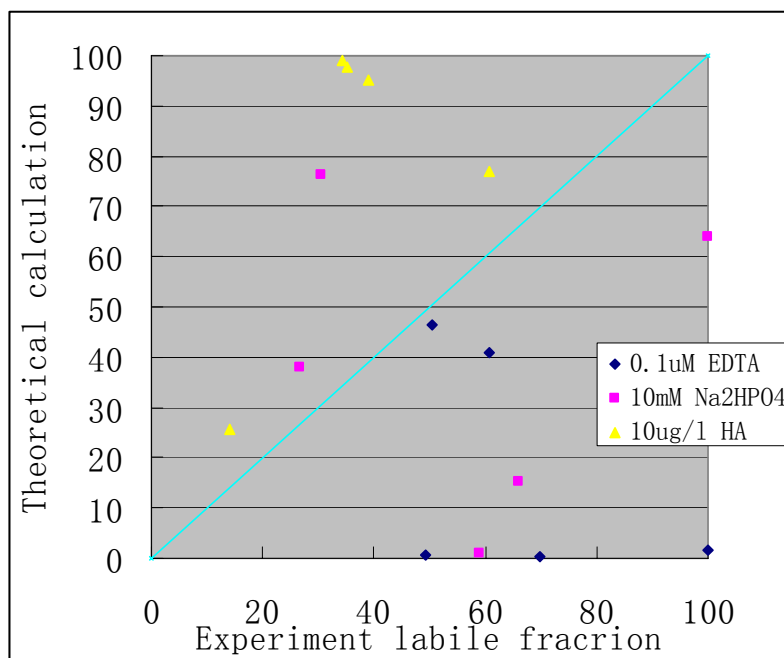


Figure 16 The correlation of experiment labile fractions of ions with calculation in double-layer CA-ME beaker experiments.

The green line is a linear formula of $y=x$. Although the plot data is unevenly distributed on the upper and lower side of the line, it shows the correlation between experimental and theoretical data somehow in the double-layer CA-ME beaker experiment. This similar correlation can also be found in other beaker experiments (see Appendix 6).

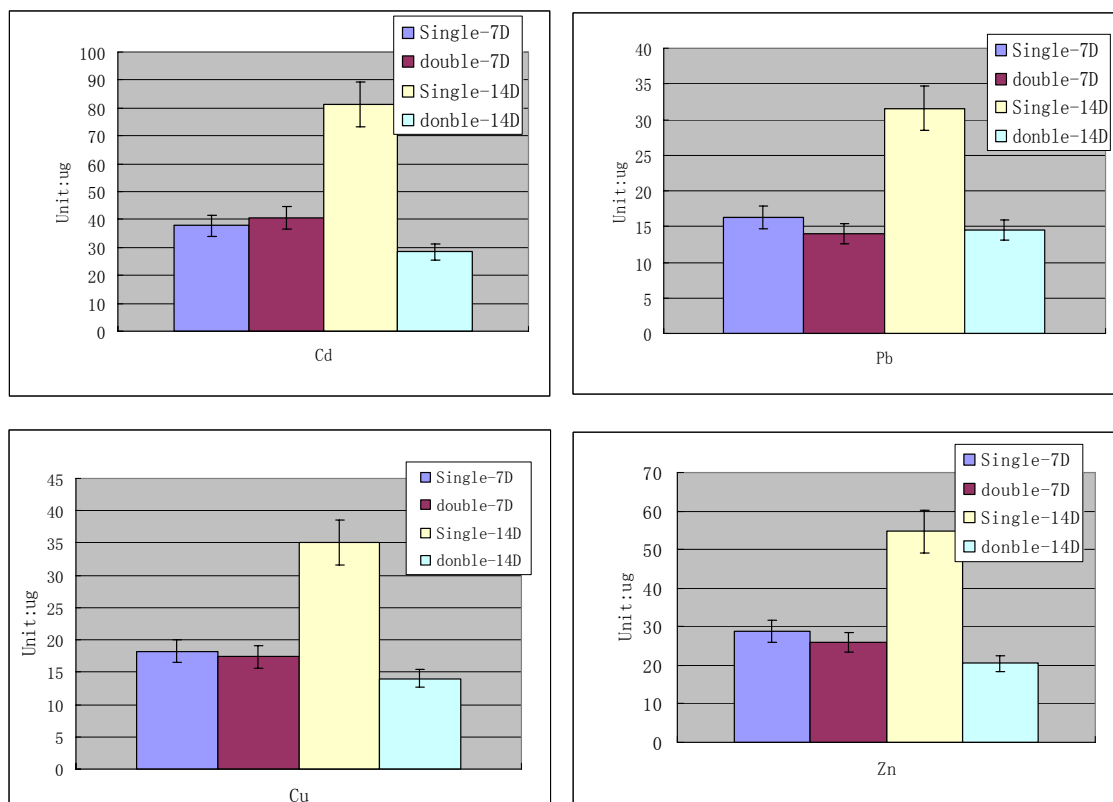
5.4 Exposure in Synthetic Fresh Water Medium

Simulating the exposure in natural water is to take more factors into account to increase the complexity of sampled medium. The contaminants in water were maintained relative constant. A test of passive samplers expose in a stable level of metal ions in water offers a reference of what configuration of the device is suitable for the real natural water and how long the exposure time is needed. The Figure 16 demonstrates result of the passive samplers with either one layer of CA-ME or two and exposure time of 7 days and 14 days. As we can see, for the first 7 days' exposure

the amount of ions that was caught by the chemcatchers with single and double filters was not diverse much, less that 10%. But when the exposure elongated to 14 days, the contaminants caught in the passive samplers with single layer filter was much more that that with double layers filters. And this is true for all the metals.

Now let us make the comparison among different layer samplers with different exposure time. For the single layer samplers, the amount of ions detected caught on the 14 days exposure passive samplers is as much as nearly twice that was on the 7 days exposure samplers for all the analysis metals. Although it is early to conclude that within the 14 days exposure period, the metal ions were caught linearly by the samplers, it is quite obviously that the samplers uptake the contaminants effectively.

Interestingly, the results of double layers samplers are very different. Lead and nickel uptake by the samplers increased slightly and ions cadmium copper and zinc decline a little bit as the elongation of exposure day. These up and down deviations show agreement with the metals concentration changes in the synthetic fresh water. In other word, the uptake equilibriums between the receiving phase and aquatic phase had been reached in a brief time (could be less than 7 days) and shifted with the concentration fluctuation in water. Therefore, the amount of metals caught by the passive samplers fluctuated with time. However, this could suggest that less exposure time is needed for the double layer passive samplers because it might take less than 7 days for these samplers to be saturated.



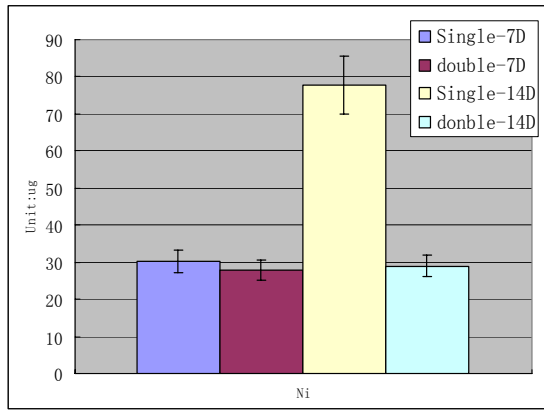


Figure 17 The ions mass caught by passive samplers in the simulation experiment of synthetic fresh water medium

6. Conclusions

Several interesting conclusions can be drawn from the experiment data. The uptake rate is reversely proportional to the thickness of filter. That is the thicker the filter is, the lower uptake rate the passive sampler has. This had been observed in the experiments with ligands EDTA, humic acid and without ligand. However in the beaker experiment with 0.01M NaH_2PO_4 as ligand, different observation had been made. The metal contents in water dropped faster in beaker 2 which has two layer filters than beaker 3 which has only one layer of filter for all the metal ions except cadmium. This also can be concluded that interactions between filter and metal ions vary with the filter materials.

The filter made from polysulphone make the ions diffuse more easily than that of CA-ME filter which is made from cellulose acetate mixed with esters. This conclusion can be found from all experiments or parts of the experiments.

The passive samplers show diverse effectiveness in different circumstances, different ligands, different concentrations of same ligands and the like. In our EDTA, and NaH_2PO_4 (beaker 1 and beaker 2) experiments regular results are obtained. The free metal ions fractions in double layers beakers are higher than in the single layer beakers which are the result we expected. Also, these values are higher in CA-ME beakers than in supor-450 beakers in EDTA experiment. However, in humic acid experiments, the free fractions of metal ions are higher in single layer beakers than in double layers beakers. This is hard to explain and need further investigation.

In comparison of metal ions free fractions values among different experiments with CA-ME as filter, metal-EDTA complex seems much more stable because free metal ions exist in single layer beaker are less with EDTA as ligand. But in the double layer beakers metal-EDTA complex seems fragile. The fractions of free ions are more in EDTA experiment than others. It makes us conclude that there are several factors or mechanisms affecting the uptake of ions. In A condition, X (like number of filter layers) is the major factor in determining the uptake rate while in B condition is others (such as the concentration of ligands).

The theoretical calculations of labile fractions of metal ions by the software CHEAQS show correlation obtained from the practical experiments.

In the simulation experiment, we conclude that 7 days exposure will be enough for the double layers passive samplers. Because there is almost no difference of uptake amount of metals when we include considering the fluctuation of the metal concentrations in synthetic fresh water medium. During this 7 days period, the receiving membrane in the samplers has been saturated and become balancing.

Acknowledgement

I would like to thank my practical supervisor Jesper Knutsson. Without his patience and help, I will not be able to go so far with my thesis. I also would like to thank my parents and their self-giving supports.

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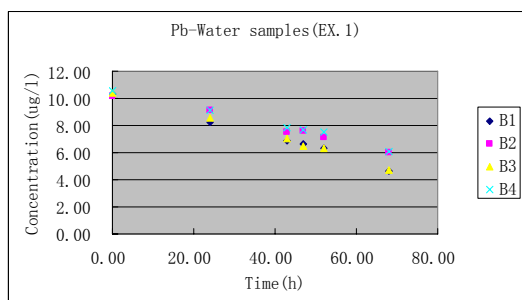
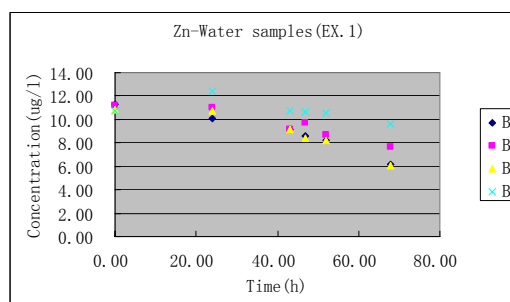
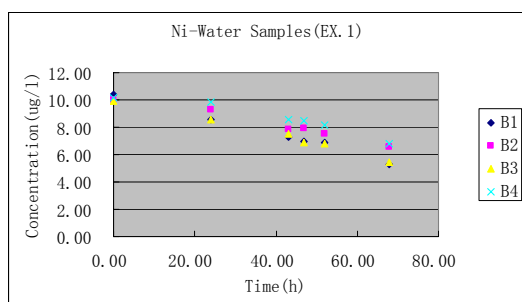
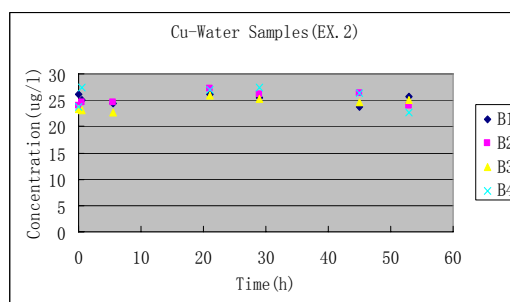
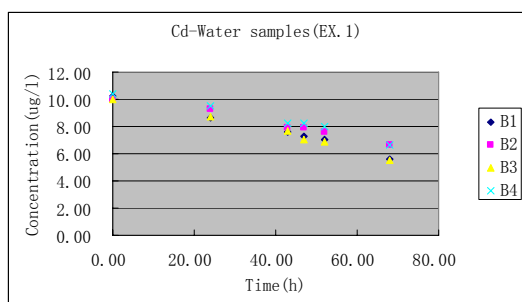
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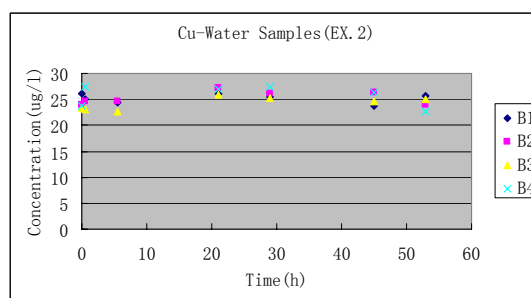
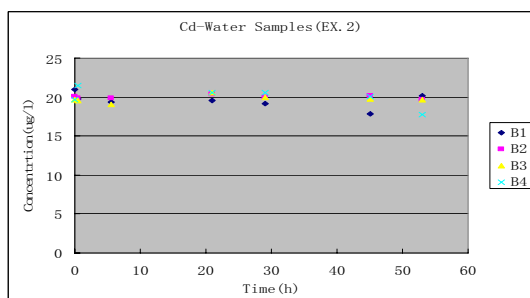
8. Appendices

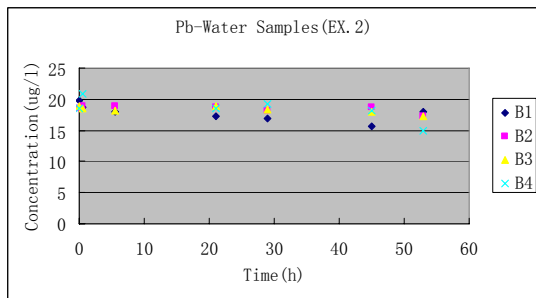
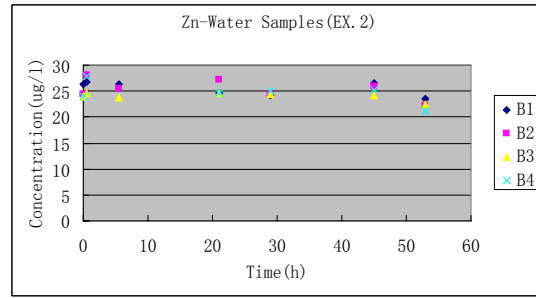
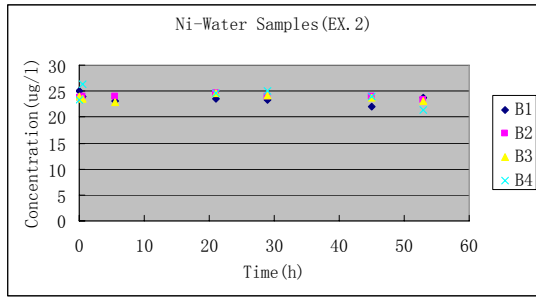
Appendix I Water samples in beaker experiments

Experiment 1 No ligand I

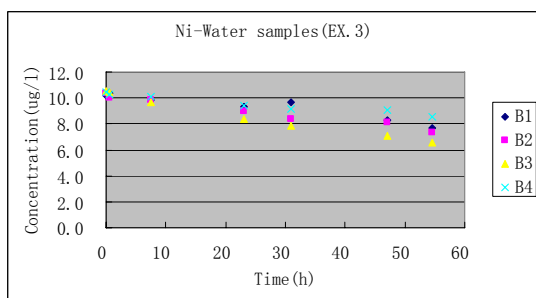
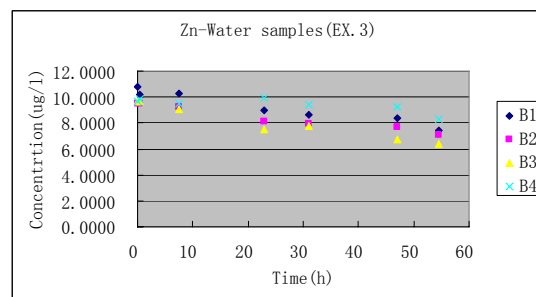
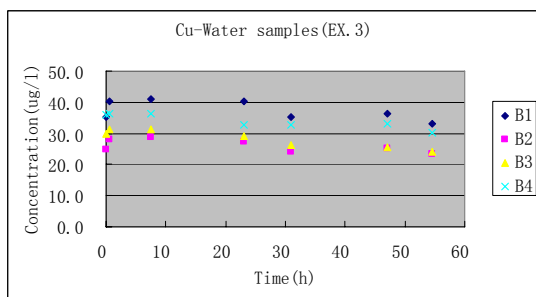
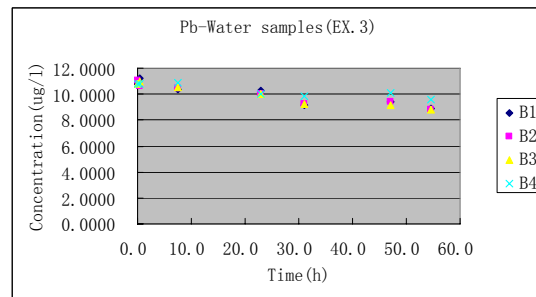
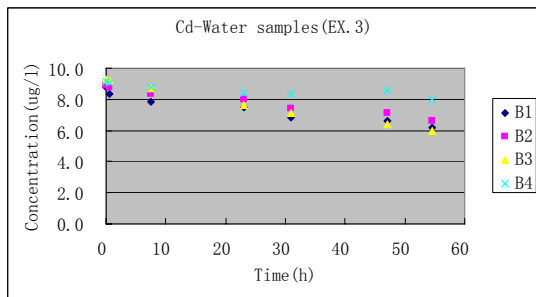


Experiment 2 Ligand 0.1μM EDTA

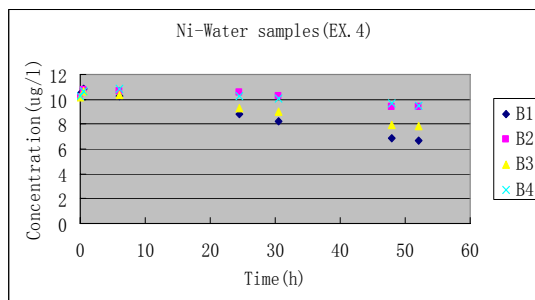
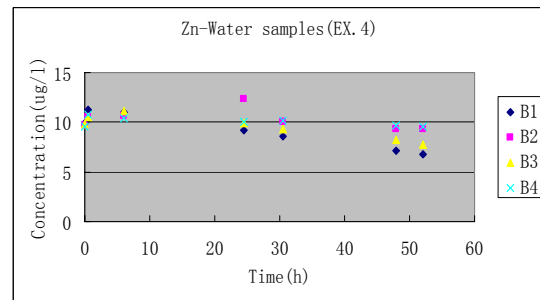
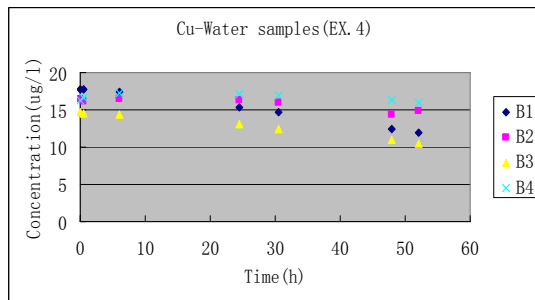
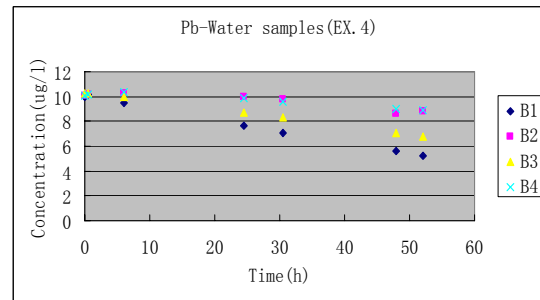
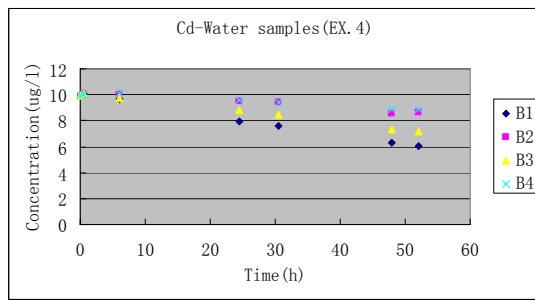




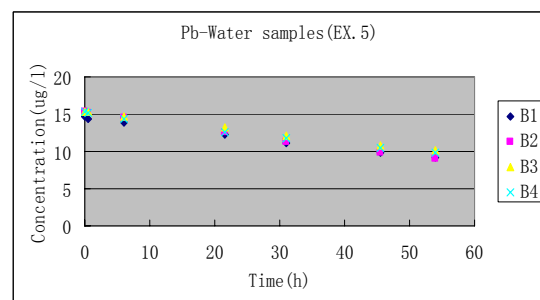
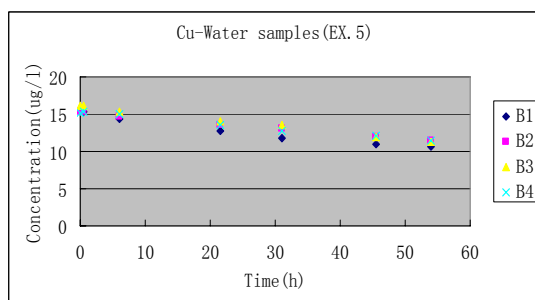
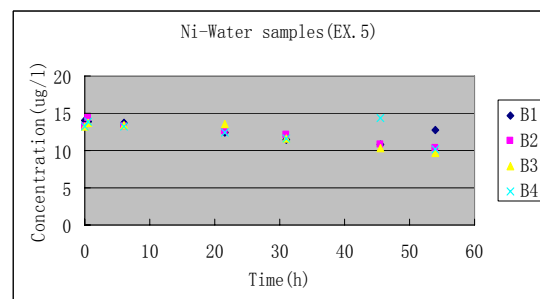
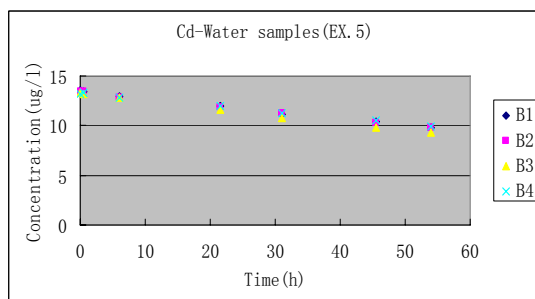
Experiment 3 Ligand 0.01M Na₂HPO₄

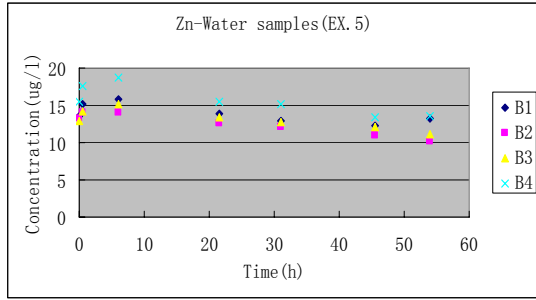


Experiment 4 Ligand 10 μ g/l humic acid

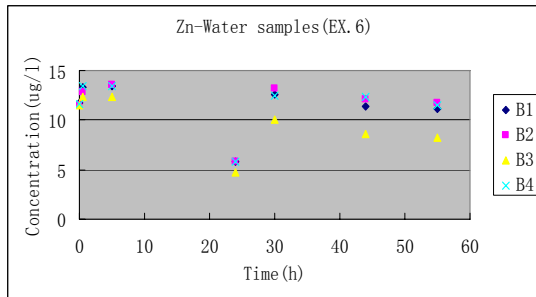
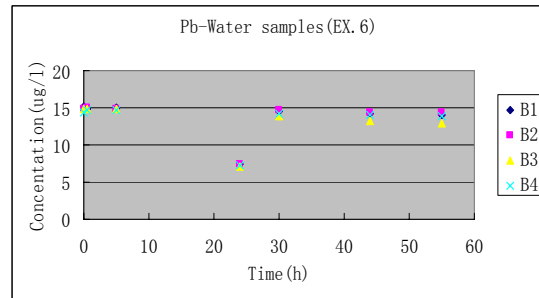
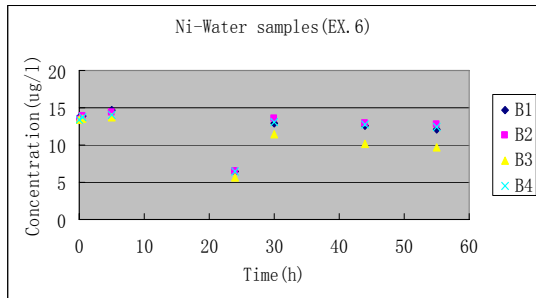
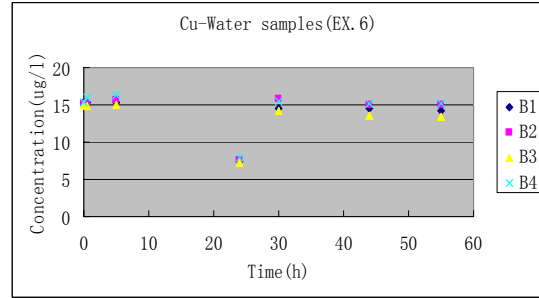
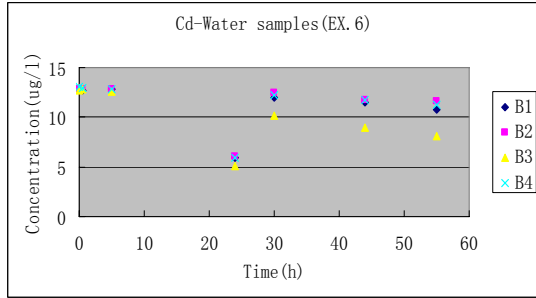


Experiment 5 No ligand II





Experiment 6 Ligand 13.59mg/l humic acid (5mg/l DOC)



Appendix II Both experimental and calculated k values

Experimental k values

Experiment 1

Analytes	Cd	Cu	Ni	Pb	Zn
k(Beaker1)	8.337	9.761	9.316	11.073	8.166
k(Beaker2)	6.057	6.226	6.205	7.709	5.674
k(Beaker3)	8.464	8.621	8.603	11.133	8.099
k(Beaker4)	6.341	4.352	5.639	7.774	1.971

Experiment 2

Analytes	Cd	Cu	Ni	Pb	Zn
k(Beaker1)	0.666	0.579	0.755	1.381	1.772
k(Beaker2)	1.074	1.219	0.994	2.100	2.600
k(Beaker3)	1.190	0.705	1.305	2.367	1.648
k(Beaker4)	3.118	3.033	2.841	4.688	3.799

Experiment 3

Analytes	Cd	Cu	Ni	Pb	Zn
k(Beaker1)	5.745	2.283	4.709	3.714	5.926
k(Beaker2)	4.970	2.402	5.708	3.561	5.074
k(Beaker3)	7.989	4.476	8.512	4.003	7.550
k(Beaker4)	1.919	2.861	3.306	2.064	2.069

Experiment 4

Analytes	Cd	Cu	Ni	Pb	Zn
k(Beaker1)	9.884	7.590	9.099	12.442	8.763
k(Beaker2)	2.960	2.303	2.169	3.049	1.644
k(Beaker3)	6.473	6.119	5.689	8.050	5.529
k(Beaker4)	2.467	0.610	1.980	2.652	1.196

Experiment 5

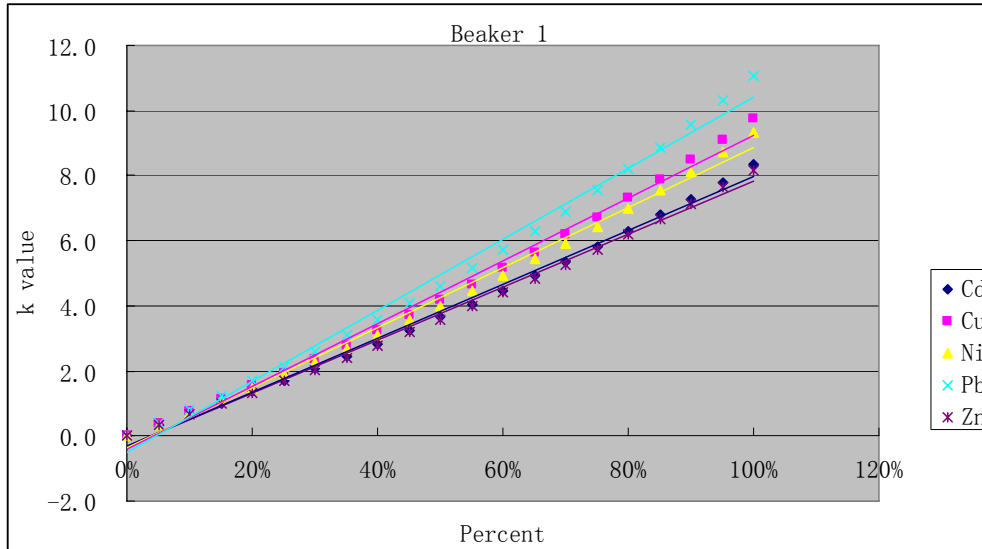
Analytes	Cd	Cu	Ni	Pb	Zn
k(Beaker1)	5.940	6.946	3.438	7.687	2.924
k(Beaker2)	5.814	5.395	5.180	7.983	5.367
k(Beaker3)	6.598	6.441	6.189	9.624	4.751
k(Beaker4)	5.248	5.376	2.935	8.707	3.857

Experiment6

Analytes	Cd	Cu	Ni	Pb	Zn
k(Beaker1)	3.233	1.675	3.088	1.634	2.869
k(Beaker2)	2.215	0.565	1.850	1.164	1.255
k(Beaker3)	8.622	2.442	6.749	3.052	7.675
k(Beaker4)	2.755	1.166	2.151	1.240	1.829

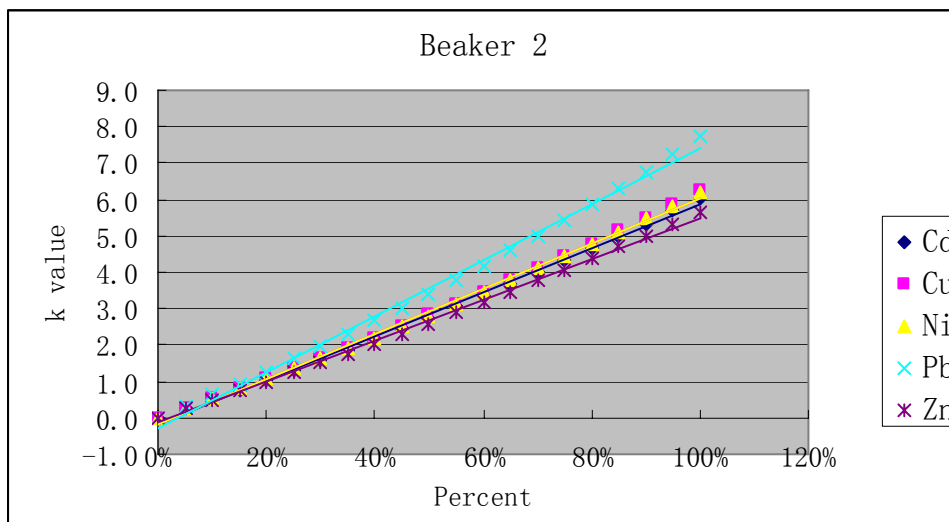
Calculated k values**Beaker 1**

Percent	Cd	Cu	Ni	Pb	Zn
1	8.337	9.761	9.316	11.073	8.166
0.95	7.804	9.110	8.703	10.305	7.647
0.9	7.288	8.483	8.112	9.570	7.143
0.85	6.786	7.879	7.540	8.865	6.654
0.8	6.299	7.295	6.986	8.188	6.178
0.75	5.826	6.730	6.451	7.537	5.716
0.7	5.366	6.184	5.931	6.910	5.266
0.65	4.918	5.655	5.428	6.306	4.828
0.6	4.482	5.142	4.939	5.723	4.401
0.55	4.057	4.645	4.464	5.160	3.985
0.5	3.643	4.162	4.003	4.615	3.579
0.45	3.239	3.694	3.555	4.088	3.183
0.4	2.845	3.238	3.118	3.578	2.796
0.35	2.460	2.795	2.693	3.084	2.418
0.3	2.084	2.364	2.279	2.604	2.050
0.25	1.717	1.945	1.875	2.139	1.689
0.2	1.359	1.536	1.482	1.687	1.336
0.15	1.008	1.137	1.098	1.248	0.991
0.1	0.665	0.749	0.723	0.820	0.654
0.05	0.329	0.370	0.357	0.405	0.324
0	0.000	0.000	0.000	0.000	0.000
slope	8.282	9.674	9.240	10.946	8.115
functions	y=8.282x	y=9.674x	y=9.240x	y=10.946x	y=8.115x

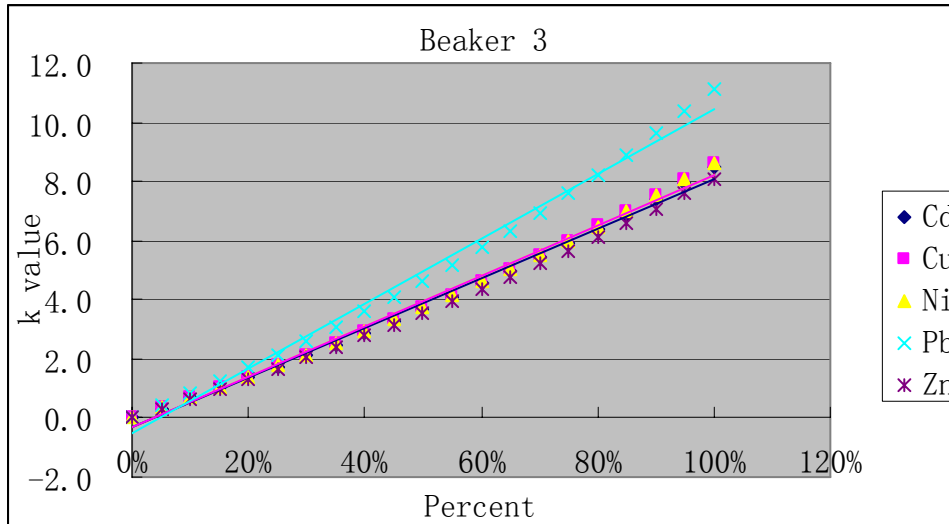


Beaker 2

Percent	Cd	Cu	Ni	Pb	Zn
1	6.057	6.226	6.205	7.709	5.674
0.95	5.695	5.852	5.833	7.226	5.339
0.9	5.341	5.487	5.469	6.756	5.011
0.85	4.995	5.129	5.112	6.298	4.688
0.8	4.655	4.779	4.763	5.853	4.372
0.75	4.322	4.436	4.421	5.419	4.062
0.7	3.995	4.099	4.086	4.996	3.758
0.65	3.675	3.770	3.758	4.584	3.458
0.6	3.361	3.447	3.436	4.181	3.165
0.55	3.053	3.130	3.120	3.788	2.876
0.5	2.750	2.819	2.810	3.405	2.592
0.45	2.453	2.514	2.506	3.030	2.314
0.4	2.161	2.214	2.208	2.663	2.040
0.35	1.875	1.920	1.914	2.305	1.770
0.3	1.593	1.631	1.627	1.955	1.505
0.25	1.316	1.348	1.344	1.612	1.244
0.2	1.044	1.069	1.066	1.276	0.987
0.15	0.777	0.795	0.792	0.947	0.735
0.1	0.513	0.525	0.524	0.625	0.486
0.05	0.255	0.261	0.260	0.309	0.241
0	0.000	0.000	0.000	0.000	0.000
slope	6.036	6.203	6.182	7.666	5.657
functions	y=6.0360x	y=6.203x	y=6.182x	y=7.666x	y=5.656x

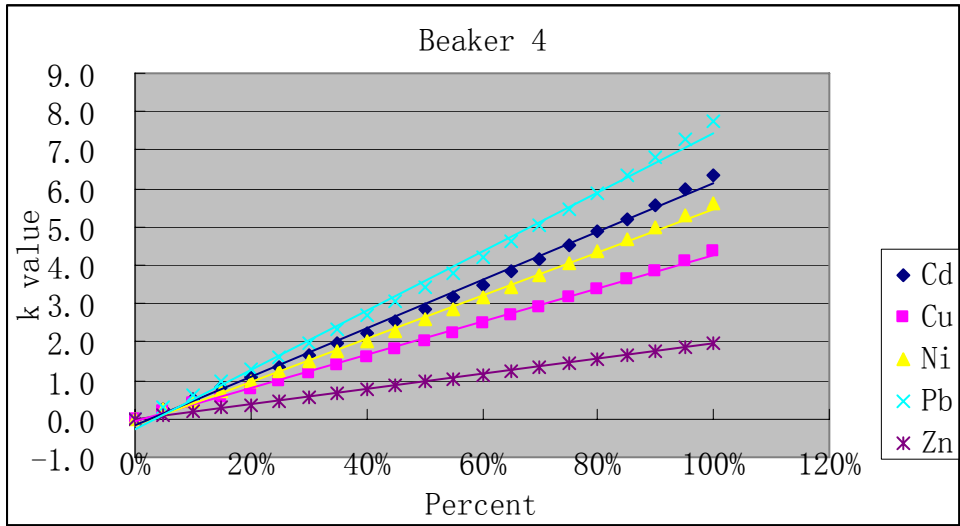


Percent	Cd	Cu	Ni	Pb	Zn
1.00	8.464	8.621	8.603	11.133	8.099
0.95	7.921	8.066	8.049	10.360	7.585
0.90	7.395	7.528	7.512	9.620	7.087
0.85	6.885	7.006	6.992	8.910	6.602
0.80	6.389	6.500	6.487	8.229	6.131
0.75	5.908	6.009	5.997	7.574	5.673
0.70	5.440	5.532	5.521	6.943	5.227
0.65	4.985	5.068	5.058	6.335	4.792
0.60	4.542	4.616	4.608	5.749	4.369
0.55	4.111	4.177	4.169	5.183	3.956
0.50	3.690	3.749	3.742	4.635	3.553
0.45	3.281	3.332	3.326	4.106	3.160
0.40	2.881	2.925	2.920	3.593	2.777
0.35	2.491	2.529	2.525	3.097	2.402
0.30	2.110	2.142	2.138	2.615	2.036
0.25	1.738	1.764	1.761	2.147	1.678
0.20	1.375	1.395	1.393	1.693	1.328
0.15	1.020	1.034	1.033	1.252	0.985
0.10	0.672	0.682	0.681	0.823	0.650
0.05	0.333	0.337	0.337	0.406	0.321
0.00	0.000	0.000	0.000	0.000	0.000
slope	8.407	8.561	8.543	11.004	8.049
functions	y=8.407x	y=8.561x	y=8.543x	y=11.004x	y=8.049x



Beaker 4

Percent	Cd	Cu	Ni	Pb	Zn
1	6.341	4.352	5.639	7.774	1.971
0.95	5.959	4.105	5.306	7.286	1.867
0.9	5.586	3.861	4.980	6.811	1.763
0.85	5.221	3.621	4.660	6.349	1.660
0.8	4.863	3.385	4.346	5.899	1.557
0.75	4.513	3.151	4.038	5.461	1.456
0.7	4.170	2.921	3.736	5.035	1.354
0.65	3.834	2.694	3.439	4.618	1.254
0.6	3.505	2.471	3.147	4.213	1.154
0.55	3.182	2.250	2.860	3.816	1.055
0.5	2.865	2.032	2.578	3.430	0.956
0.45	2.555	1.817	2.301	3.052	0.858
0.4	2.250	1.605	2.028	2.682	0.760
0.35	1.951	1.395	1.760	2.321	0.663
0.3	1.657	1.188	1.497	1.968	0.567
0.25	1.369	0.984	1.237	1.623	0.471
0.2	1.085	0.782	0.982	1.285	0.376
0.15	0.807	0.583	0.731	0.953	0.281
0.1	0.533	0.386	0.483	0.629	0.187
0.05	0.264	0.192	0.240	0.311	0.093
0	0.000	0.000	0.000	0.000	0.000
slope	6.317	4.344	5.622	7.730	1.970
functions	$y=6.317x$	$y=4.344x$	$y=5.622x$	$y=7.730x$	$y=1.970x$



Appendix III Free fraction of metals in water sample

Experiment 2

Analytes	Cd (%)	Cu (%)	Ni (%)	Pb (%)	Zn (%)
Ψ_{cc} (Beaker1)	8.0	6.0	8.2	12.6	21.8
Ψ_{cc} (Beaker2)	13.0	12.6	10.8	19.2	32.0
Ψ_{cc} (Beaker3)	14.4	7.3	14.1	21.6	20.3
Ψ_{cc} (Beaker4)	37.6	31.4	30.7	42.8	46.8

Experiment 3

Analytes	Cd (%)	Cu (%)	Ni (%)	Pb (%)	Zn (%)
Ψ_{cc} (Beaker1)	69.4	23.6	51.0	33.9	73.0
Ψ_{cc} (Beaker2)	60.0	24.8	61.8	32.5	62.5
Ψ_{cc} (Beaker3)	96.5	46.3	92.1	36.6	93.0
Ψ_{cc} (Beaker4)	23.2	29.6	35.8	18.9	25.5

Experiment 4

Analytes	Cd (%)	Cu (%)	Ni (%)	Pb (%)	Zn (%)
Ψ_{cc} (Beaker1)	100.0	78.5	98.5	100.0	100.0
Ψ_{cc} (Beaker2)	35.7	23.8	23.5	27.9	20.3
Ψ_{cc} (Beaker3)	78.2	63.3	61.6	73.5	68.1
Ψ_{cc} (Beaker4)	29.8	6.3	21.4	24.2	14.7

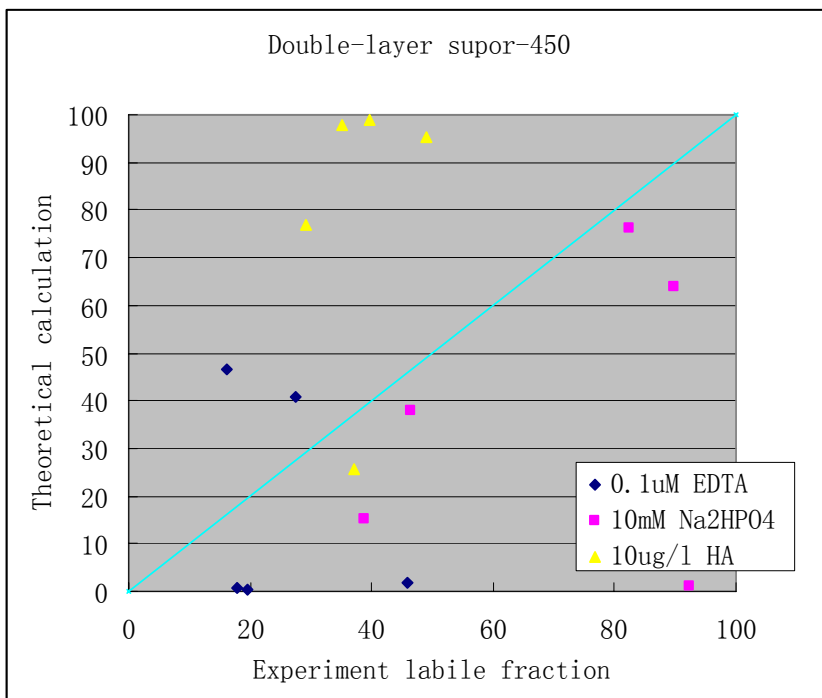
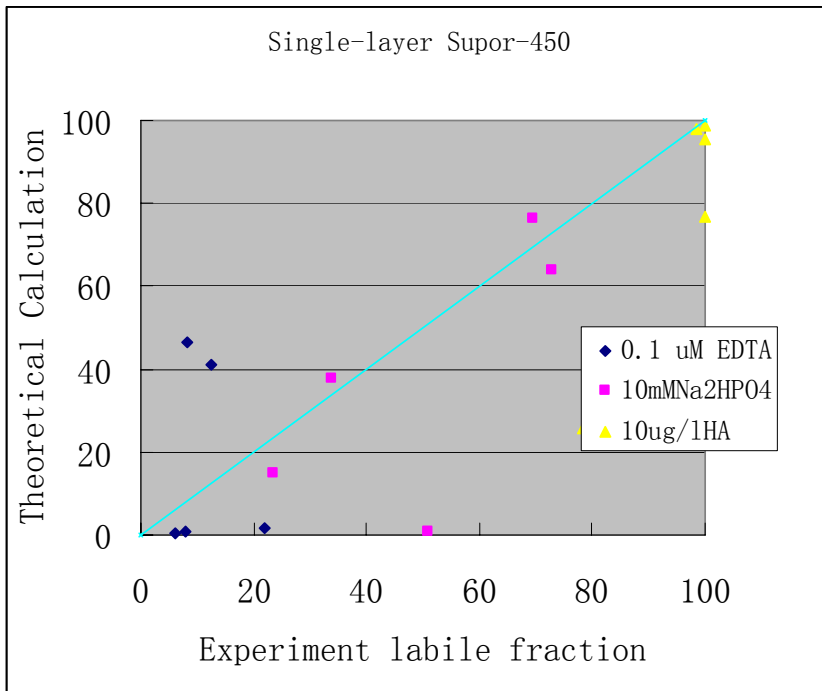
Experiment 5

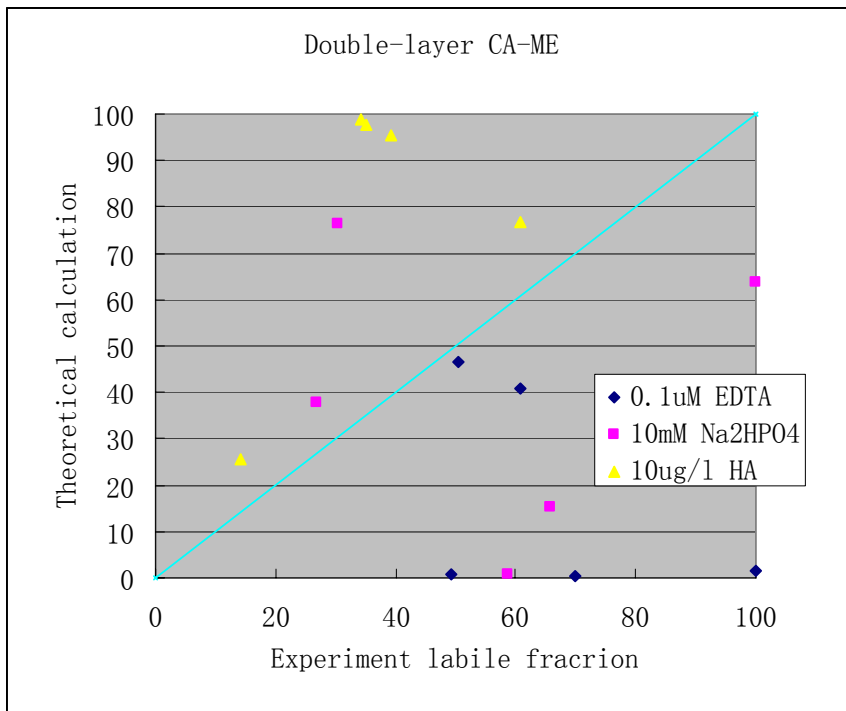
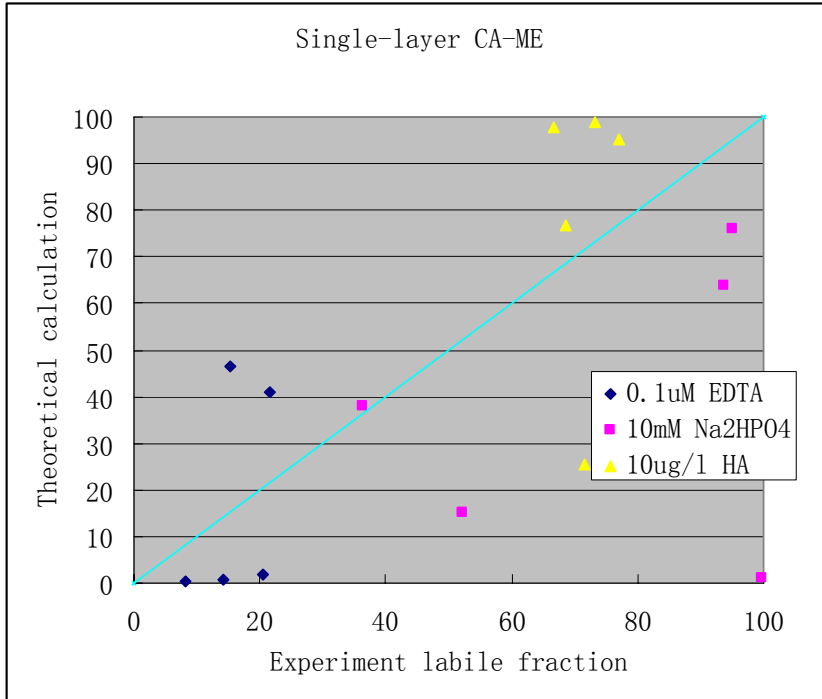
Analytes	Cd (%)	Cu (%)	Ni (%)	Pb (%)	Zn (%)
Ψ_{cc} (Beaker1)	71.7	71.8	37.2	70.2	36.0
Ψ_{cc} (Beaker2)	70.2	55.8	56.1	72.9	66.1
Ψ_{cc} (Beaker3)	79.7	66.6	67.0	87.9	58.5
Ψ_{cc} (Beaker4)	63.4	55.6	31.8	79.5	47.5

Experiment 6

Analytes	Cd (%)	Cu (%)	Ni (%)	Pb (%)	Zn (%)
Ψ_{cc} (Beaker1)	39.0	17.3	33.4	14.9	35.4
Ψ_{cc} (Beaker2)	26.7	5.8	20.0	10.6	15.5
Ψ_{cc} (Beaker3)	100.0	25.2	73.0	27.9	94.6
Ψ_{cc} (Beaker4)	33.3	12.1	23.3	11.3	22.5

Appendix IV Correlation of metal ions labile fractions between theoretical calculations and experiments





Appendix V 7 and 14 days exposure in synthetic fresh water medium

