the 2nd International Conference Proceedings

Transport, Fate and Effects of Silver in the Environment

The University of Wisconsin-Madison
September 11-14, 1994

Editors

Anders W. Andren
University of Wisconsin Sea Grant Institute

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A special thanks to Delphine Skinner for her assistance in helping to organize the conference, to Michael Murray for the scientific transcription, to Gloria Gardner for word processing and to Tina Yao for graphic design.

University of Wisconsin Sea Grant Publication No. WISCU-W-94-002. Publication No. (Library of Congress TD/196/.A52/1994) (National Technology Information Services PB97-133623) (ISBN 0-936287-02-0). This work was funded in part by the University of Wisconsin Sea Grant Institute under grants from the National Sea Grant College Program, National Oceanic & Atmospheric Administration, U.S. Department of Commerce, and from the State of Wisconsin. Federal grant no. NA46RG0481, project A/AS-2.

Sea Grant
University of Wisconsin

printed in the United States of America
First Printing April 1997

TABLE OF CONTENTS

EXTENDED ABSTRACTS

SESSION A: Metal Speciation in Aquatic and Terrestrial Systems

SESSION B: Environmental Cycling of Silver

Session I

Session II

Session III

SESSION C: Toxicity of Metals to Aquatic Organisms

SESSION D: Food Chain Transfer of Metals in the Aquatic and Terrestrial Environment

SESSION E: Environmental Analytical Chemistry of Silver

PANEL DISCUSSION

POSTER SESSION

PARTICIPANTS

Welcome to Madison

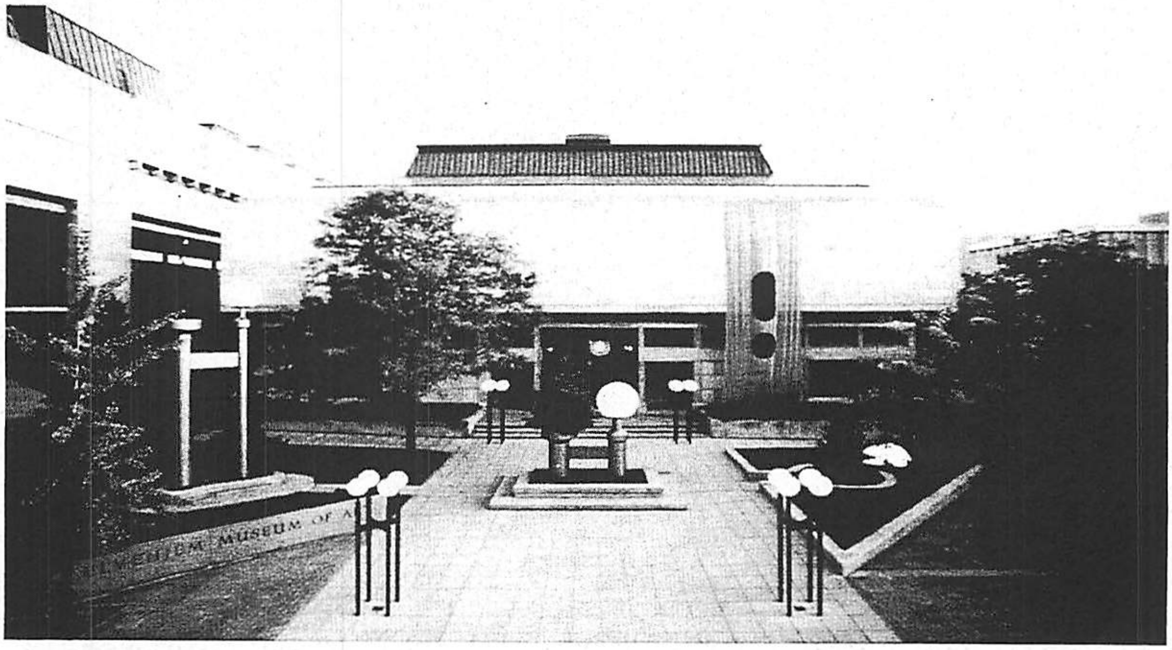

photo / Madison Visitors Bureau

It is a pleasure to welcome you to the University of Wisconsin-Madison. The UW-Madison enjoys a world-class reputation, and those of us associated with it are proud of our accomplishments. We are especially proud of our pioneering efforts in the area of environmental and multidisciplinary research. Although the majority of environmentally related research is carried out in traditional departments, many efforts on the campus are supported and focused in the Center for Limnology, Water Chemistry Program, Environmental Toxicology Program, the Sea Grant Institute and the Institute for Environmental Studies. These programs are all striving to put "The Wisconsin Idea" into action. That is the idea that the university serves as the research arm of the state, and as such we strive to quickly transfer new information and new technologies to a number of user groups. These include federal, state and local governments, industry, advocacy groups and the public.

This conference brings together experts from the international research community to exchange state-of-the-art information on the sources, transport, fate and effects of silver in the environment. The behavior of metals in the environment is certainly not a new issue. However, the first conference on the topic of silver in the environment, held in Madison last year, clearly showed that our information on the behavior of this metal clearly lags far behind our knowledge of other metals, such as mercury, lead and copper. Recent analytical advances in trace metal chemical analyses that use "clean techniques" make this an ideal time to reassess our understanding regarding the environmental cycling and impact of anthropogenic silver.

This conference, then, provides a forum for disseminating up-to-date research results on sources, biogeochemistry, environmental cycling and biological effects of silver in the environment. By synthesizing current knowledge, we hope to more accurately interpret the environmental behavior and potential impacts of silver. We also hope that information presented at this conference will serve to identify future research informational needs.

Again, it is indeed a pleasure to welcome you on behalf of the organizing committee and the UW-Madison. We hope you enjoy both the conference and what Madison has to offer.

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Extended Abstracts

Transport, Fate and Effects of Silver in the Environment

The University of Wisconsin-Madison

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Session A

Metal Speciation in Aquatic and Terrestrial Systems

J.R. Kramer and A.W. Andren
Session Chairs

Examining Trace Metal Complexation by Hydrogen Sulfide Species at Nanomolar Concentrations: New Approaches and Implications for Silver

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The biological and geochemical reactivities of dissolved trace elements are strongly controlled by their chemical speciation, the oxidation states and the ligand-metal complexes in which they are found in solution. While most early speciation studies focused on inorganic complexation, the discovery of organic ligands with very high metal-ligand formation constants has held the interest of environmental chemists since the early 1980's. However, the recent discovery of pico- to nanomolar concentrations of hydrogen sulfide species in oxygenated waters has renewed interest in inorganic complexation. In anoxic waters, reactions with hydrogen sulfide species play a dominant role in metal cycling, but is this the case for oxic waters where both metals and total sulfide are at nanomolar concentrations? While one can approach this problem with multiple equilibrium computer programs, literature values for metal-sulfide formation constants suggest equilibrium behaviors that are at odds with field observations. This has prompted a re-examination of metal-sulfide formation constants at nanomolar concentrations.

The chemical speciation and analytical chemistry of dissolved hydrogen sulfide require a specific nomenclature to avoid confusion. In this work, "free sulfide" is defined as the sum of the uncomplexed hydrogen sulfide species (H_2S_{aq} + HS^- + S^{2-}), "total dissolved sulfide" (TDS) is the sum of the free sulfide and sulfide complexed with metals, and "particulate sulfide" is the sulfide bound in insoluble metal sulfides that are retained on a 0.4 µm filter. Water samples are taken using trace metal-clean Go-Flo sampling bottles, the water is transferred into polyethylene cubitainers using nitrogen pressure and removal of all atmospheric headspace, and samples are returned to the shipboard clean lab for analyses. Total dissolved sulfide is determined using acidification, gas stripping, cryogenic trapping of the evolved H_2S, and quantification using a gas chromatograph with flame photometric detector; the detection limit is 0.2 pmol/L. Free sulfide is determined by injecting a known volume of helium headspace into a cubitainer containing 3 L of sample; the headspace gas is then analyzed for H_2S_g. Knowing the pH, salinity, and temperature of the sample, the concentration of free sulfide can be calculated (see below); the detection limit is 50 pmol/L.

CALCULATION OF FREE (UNCOMPLEXED) SULFIDE

$$S^{-2} + 2H^+ \overset{K_2^*}{\Longleftrightarrow} HS^- + H^+ \overset{K_1^*}{\Longleftrightarrow} H_2S_{aq} \overset{K_d^*}{\Longleftrightarrow} H_2S_g$$

K_1^*, K_2^*, and K_d^* are conditional constants (corrected for temperature and salinity)

$$C_{free} = ([H_2S_g]/\alpha)(K_d^* + V_g/V_{samp})$$

$$\alpha = (1 + K_1^*/[H^+] + K_1^* K_2^*/[H^+]^2)^{-1}$$

To estimate the conditional formation constants for metal sulfide complexes, 30 L of water are collected using trace metal-clean procedures, and 2.5 L of sample are partitioned into clean cubitainers. The cubitainers are amended with different metal concentrations, a known amount of H_2S_g added, and the concentration of H_2S_g (and therefore free sulfide) determined over a period of an hour (to check for slow equilibration). The metal and free sulfide titration data are then used to calculate the conditional formation constants.

CALCULATION OF CONDITIONAL FORMATION CONSTANTS

FOR THE REACTION BETWEEN A FREE METAL AND FREE LIGAND (BISULFIDE):

$$M' + L' \Longleftrightarrow ML$$

$$K_{cond}' = \{ML\}/\{M'\}\{L'\}$$

MASS BALANCES:

$$L_T = ML + L'$$

$$M_T = ML + M'$$

WITH REARRANGEMENT,

$$K_{cond}' = (L_T - L')/(L'(M_T - L_T + L'))$$

ALTERNATIVELY,

$$L'/(L_T - L') = L'/M_T + 1/(K_{cond}'M_T)$$

LINEAR PLOTS OF $L'/(L_T - L')$ VS. L' YIELDS A SLOPE OF $1/M_T$ AND AN INTERCEPT OF $1/(K_{cond}'M_T)$

Subsequently, the redetermined constants are added to the thermodynamic data base for the equilibrium program MINEQL 2.0 and predictions for metal and TDS speciation calculated. An iterative approach is then utilized to see if the model predictions match the field results (e.g., does the predicted concentration of free sulfide match the field data?).

The results to date of our experiments for seawater show that many of the literature constants for metal-sulfide complexes are off by more than 2 orders of magnitude. The metals copper, zinc, nickel, and cadmium appear to play a role in controlling hydrogen sulfide speciation in surface seawater. However, hydrogen sulfide only plays a minor role in controlling their speciation due to picomolar concentrations of TDS. Calculations using existing constants for silver indicate that chloride complexation dominates in seawater, but in freshwater, silver should react with free sulfide to form precipitates and soluble complexes. However, it is clear that the formation constants for metal-sulfide complexes in fresh waters, especially for mercury and silver, need to be redetermined.

Q. KOSTAS DASKALAKIS (NOAA, NOS): You referred to stability constants from recent and earlier work. But these are not experimental constants. They base these constants on linear free energy. Now I want to bring to your attention some work that we did a few years ago with cadmium and zinc and, most recently, in another paper, copper. It's by Richard Thompson. Did you use any of these stability constants?

A. Yes, we did, in that original seawater compilation. That was done. The problem is, when my student went to France, he also took the data disk with him. So I just have those calculations which I show in the table. Yes, they were just using the existing thermodynamic data.

Q. Because I think you have a better chance of explaining, without going back to doing the experiments and getting the stability constants yourself.

A. The experimental work is very close to this, in fact. I would suggest that, actually, Gerson's work was from the dithiozone extraction, so, and I still have a problem even with George's work when you do it at millimolar concentration.

Q. Everybody has a problem with that, but at least I know it works for me.

A. Well, no, I have another way to do it.

Q. George Lunzer is doing it in a different way.

A. George Lunzer is doing it at micromolar levels, and the advantage to his electrochemical method is that he can, as well, get the stoichiometry.

Q. Yes, but he can never say whether this is a real complex or a compound.

KRAMER: I'm going to have to interrupt this. Because I think later on we can all fight over our numbers, but there's one more question.

Q. ARUN MUKHERJEE (Univ. of Helsinki): You maintain that silver in seawater is in the form of chloride. What happens in river water or stream water? Is it in chloride, or carbonate, or something else?

A. Let's see. The first table that I showed suggested, no, that only maybe 15 percent was in chloride, and my calculations, done with the caveat that they're just the literature values that I could dig up very quickly, were that about five percent were complex-insoluble H_2S, with soluble H_2S complexes, and about 50 percent were as a precipitate.

Q. Do you think that chloride complexes both with cadmium and silver in seawater?

A. Oh, yes. I mean the chloride complexation of cadmium is much less.

Q. ANDERS ANDREN (Univ. of Wisconsin): Do we know anything about oxidation kinetics? These sulfides are formed in oxygenated water. Do they oxidize?

A. Yes, they do. The half-life with respect to oxidation by oxygen is about 48 hours. The real problem oxidant is iodate. The existing data for iodate would suggest that the oxidation would give a half-life, with respect to iodate, of about an hour. Now, if that was the case, we'd never be able to measure it. So we believe that the iodate data are incorrect, and we're redoing them. We believe that most of these data are for the free hydrogen sulfide oxidation, and not that with metal. We have samples that have been stored for a year or two, and we still have hydrogen sulfide in them. So I believe that the metal sulfide complexes are more stable.

Photo-Enhanced Sorption of Silver to Bentonite

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The chemical speciation of silver influences its toxicity, bioavailability, solubility and sorption to mineral surfaces. Most of the silver released to surface waters from anthropogenic and natural sources is in the form of Ag(I), and calculations based upon thermodynamic data indicate that Ag(I) will be the dominant oxidation state in aerobic environments (Lindsay and Sadiq, 1978). Based upon these facts, many recent studies of silver toxicity and environmental fate and transport have ignored the possible presence of Ag^o in surface waters. However, as anyone familiar with the principles of black and white photography is aware, many Ag(I) salts readily undergo photochemical reactions which result in the reduction of Ag(I). Results of preliminary experiments in our laboratories indicate that the exposure of Ag(I)-containing solutions to visible light significantly enhances the adsorption of silver to bentonite, possibly through photoreduction of adsorbed Ag(I) at the particle surface.

To understand how photochemical reactions could result in the formation of a thermodynamically unstable species, such as Ag^o, it is instructive to consider the redox reactions of dissolved iron:

$$\mathrm{Fe(III)} + e^- \longleftrightarrow \mathrm{Fe(II)} \qquad E^o = +0.771\ \mathrm{V} \qquad (1)$$

In aerobic environments, the use of thermodynamic data would lead us to predict that Fe(II) will be oxidized by oxygen:

$$\mathrm{Fe(II)} + \frac{1}{2}O_2 + 2\,H^+ \longrightarrow \mathrm{Fe(III)} + H_2O \qquad (2)$$

However, this reaction is strongly pH dependent and, under acidic conditions, the oxidation of Fe(II) is very slow (at $pH \leq 4$ less than 1% of the Fe(II) is oxidized per day [Stumm and Morgan, 1981]). In sunlit acidic waters, such as those encountered in cloud droplets and in acid mine drainage streams, reactions of dissolved Fe(III) with photoproduced superoxide and direct photochemical reactions of Fe(III) compounds and Fe(III) minerals result in the production of Fe(II) at rates which are much faster than the rate at which it is reoxidized by oxygen. Field measurements (McKnight *et al.*, 1988; Behra and Sigg, 1990; Sedlak *et al.*, 1994) and laboratory experiments (Waite and Morel, 1984; Sedlak and Hoigné, 1993; Voelker and Sedlak, 1994) have demonstrated that Fe(II) can, under some conditions, be the dominant form of dissolved iron in aerobic surface waters.

The redox reactions of silver could also result in the presence of thermodynamically-unstable Ag^o in aerobic surface waters. For the production of *dissolved* Ag^o it is possible to write the following half reaction:

$$Ag(I) + e^- \longleftrightarrow Ag^o \qquad E^o = -1.8\ V \qquad (3)$$

The strongly negative potential for reaction 3 indicates that dissolved monomeric Ag^o can only be formed through reactions with very strong reductants. However, the production of *solid* elemental silver occurs more readily because the Ag^o is stabilized by the phase change:

$$Ag(I) + e^- \longleftrightarrow Ag^o_{(s)} \qquad E^o = +0.799\ V \qquad (4)$$

The photoreduction of Ag(I) is therefore unlikely to occur in the absence of a solid phase but, in the presence of a suitable solid, could occur in a manner analogous to that observed for the photoreduction of Fe(III). Many known heterogeneous photochemical processes are capable of reducing metals such as Ag(I) and Fe(III). In fact, the photoreduction of Ag(I) on titanium dioxide semiconductors (Hada *et al.*, 1982) and on anthracene colloids (Tennakone *et al.*, 1994) have been developed as means of removing Ag(I) from wastewater.

In sunlit natural waters, the heterogeneous photoreduction of silver could possibly occur on common minerals and on natural organic particles. If we wish to consider the adsorption of Ag(I) to particulates in the absence of light, we only need to consider the following equilibrium reaction:

$$Ag(I) + {=}S \longleftrightarrow Ag(I){=}S \qquad (5)$$

where =S represents the solid phase. If the adsorbed Ag(I) also undergoes heterogeneous photoreduction we must consider an additional reaction:

$$Ag(I){=}S + h\nu \longrightarrow Ag^o{=}S \qquad (6)$$

When this additional reservoir for adsorbed silver is included, both the rate at which silver is adsorbed and the overall amount of silver adsorbed at equilibrium could increase.

Our experimental results indicate that the adsorption of silver to bentonite (a representative clay particle) is greatly enhanced when particle-containing solutions are exposed to light from a xenon lamp. Figure 1 illustrates the results from an experiment in which silver adsorption to bentonite was measured over a period of three hours. In the dark, approximately 20% of the Ag(I) adsorbed to the bentonite during this period. Most of the dark adsorption occurred during the first hour. When the experiment was repeated in the presence of light, the percentage of adsorbed bentonite steadily increased to approximately 70% of the total over three hours. Similar results were also observed at different concentrations of bentonite (Figure 2). As the concentration of bentonite increased, the difference between the adsorption in the light and the dark also increased.

Although further experiments will be necessary to determine the rates of photoreduction of Ag(I) on other representative natural particles and under other conditions, our preliminary results indicate that photochemical reactions do enhance the sorption of silver to bentonite. If these photochemical reactions result in the formation of Ag^o, it may be necessary to reconsider some of our concepts of silver cycling in aquatic environments. In particular, it may be necessary to reevaluate our models of how silver is adsorbed by particles, as well as its bioavailabilty and release from sediments.

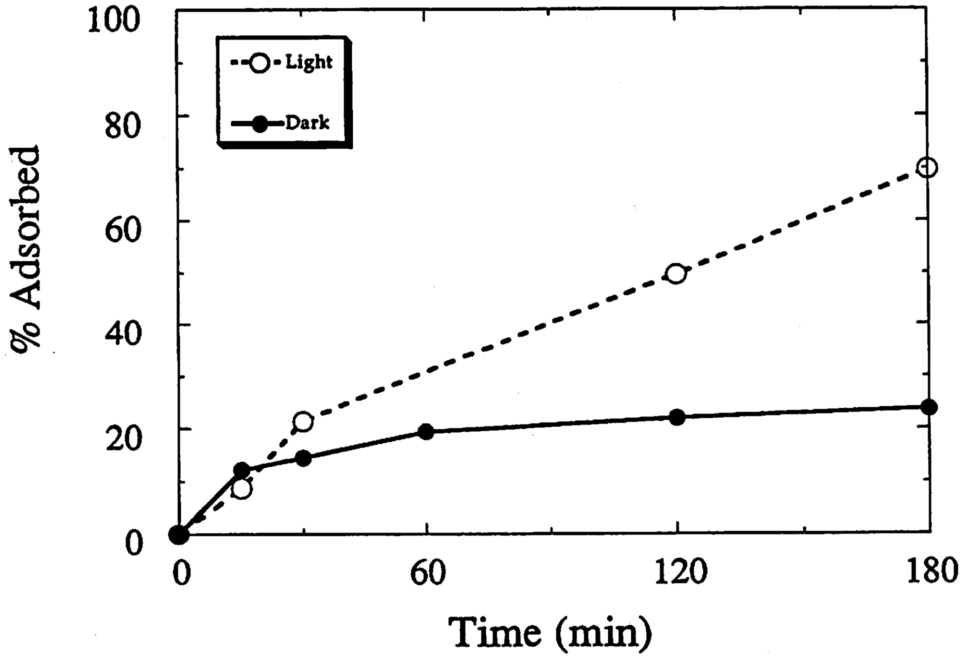

Figure 1: The adsorption of silver to bentonite as a function of time. Hollow circles depict samples that were exposed to a 120 Watt xenon lamp (which provided visible light with a spectral distribution and intensity similar to that of noon summer sun). Filled circles depict dark control. Conditions: $[Ag(I)]_{initial}$ = 100 nM; bentonite = 100 mg/L; pH = 8.0 (buffered with 10 mM $NaHCO_3^-$).

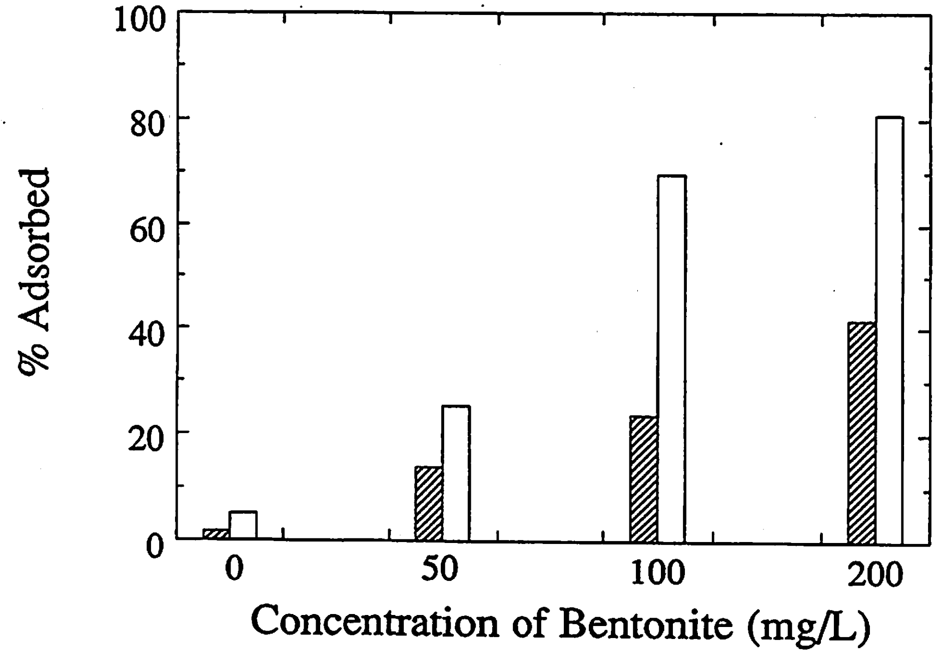

Figure 2: Comparison of the percent of adsorbed silver after three hours of adsorption as a function of bentonite concentration. Hollow bars depict samples that were exposed to light, shaded bars depict dark control. Conditions are identical to those listed for Figure 1.

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Questions & Answers: Photo-Enhancement Sorption of Silver to Bentonite

Q. JEROME NRIAGU (Univ. of Michigan): Would you care to comment on the role of organics, especially humic and fulvic acids, in the photoreduction of silver? We know that some of these colored compounds will absorb solar photons and, in the process, they get activated and will reduce some of the metals, specifically mercury, and possibly silver.

A. Like I said before, there hasn't been a lot done on this subject. With silver(I) organo complexes, you'd expect a ligand-to-metal charge transfer for the reduction. There has been some work a number of years ago by Balzani and others, where they had a very specific ligand for silver(I) — I don't remember the name of it offhand — but they saw some photoreduction with near-UV light. I hate to speculate about some of the natural organics, because whenever we get into this question, it's quite a mess. With humics and fulvics, we can't separate, for example, hydrated electrons being produced on natural organic matter, or superoxide radicals being produced, but it's likely it happens there as well.

Q. KEN ROBILLARD (Eastman Kodak): You showed the results of a concentration series with bentonite. I didn't catch the data at the very beginning of that curve or bar chart. Did you do it without bentonite present, and what results did you see?

A. Yes, that's the first one. I kind of rushed through it. The first data point here at zero, we see about — oh, that's the one I didn't even show. Thank you. Well it's the same data. What we have here is maybe two or three percent in the dark, and maybe five or six percent in the light. And I'm not sure that these are statistically different. I think we have some silver sorbing to the bottles — we use high density polyethylene.

Q. NORMAN NEWMAN (3 M): I would contend that one of the things that you need to consider is that silver, in very low concentration, individual type atoms, are extremely reactive. From the photochemical side of photoemulsions, we get into latent image issues where we have one or two silver atoms that are formed from photochemical transformation, and these regress back to silver bromide or chloride in the grain. So one of the interesting experiments I think you need to do is, having formed the silver on the bentonite, putting that back in the dark, and seeing how much regresses back into silver. I think you'll find that your estimate of a slow desorption is going to be in error, and that it's going to go back. The driving force of reaction in the environment, low concentrations of chloride or bromide, are just going to drive it.

A. That's interesting. I wouldn't really suspect that because I think it's a much different case when you have it on an inorganic particle like a clay, as opposed to in an emulsion or in solution.

Q. It's not in solution in the grain. In the grain, it's sitting generally on the surface of the silver halide. But what you're really talking about is the solid state physics that's driving it. And it comes down to the fact that an independent, single silver atom is a very reactive species, and unstable.

A. Well, if I could add just one more thing. In these experiments, I think the lag time between actually exposing the sample and working it up, getting to the extraction, was probably 15 or 20 minutes, and we don't see much variability between 15 minutes and 30 minutes in that extraction. So if there's a half-life, it's got to be on the order of hours and not minutes. What I showed from the example with iron is that, if the half-life for oxidation is on the order of hours or days, we'd still see it produced during daytime. But the question of desorption from sediments is probably still relevant.

KRAMER: I've got to cut this short. It sounds to me like there's some good industrial experiences here that you two might want to compare notes on and see what the differences and similarities are.

Development of a Sediment Quality Criteria for Silver

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The proposed sediment quality criteria for the five metals (Cd, Cu, Ni, Pb, Zn) are based in part on the criteria that the ratio of SEM (Simultaneously Extracted Metal) to AVS (Acid Volatile Sulfide) should be less than one. Since silver forms an insoluble sulfide, it is likely that this requirement would apply to it as well.

We will report on the progress being made in examining the validity of the assumptions and procedures used for the five metals mentioned above when applied to silver.

Questions & Answers: Development of a Sediment Quality Criteria for Silver

Q. NICHOLAS FISHER (SUNY-Stony Brook): I have a question about the organic carbon-metal complexation in the sediments. You have deposit-feeding organisms, which ingest sediment and try to assimilate the organic carbon out of the sediment, and presumably would be exposed to the metal that's complexed to that organic carbon during that process. So I could understand why the arthropods, for example — which are swimming around, or hopping around on the surface — are going to be exposed principally, perhaps, to the dissolved phase. And while your picture holds for an arthropod, it may not hold for a deposit-feeding organism.

A. That's a very good point, Nick. As far as I know, there are no experiments that we've done with oligochaetes, that would confirm or deny what you've said. One would expect, by analogy, that it probably would work the way an organic chemical might work, that is to say, there would be a competition between the organic carbon phase and whatever the binding phases are within the organism for metals. So one could imagine that we're into a bioconcentration factor kind of analysis. But it's an interesting experiment to contemplate, and one I think we'd have to do if we want to utilize carbon binding as part of the criteria.

Coupled Sorption/Reduction of Silver and Other Multivalent Metals by Ferrous Micas: Insights From Electron Microscopy and XPS

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Experimental studies have shown that oxidation-reduction reactions between aqueous species and structurally bound iron on or beneath the surface of both silicates and oxides can control the redox state of solutes (see reviews by; HERING AND STUMM, 1990; WHITE, 1990; WERHLI et al., 1989). WHITE and YEE (1985) demonstrated that ferrous iron in biotite, augite, and hornblende was a stronger reducing agent over a broad range of conditions than $Fe(II)_{aq}$. They concluded that the electron transfer from iron in ferrous silicates to aqueous species was coupled to the transfer of cations to solution in order to maintain charge balance in the oxidized solid, and they used the term coupled electron-cation transfer reaction to describe this process. An implication of their study was that iron *in* ferrous silicates could be a particularly important electron donor in dilute, poorly poised near-surface waters. In this regard, biotite is a particularly important mineral for study because it is a ubiquitous Fe(II)-bearing mineral with accessible exchange sites. Here, we present results from experiments on the interaction of Ag(I), Cu(II), Cr(VI) and Cr(III) bearing aqueous fluids with biotite, an Fe(II)-rich mica.

Our experimental design differed from most sorption studies because we used large single crystals instead of powders. Near end-member phlogopite grains (i.e., Mg-rich biotite) were used as internal controls (relatively redox inert). In order to minimize homogeneous reduction of the metals by $Fe(II)_{aq}$, both mica surface area/fluid ratios and the concentrations of anions that could promote the dissolution of iron in biotite were kept low. We used high-resolution scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) to check for precipitates and potential transformation reactions. Precipitates and alteration assemblages were identified with selected area electron diffraction (SAED), condensed area electron diffraction (CBED), and analytical electron microscopy (AEM). Diffusion profiles were obtained from electron microprobe analyses and compositional X-ray mapping. For the chromium experiments, we also used X-ray photoelectron spectroscopy (XPS) to determine the compositions of the mica surfaces and the oxidation states of near-surface iron and sorbed chromium. One advantage of using relatively large biotite crystals was that we could easily compare and contrast the reactivity of the (001) surfaces, or basal planes, with the (hk0) crystal edges using XPS. Another advantage was that solution compositions and pH did not vary appreciably, due to the low mica surface area/fluid volumes in the experiments. The disadvantage of the experimental setup was that the concentrations of dissolved iron and potassium were near or below the detection limit of the ICP, and changes in metal concentrations in solutions were indiscernible. Consequently, it was not possible to derive mass balances between the solutions and the solids.

HRTEM/AEM and SEM studies of biotite reacted with 9×10^{-6} to 4.5×10^{-3} M Ag silver sulfate solutions, at 25°C and 1 atm., showed that biotite absorbed silver along the interlayers and that silver was quantitatively reduced to the metallic state. In contrast, phlogopite from the same experiments (near Fe free biotite) did not accumulate silver metal precipitates. This work differs from Sayin et al.(1979) in that Sayin et al. worked at higher temperatures, used silver nitrate, and extracted potassium from biotite before reaction with silver solutions. SEM images show columnar growths of native silver precipitates that cling to and have overgrown biotite edges. TEM images of interior basal plane surfaces of reacted biotite show numerous psuedohexagonal platelets of metallic silver. The morphology of the silver precipitates is probably controlled by the structure of biotite. Electron microprobe and X-ray mapping show a strong negative correlation between silver and potassium concentrations in biotite, but silver is not correlated to any other element in biotite. Despite this correlation, analytical TEM shows that silver is not detected in altered biotite domains (e.g., vermiculite) and that most silver is present in biotite as submicroscopic native silver inclusions in the interlayer region. The fact that biotite was capable of sorbing and reducing silver in solutions that contained only 9×10^{-6} M Ag, at pH = 3, illustrates that Fe(II) in ferrous silicates is a potentially stronger reducing agent than $\mathrm{Fe(II)}_{aq}$

HRTEM studies of copper-rich biotites from natural and experimental assemblages show that biotites can acquire appreciable concentrations of copper during low temperature (25°C) events, such as weathering (ILTON et al.1992; ILTON and VEBLEN 1993). The mode of copper incorporation in "biotite" is complex, but the most common form is substitution of copper into expanded interlayers or vermiculite-like intergrowths. Copper concentrations are positively correlated with the density of expanded interlayers. Highest copper concentrations (up to 13 wt. % CuO) are found in narrow (up to a few microns) alteration domains that consist of an ordered mixed layer phase with alternating 10 and 12-14 Å layers. Copper also appears as rare, but occasionally locally abundant, submicroscopic inclusions of native copper and as a substitute for iron in submicroscopic iron oxide inclusions. Whereas biotite easily reduces silver to the metallic state, copper appears to be on the border-line of what biotite is capable of reducing.

Better constraints on the low-temperature geochemistry of chromates are of great interest because they are very soluble, known carcinogens, and common anthropogenic pollutants. Reduced forms of chromium, such as trivalent species, are less toxic than chromates and only sparingly soluble (SASS and RAI, 1987; RAI *et al.*, 1987). Therefore, redox reactions are critical to understanding the behavior of and the threat posed by chromium in the environment. Here and in ILTON and VEBLEN (1994), we provide further constraints on the mechanisms by which ferrous sheet silicates can control the fate of chromium in the near-surface environment. More specifically, we present results from a series of reconnaissance experiments that were designed to test whether chromate can be reduced to Cr(III) at the biotite-solution interface by structurally bound $\mathrm{Fe(II)}_{bio}$. An important goal of the research was to compare the reactivity of the edges to that of the basal planes.

Large single crystals of biotite and near end-member phlogopite were reacted with acidic Cr(VI)- and Cr(III)-bearing solutions, at 24°-27°C and 1 atm. After reaction of the micas with Cr(VI) solutions, XPS analyses of biotite and phlogopite edges indicated little or no chromium on phlogopite but elevated concentrations of chromium on biotite. The binding energies for Cr2p are consistent with a Cr(III) species. XPS and SEM of biotites reacted with Cr(VI) solutions indicate that chromium is strongly sorbed by the edges of mica books relative to the basal plane. In fact, much of the chromium associated with the basal plane is sorbed by steps and micron-sized biotite flakes, or, in other words, by layer edges. TEM and SEM of biotite basal planes and edges show no chromium-rich precipitates. After reaction of the micas with Cr(III) solutions at pH = 3, XPS shows similar concentrations of a Cr(III) species on *both* biotite and phlogopite, and on the edges and basal planes. These results stand in strong contrast to the results from Cr(VI) solutions. XPS indicates that near-surface iron in biotite is more oxidized after reaction with Cr(VI)- relative to Cr(III)-solutions.

A comparison of biotites and phlogopites from the Cr(VI) and Cr(III) experiments provides convincing evidence for coupled sorption and reduction of $Cr(VI)_{aq}$ at the biotite edge-fluid interface. Experiments with additions of potassium and sodium perchlorate confirm the importance of potassium in the heterogeneous coupled cation-electron transfer reaction. Initial observations indicate that biotite tends to concentrate Cr(III) more strongly in Cr(VI) solutions than in Cr(III) solutions, at pH = 3 and ionic strength $\approx 10^{-3}$, despite the fact that there was order-of-magnitude more $Cr(III)_{aq}$ in the Cr(III) solutions than in the Cr(VI) solutions. Much more work is required to understand this observation, but one possibility is that, under these conditions, the kinetics of coupled sorption/reduction of Cr(VI) is faster than the the sorption of Cr(III). Interestingly, this would imply that $Cr(VI)_{aq}$ could be more mobile than $Cr(III)_{aq}$, at least in some reducing environments.

In summary, ferrous micas such as biotite can attenuate the transport of redox sensitive metals in the environment by coupled sorption/reduction reactions. The efficiency of this process will be affected by many factors, but one of the most important parameters is the concentration of dissolved potassium. Dissolved potassium can block absorption of silver and copper by interlayer exchange sites. Further, high potassium concentrations can block electron transfer from biotite to sorbed species by inhibiting the dissolution of biotite and, consequently, the loss of charge compensating cations.

ACKNOWLEDGEMENTS

This research was funded by DOE contract DE-FGO2-89ER 14074. Support by the DOE for this work does not constitute an endorsement by the DOE of the views expressed in this abstract. Electron microscopy was performed at the Johns Hopkins HRTEM/AEM lab, which was established with partial support from NSF grant EAR 83-00365. XPS was performed with the Scienta ESCA-300 X-ray photoelectron spectrometer housed in the Zettlemoyer Center for Surface Studies, Lehigh University.

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Questions & Answers: Coupled Sorption/Reduction of Silver and Other Multivalent Metals by Ferrous Micas: Insights From Electron Microscopy and XPS

Q. DAVID SEDLAK (Univ. of Wisconsin): Your technique necessitated that you used very high concentrations of your metals. I also saw from your picture that you hadn't tried to cover them from exposure to light during the hours to days that you did your experiments. At the concentrations of silver that you used, miniscule amounts of chloride would form silver chloride precipitates in your solutions. How much silver chloride photochemistry could you have been seeing, and is there a way to try to look at this in some further experiments?

A. Well, I mean there's no measurable chloride in my experiments. When I characterized the precipitates, I didn't find any silver chloride. Also, I put in redox-inert controls — phlogopite — there were no silver precipitates on that phlogopite. So if it was just "chemistry," I would expect to find silver precipitates also on the phlogopite. The phlogopite surface characteristics are very similar to the biotite. The only difference is you get a removal of iron. Electrostatically these are the same. I would suspect that the thing would be sorbing just as readily to the phlogopite as to the biotite. So I think it's a fairly good control.

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Session B

Environmental Cycling of Silver

A. Sodergren and T.W. Bober
Session Chairs

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Session B

Environmental Cycling of Silver

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Session Chairs

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Session I

Partitioning of Trace Metals Among Macroparticles, Colloids and Solution

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Partitioning of trace elements between solution and solid phases is probably the single most important factor controlling their transport, reactivity, bioavailability, residence time, and fate in aquatic systems. For this reason, it is crucial to understand partitioning and to be able to predict it quantitatively. Surface complexation models (SCM's) are the most sophisticated tool available at present to describe reactions at the solution-solid surface interface. Unfortunately, adequate data to apply SCM's rarely exist for real systems. Instead, scientists, engineers, and modelers often rely on a simpler, empirical partition coefficient defined as:

$$K_d = \frac{\text{mass of filter-retained metal/mass solids}}{\text{mass of filter-passing metal/volume water}}$$

K_d is not a strict thermodynamic constant, in the sense that it cannot be directly related to the free energy change of a specific chemical reaction. However, K_d may behave much like a thermodynamic constant across a broad physicochemical environment if a few conditions are satisfied: 1) the abundance of surface complexation sites is proportional to the mass of suspended solids, 2) a given trace metal reacts with an approximately homogeneous reaction site type, and 3) the concentration of metals measured on solids corresponds to a pool that is labile with respect to surface-solution reactions. These conditions may be satisfied when: 1) there is an approximately constant particle size distribution, 2) the concentration of a trace metal is very small compared to that of the surface sites with which it reacts, and 3) an appropriate method has been selected to extract and measure the particle-bound metal fraction.

Whether it is a strict thermodynamic constant or not, there is no reason to expect that K_d will vary in any systematic way with the concentration of suspended solids (TSS). To do so would be similar to a Henry's law constant being a function of the size of water body with which a gas phase interacted. Nevertheless, contrary to expectation, K_d has been found to be proportional to TSS in both natural and experimental aquatic systems. Generally it is observed that:

$$\log(K_d) = k - n \times \log(TSS), \tag{1}$$

where k and n are constants with values near 6 and 0.7, respectively. This phenomenon, termed the "particle concentration effect" (PCE) is well documented for Th isotopes and some metals in the world ocean, and also for elevated metal concentrations in experimental systems. The PCE is not a subtle effect, since it reflects a change of partitioning behavior spanning at least three orders of magnitude across the normal range of TSS encountered in real systems. The current research extends these observations to Pb, ^{210}Pb, Ag, Cu, Cd, and Zn in estuaries and fresh waters.

In six estuaries that represent all but two of the major rivers in Texas, Ag, Cu, Pb, and Zn conform to the PCE. Their average slope is near -0.7, and their intercepts fall in the order $Cu < Zn \leq Ag < Pb$. (Pb is sorbed to particles most effectively and Cu least.) Balls (1989) observed similar results for a compilation of studies on trace metals in European coastal waters.

We have also completed measurements for Pb in three surface freshwater bodies with a broad range of background water chemistry (i.e., pH, ANC, ionic strength), suspended particle load, and total trace metal levels. Pb conforms to the PCE with a high degree of significance ($r = 0.91$, $N = 64$, $P << 0.001$). The slope is indistinguishable from the value for Texas estuaries, but the intercept is higher by about one log unit. Pb is bound about 10 times more effectively by freshwater suspended particles. Curiously, 210Pb in two lakes has a lower intercept than that of stable Pb (0.6 log units), but the same slope. The significance of the correlation is again very high ($r = 0.77$, $N = 118$, $P << 0.001$). The dissimilarity between 210Pb and stable lead may be due to difference in speciation of the source material, and is under investigation.

The data also show that suspended solids ranging in composition from clays and silts, to organic matter and cells, to freshly precipitated iron oxyhydroxides, all partition 210Pb according to a single trend. Thus neither background chemistry nor surface composition seem to have a significant influence on lead partitioning in these five water bodies. This is the opposite of what is predicted by surface complexation models.

We interpret these anomalous observations as resulting from the existence of colloidal forms of the metals. By "colloidal forms" we mean metal associated with particles in the size range from approximately 1 - 400 nm. Particles in this size class can pass through conventional ≈ 0.5 μm pore-size filters and are not readily removed by gravitational settling. Metals associated with colloids behave physically as if they were in true solution (e.g. in terms of transport), but chemically they behave like a solid phase (in terms of chemical reactivity and bioavailability).

Ordinary filtration, designed to separate dissolved from solid fractions, actually segregates between macroparticles (> 0.5 μm) and a combination of metal in true solution and associated with colloids. The apparent partition coefficient, K_d, is thus correctly:

$$K_d = \frac{\text{mass of filter-retained metal/mass solids}}{\text{dissolved metal/volume water + colloidal metal/volume water}} \qquad (2)$$

When the amount of metal associated with colloids is greater than that in true solution, equation 2 reduces to:

$$K_d = \frac{\text{mass of filter-retained metal/mass solids}}{\text{colloidal metal/volume water}}$$

(The case when truly dissolved metals are greater than those associated with colloids is discussed later.) This last equation can be transformed to:

$$K_d = \frac{K_{part}}{K_{coll}} \times \frac{1}{CSS}$$

Where K_{part} is the partition coefficient between macroparticles and true solution, K_{coll} is the partition coefficient between colloids and true solution, and CSS is the mass of colloids per volume of solution. It follows that:

$$\log(K_d) = \log(K_{part}/K_{coll}) - \log(CSS) \qquad (3)$$

The observed decline in K_d with increasing TSS can be explained if the amount of colloidal suspended solids is related to the amount of macroparticulate suspended solids:

$$CSS = x(TSS)^n \qquad (4)$$

Substituting eqn. 4, eqn. 3 becomes:

$$\log(K_d) = [\log(K_{part}/K_{coll}) - \log(x)] - n \times \log(CSS)$$

This is the same as eqn. 1, if $(K_{part}/K_{coll})/n = k$.

If truly dissolved metals are greater in concentration than those associated with colloids, then eqn. 2 reduces to :

$$K_d = K_{part} \tag{5}$$

That is, K_d becomes constant. If eqn. 4 correctly describes the particle size distribution, then eqn. 5 should hold true in the region where TSS, and consequently CSS, is low. This condition may occur in lakes with extremely clear, particle-free water, such as Crater Lake, Oregon, and Ungava Crater Lake, Territoire de Nouveau Québec. These unusual systems are worth studying in order to test this hypothesis.

Equation 4 implies a fixed relationship between macroparticles and colloids. The simplest possibility would be if there were a constant relative size distribution with a consistent "tail" falling in the colloidal size class. In this case, the value of n would be 1.0. Since the actual observed values tend to be closer to 0.7, additional factors are probably contributing to control of the particle size distribution spectrum. Further measurement of the partitioning behavior of several metals in a variety of aquatic systems may help to elucidate dynamic self-regulation of size distribution, which occurs through the interaction and competition among processes of aggregation (Brownian, shear, and differential settling types), disaggregation, and generation of new colloids.

Q. MICHAEL BOTHNER (USGS, Woods Hole, Mass.): I'm just curious to know — you're concerned about artifacts, and that's well expressed. I just wondered if, when you're filtering the water through a filter, and you have a lot of suspended matter, whether you can take into account the fact that it might be a more efficient filter, when you have a clump of cake deposited on the filter, than when you have a real clean water system and you know the colloids are going through more readily.

A. Yes, that's clearly one [factor] that's very important. The way that we're trying to deal with that is, we monitor the back pressure on the filter, and we stop at a standard back pressure. We're also doing a series of experiments to see, for a given sample, collected repeatedly at different filter loads, how that might be changing. Yes, that's a good point. That's actually what I was thinking might be the problem between stable lead and lead-210. You could use a different filter size — the same material — but a different filter size. But when we calculated the load of suspended particles on the two filters, it turns out that the effects, if anything, would have been causing an opposite change of lead-210 vs. stable lead. Yes, point very well taken.

Q. NICHOLAS FISHER (SUNY-Stony Brook): Revisiting your nightmare question, when you have very low suspended particle load, say a tenth of a milligram per liter, and you're finding K_d values in excess of 10^7, which seems very high, to me, for lead, to what extent is there adsorption of the lead to the filter material itself? Have you corrected for that? Is that a big problem? And what kind of filter are you using, pore size? I didn't catch that information.

A. We're having a problem — and I didn't spend a lot of time talking about colloidal breakthrough at the beginning because everybody here must have experienced that. We found that we were having problems of adsorption, at least for some of the metals, on the one type of filter that we were using. As a result, we wound up using Nucleopore material as a filter, and the adsorption was much lower. At this very low concentration range, our detection becomes more difficult. But we are doing that now. If you have any recommendations, I'll be glad to listen to them.

Q. We find Nucleopore polycarbonates work best for us. But at very low suspended particle loads, I didn't know whether or not the data you presented were corrected for the adsorption blanks.

A. Yes, they are. In fact, the good point about that is it's clearly an artifact which would have a systematic nature, which is the kind we see. The problem that we have is that with the preloaded Teflon filter holders, because we can't change them and keep them clean, and the type that we use has such a large grid size in the platform that Nucleopore by themselves pop under the pressure of the water.

Q. ANDERS ANDREN (Univ. of Wisconsin): Colloid particles physically have a certain time constant, vis-a-vis their stability. They tend to agglomerate. You were saying that, perhaps in a transport sense, colloidal material behaves more like dissolved. They won't necessarily stick, but there might be some agglomeration. I just wonder if you've given some thought about the time constant stability, and this sort of continual movement towards larger particles, and if that can be modeled yet.

A. Well, I certainly haven't done it in a very rigorous way — I'm still doing some calculations of a modeling nature. But I certainly see information that suggests that the time scale of that process is on the order of days, or even a couple of weeks. So, for a lot of freshwater systems that I'm interested in, the metals are getting moved at that same rate. Probably, the rate of transfer from a colloid-type particle to a large particle, and the rate of settling, are about the same.

Q. DAVE ARMSTRONG (Univ. of Wisconsin): My question is about DOC, which you mentioned. Do you see a relationship between your K_d's and DOC, and also between DOC and SPM in your data?

A. I don't yet, and the problem is that most of the waters I've looked at have a relatively narrow range of DOC and SPM. So even if they were detected, it wouldn't really show up. One of the things I'd like to do is to look at a greater number of water bodies, some of which have much higher DOC values. Most of these are pretty low levels — milligrams per liter, something like that. But, yes, that's certainly something you'd expect to see.

Silver Production and Mercury Pollution in South America Between 1580 and 1900

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Introduction

Bartolome de Medina's development of the *patio* (mercury amalgamation) process into an industrial scale operation in 1554 stimulated the production of silver in South America at unprecedented levels for over four centuries (Figure 1). The patio process, often regarded as one of the most remarkable inventions of Ibero-America (Bakewell, 1984), was ideally suited for the low grade ores and some unique ore minerals (such as argentite and cerurgyrite) common in the New World, and also solved the problem of fuel scarcity which had plagued the early resource extraction industry in the region (Brading and Cross, 1972). Te patio process depended on a cheap and plentiful supply of mercury which was easily met by the production of unparalled quantities from the mercury mines at Almaden in Spain, Huancavelica in cetral Peru and Idrija in Slovania (Bethell, 1984; Blanchard, 1989). While volumes have been written on various facets of the Spanish silver, little has been said or is known about the massive mercury pollution associated with the silver production.

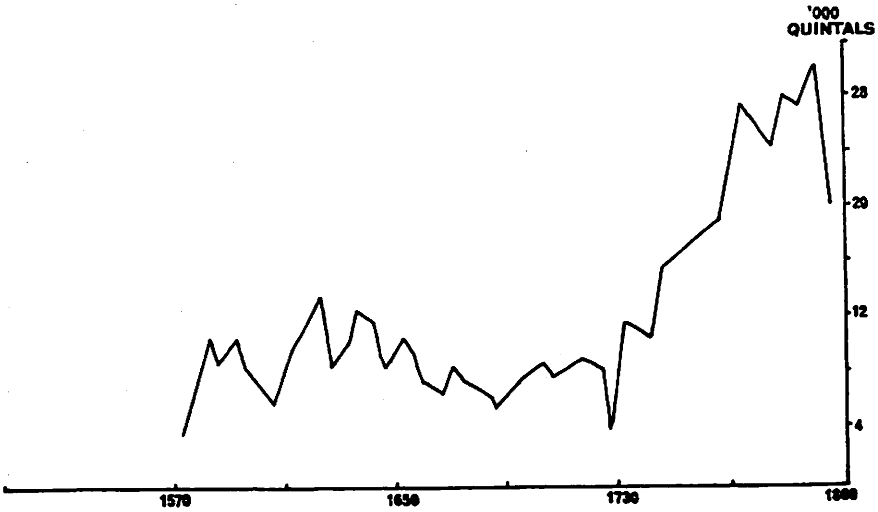

Figure 1. Total production from the mercury mines of Almaden, Huancavelica and Idrija. From Blanchard, 1989.

The Patio Process

In its original cold form, the amalgamation was done on a large, flat stone-paved surface (the *patio*). The finely pulverized ore (*harina*) was piled in heaps (*montones*) of 1-1.5 metric tonnes on the patio and mixed with salt (about 1.0 kg per *quintale,* roughly 50 kg, of ore) and water to form the *ripasos* (mud). Lime was added if the mixture turned "hot" but if no heat was generated the *magistral* (roasted copper or iron pyrites) was used. Mercury was then mixed in, typically at a rate of 3-6 kg per quintale of ore and the mixture spread out as large cakes (*torta*) up to 85 m across which was treaded at intervals by men, horses or mules. The reaction of the mercury and silver took 3 weeks to 5 months depending on the ambient temperature, the nature of the ore and the refining skills of the *azoguero* or *beneficiador.* At high altitudes where the temperature is lower, such the Potosi mines located in the Andes mountains, the reaction was often speeded up by warming the mixture in large stone tanks (*cajones*) or the copper-bottomed tubs invented by Alonso Barba (1590). The finished cakes were shovelled into a large vat (*tina*) equipped with beaters to separate out the silver amalgam (*pella*). Excess mercury was expelled from the *pella* in canvas bags and the amalgam heated in a retort (*capellinas*) to free the silver and recover some of the mercury (Motten, 1972; Prieto, 1973; Bethell, 1984).

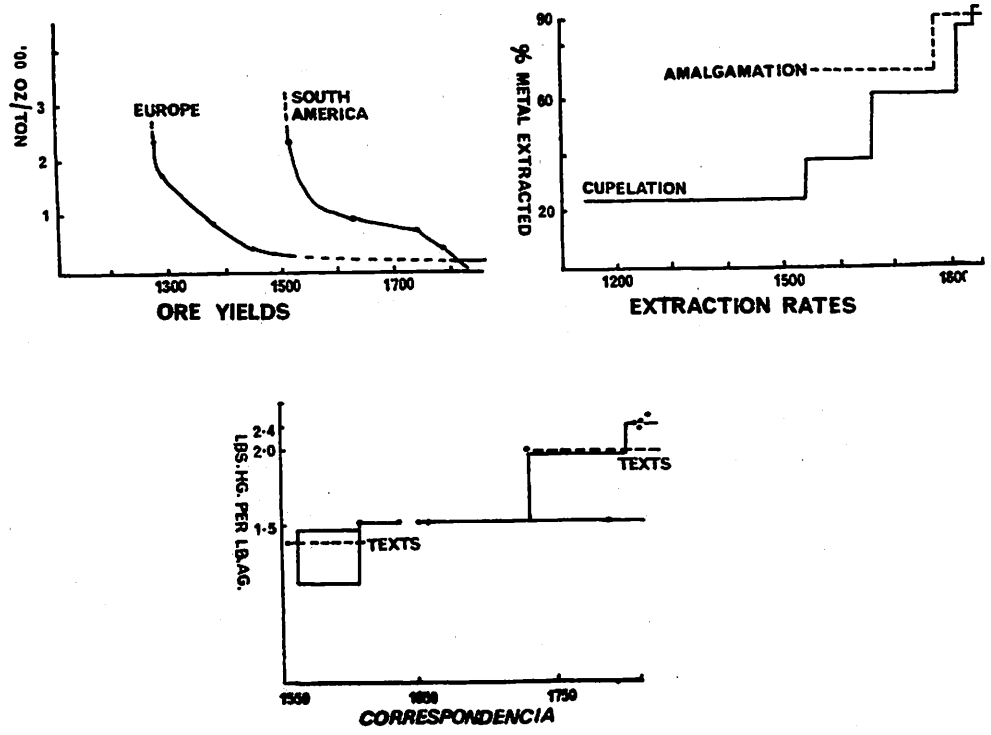

Figure 2. The ore yields, extraction rates and correspondencia for silver in South America during colonial times. (From Blanchard, 1989).

The patio process and its various adaptations made it possible for large amounts of ores containing as low as 15 oz silver per tonne of ore to be extracted profitably, a performance unmatched by any of the smelting techniques being used in Europe at that time. It remained unchallenged in South America for over 300 years; as late as 1870, about 71% of all the Mexican silver was still being produced by this process (Brading and Cross, 1972). Although it was supplanted by the "barrel amalgamation" or Born process in the late 19th century, the technological nexus between silver and mercury was not severed until cyanide amalgamation was introduced around 1900 (Brading and Cross, 1972).

The Loss of Mercury

Considerable quantities of mercury were needed to sustain the massive output of silver from the Spanish American mines and the great cycles of silver production were closely linked to the supply and price of the mercury (Whitaker, 1952; Fisher, 1977; Blanchard, 1989). Although some of the mercury used to extract the silver was recovered, a large fraction was generally wasted in the process because of the crude equipment and conditions. Until the middle of the 1740s when the profitable margin of exploitation stood at about 2 kg Ag/tonne of ore, a rule of thumb was that 1.5 kg of mercury was lost for every kg of silver produced (Bethell, 1984; Fisher, 1977). The ratio (or *correspondencia*) increased to about 2 kg Hg/kg Ag between the 1740s and 1790s when the margin of exploitation declined to about 1.1 kg Ag/tonne ore. As the margin of exploitation dropped to about 0.6 kg Ag/tonne ore between the 1790s and 1810s, the *correspondencia* values of 2.4-2.9 Hg/kg Ag became common in Potosi and many mines of Central America (Figure 2). Throughout the period the ration could be as low as 0.85 kg Hg/kg Ag for very rich ores and as high as 4.1 kg Hg/kg Ag for the impoverished ores (Prieto, 1973; Motten, 1972; Blanchard, 1989). The *correspondencia* for the colonial silver mines may be compared with the the current loss of mercury associated with gold extraction in the Amazon of Brazil estimated to be in the typical range of 1.3 to 1.7 kg per kg of gold recovered (Pfeiffer et al., 1989; Lacerda and Salomons, 1991).

Since the Almaden and Huancavelica mines produced most of the Hg for the silver and gold miners in South America, the consumption of mercury can been estimated using the import figures from these two sources and the recorded imports from the Idrija mines (see Cronshaw, 1921; Brading and Cross, 1972; Fisher, 1977; Bethell, 1984; Blanchard, 1989). During 1556-1560, about 9 t/y of mercury were discharged and by 1570-1575 the wastage had exceeded 86 t/y. Between 1580 and 1820, the calculated losses varied from 292 to 1085 t/yr (Figure 3) with the average being 527 t/yr. The divergence in the data shown in Figures 1 and 3 since 1750s can be attributed to the increasing diversion of the mercury to the gold mines in other parts of the world including West Africa, Brazil and New Granada, and the United States (Blanchard, 1989). By comparison, the input of mercury into the Amazon associated with the current gold rush is reported to be 73-232 t/yr (Lacerda and Salomons, 1991). The cumulative loss of mercury in South America between 1570 and 1820 is estimated to be 126,000 tonnes.

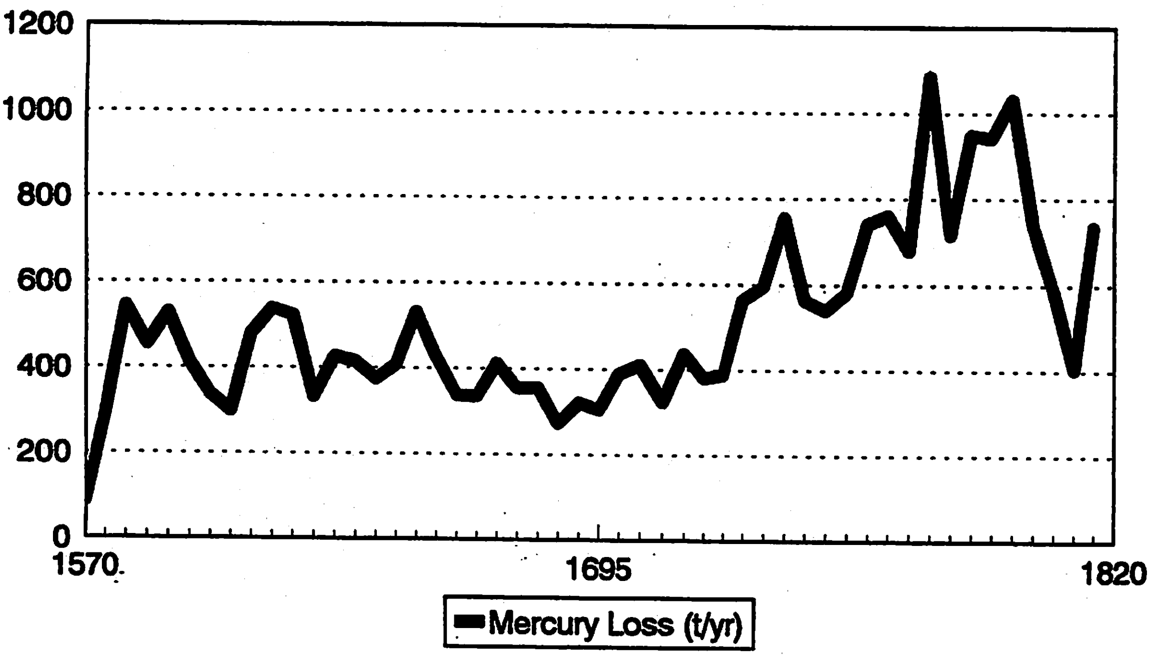

Figure 3. Mercury losses from the production of silver in Spanish America

Total silver production in South and Central America between 1820 and 1900 is estimated to be 99,400 tonnes, based on the compilations by Moshide (1985), Cronshaw (1921) and Lamey (1966). Assuming the ratio of mercury lost to silver produced to be 1:1 (actual *correspondencia* was likely to be the 2-3 kg Hg/kg Ag noted above) and that 70% of the silver was recovered by the patio process and its modifications (see above), the cumulative discharge of Hg during the 80 years is estimated to be 70,000 tonnes. From the total figure, the average discharge rate in post-independence times is estimated to be 875 t/y. For the duration of over 300 years, from 1570 to1900, when the patio process was in common use, the total discharge of mercury from silver mining in South and Central America is estimated to be 196,000 tonnes, an impressive figure indeed.

Although mercury was used in numerous silver mines, the most sustained losses occurred in the 7 important silver mining regions of South America and the 16 major centers in Central America (Figure 4). An intriguing question is, what has happened to the unprecedented quantities of mercury discharged in these silver mining areas? The old Spanish literature is completely silent on the ecological and human health effects of what would have been severe mercury pollution. One would hope that this report will encourage some investigation of this forgotten but major source of mercury in South and Central America. It has been suggested that the continuing recycling of this large mass of mercury may partly be responsible for the high background levels of mercury in the global environment (Nriagu, 1993). The current problem of mercury pollution associated with gold mining in the Brazilian Amazon can be regarded as a re-enactment of an old Spanish American tragedy.

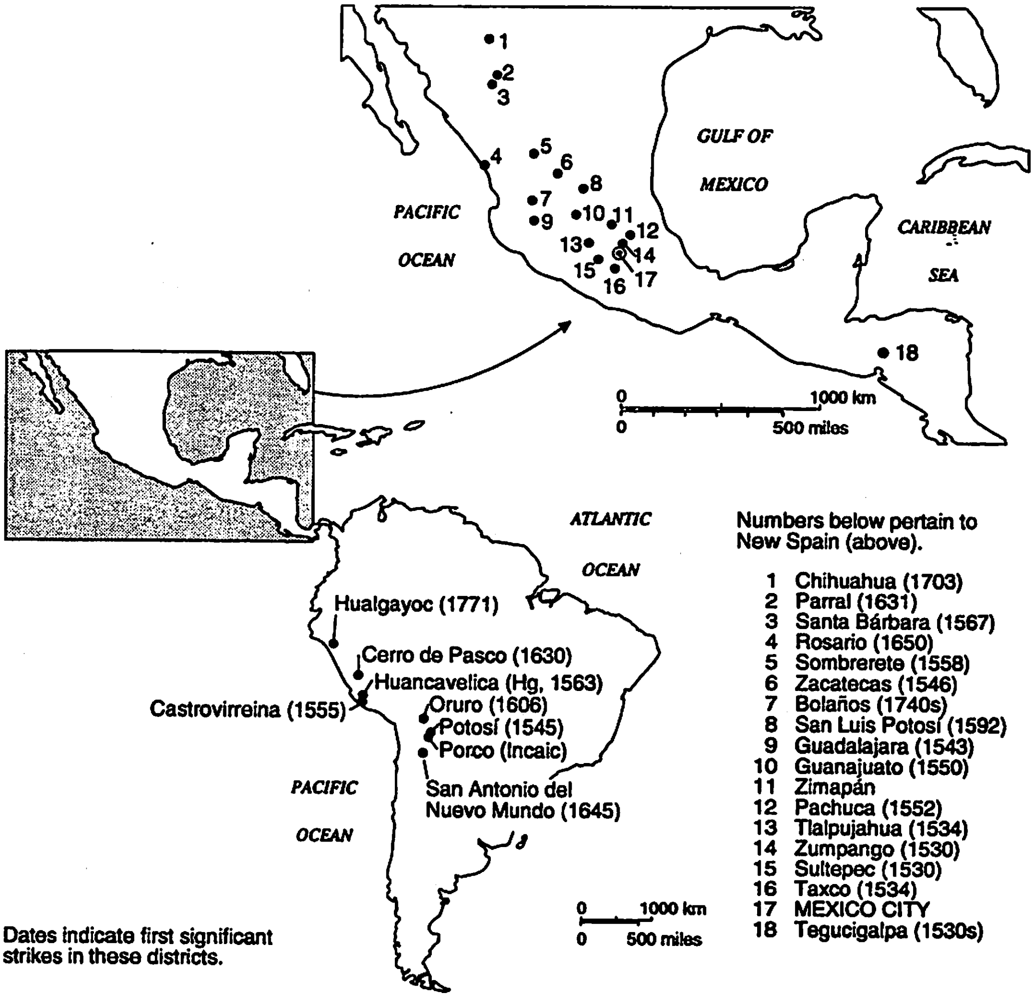

Figure 4. Major silver mining centers in South and Central America during the colonial times.

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Questions & Answers: Silver Production and Mercury Pollution in South America Between 1580 and 1900

Q. SAM LUOMA (USGS, Menlo Park): Jerome, you probably know more about this than anybody. What do you speculate has been the fate of mercury? What proportion of that mercury do you think has ended up in the atmosphere and widely dispersed, vs. mercury that might come down the rivers?

A. Well, if I go with the current estimates, I'd say 50 to 60 percent probably ended up in the atmosphere. Because what happened was, after washing up the gangue, they collected the amalgam and, in most cases the amalgam was melted in the open air. Occasionally they may have recovered some of the mercury. But then, after using the mercury once or twice, it gets dirty, so I think that they didn't bother reusing it any more. A large fraction went up to the atmosphere. On a global scale, that we've been tracing, when you go back to South America, look up some of the historical records and examine sediments or peats, or whatever, and see exactly what has happened. Now you can look at some of the biota, some of the ecosystem, to see if you do pick some of the increased levels of mercury in the biosphere.

Q. We have some sediment cores from San Francisco Bay that we've looked at recently. Interestingly enough, you don't see huge increases in mercury concentrations, at least in the one place that we've looked, around the period from — well you see increases from the late 1800s until 1930 or so — but they aren't huge increases. That's why I was curious how much would volatilize. The other thing that I noticed in looking at that, industrial emissions of mercury — at least in San Francisco Bay, which is a pretty large industrial complex — are about 0.8 tons per year, compared to what you showed up there.

A. Yes, again, you're talking about a highly industrialized area. I'm talking about going to something like an ombrotrophic bog, where you're getting mostly mercury from the atmosphere, not San Francisco Bay. I mean, if I were to go to Hamilton Harbor or something, I wouldn't see that. It gets totally masked by modern anthropogenic inputs. If you do that, you're going to have to go to an area that didn't receive a lot of direct inputs, and see what is happening, if you can see such a record. And for North America, actually, the maximum amount of these are found from about 1860 onward. So that is just a typical history. Whereas in South America, about 1900 they stopped using the process. With the newer technologies it's not a problem.

Q. TOM BOBER (Eastman Kodak): Along with the mercury, I noticed that you didn't account for about 15 percent of the silver by that process. How much silver might have been carried along as an impurity in this discarded mercury, such as, for example, into San Francisco Bay?

A. Later, they went on and resmelted some of the old mine tailings, strictly those that had residual metal, depending on the amalgam. So they went back and resmelted some more. So, in fact, yes, a lot of the silver got lost, or silver amalgam rather.

AN INITIAL ASSESSMENT OF THE PRODUCTION, CONSUMPTION AND EMISSION OF SILVER IN THE NORDIC COUNTRIES

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Abstract

This is the first attempt to provide scenarios for silver in the Nordic countries. In the Nordic countries, silver recovery from non-ferrous metallurgical plants occurs in Sweden and Finland. In Sweden, the average recovery of silver for the last 23 years is about 230 metric tons (7.4 Million Troy Oz) whereas in Finland, it is about 30 metric tons (0.96 Million Troy Oz). In addition, silver is also recovered by the secondary metal industry from photographic materials, electronic and jewelry scrap.

The silver use pattern in the Nordic countries differs somewhat from the global use pattern. The global use pattern of silver for the 1980s was maximum (38%) in the sector of photography whereas in the Nordic countries, maximum use was observed in jewelry/silverware. In Norway, the maximum amount of silver (90 tons i.e. 2.89 Million Troy Oz) was used in jewelry/silverware whereas in Finland, the total consumption of silver was noted to be 66.5×10^6 g (2.22 Million Troy Oz) per year.

An attempt has also been made to determine source categories of silver emissions and also to estimate the discharge of silver to the environment of Finland and the other Nordic countries.

Introduction

The last decades have witnessed progressive increase in the influence of industrial activities due to which there is sharp increase of the emission of toxic metals (Nriagu and Pacyna 1988; Nriagu 1990). Emission data for trace elements such as arsenic, cadmium, lead, mercury and many others from low- or high-temperature processes are available. But very limited information exists on the emission, bioaccumulation and toxicity of silver in the ecosystem. It is no doubt that dissolved silver compounds are toxic to the aquatic species.

The purpose of this study is to find out the recovery pattern of silver, its use and industrial discharge to the ecosystem of the Nordic countries. This information will be helpful to the responsible bodies to formulate policies for the prevention of heavy metal emission. In addition, information gaps between governmental authorities, industry and scientists on silver scenarios in the Nordic countries will be reduced to some extent.

Production

The quest for precious metals by primitive man has been mentioned by the early Egyptians and Babylonians and still today the same quest is followed by the modern civilization and hence the Nordic countries are no exception.

In the Nordic countries, there is no primary production of silver but it is recovered from the non-ferrous metallurgical industry in Sweden and Finland. In Sweden, the average recovery of silver for the last 23 years is about 230 metric tons (7.4 Million Troy Oz) whereas in Finland, it is about 30 metric tons (0.96 Million Troy Oz) (Fig. 1).

Silver is also recovered from photographic materials, electronic scrap and jewelry waste. The recovery of silver from photographic processes is based on several processes including electrolysis, ion exchange and oxidation of silver complexes with hydrogen peroxide (Knorre et al. 1988). It is estimated that in Denmark, Finland and Norway about 12 to 13 million m^2 of photographic materials containing 2.5 g Ag m^2 (average) were imported and the recovered silver percentage was estimated to be 95%. On the other hand, in Sweden, the import of photographic films and papers varied between 12 to 15 million m^2 in 1993. The total recovery of silver from the photography industry in the Nordic countries (excluding Iceland) was about 57 to 67 tons (1.81 to 2.15 Million Troy Oz) per year.

Silver use in the Nordic countries

The silver use pattern in the Nordic countries differs somewhat from the global use pattern. The global use pattern of silver for the 1980s was maximum (38%) in the sector of photography (Silver Institute 1994) whereas jewelry and silverware use became largest end use market in Norway, followed by Finland, Sweden and Denmark in 1993. It is amazing that about 20 g Ag per capita was used in jewelry and silverware in Norway whereas the minimal use pattern (2 g Ag per capita) was noted in Denmark (Fig. 2). The use pattern of silver in the Nordic countries is cited in Table 1. Though some data are not available for Sweden, Denmark and Norway but still this study indicates that the maximum demand of silver was noted to be 100.54 metric tons (3.23 Million Troy Oz) in Norway where the total population is about 4.2 million. However, the consumption pattern of silver varies in the following order: Norway > Sweden > Finland > Denmark.

Table 1. The Use of Silver in the Nordic Countries (Excluding Iceland), 1993.

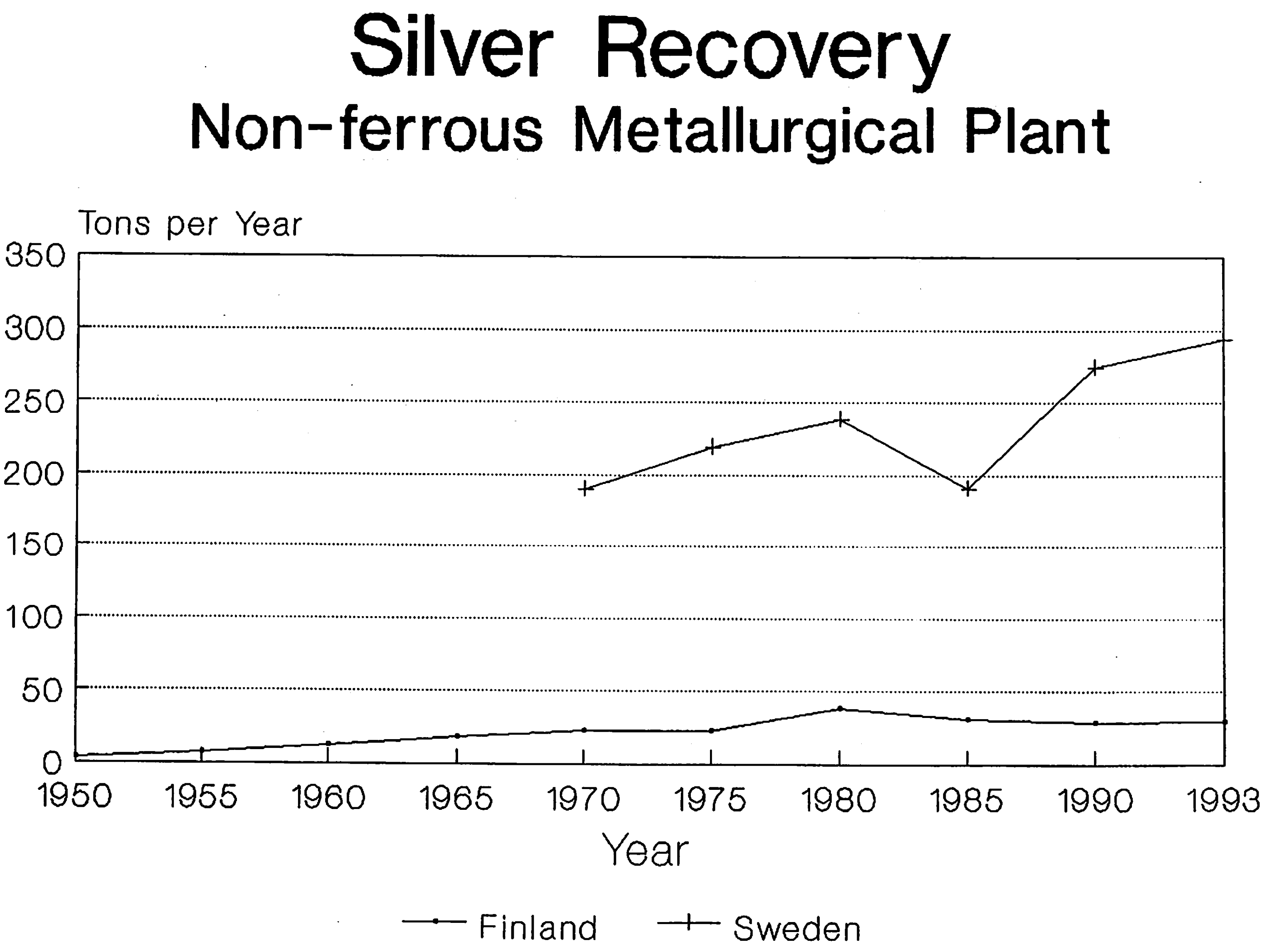
		kg* yr^{-1}		
Sources	Finland	Sweden	Denmark	Norway
Jewelry & silverware	42,000	26,000	12,000	90,000
Photography	10,000	37,000	10,500	10,000
Coinage	7,470	1,250	310	20
Electroplating	2,000	400	-	-
Brazing[1]	1,350	2,000	-	-
Mirrors[2]	700	0	0	0
Dental[3]	520	1,720	645	520
Batteries	100	-	-	-
Electronics	2,370	-	-	-
Miscellaneous, (Lab. etc)	-	1,000	-	-
Total	**66,510**	**69,370**	**23,455**	**100,540**

Note: A dash indicates that the quantity used is not available.

Note: 1. 15% Ag is in the material. 2. Calculated as pure Ag. 3. It is assumed that amalgam contains 43% Ag. 4. Scrap contains 500 to 1400 g Ag t^{1} (average value: 950 g t^{-1}).

*To convert metric ton to Million Troy Oz, divide by 31.1.

Fig. 1.

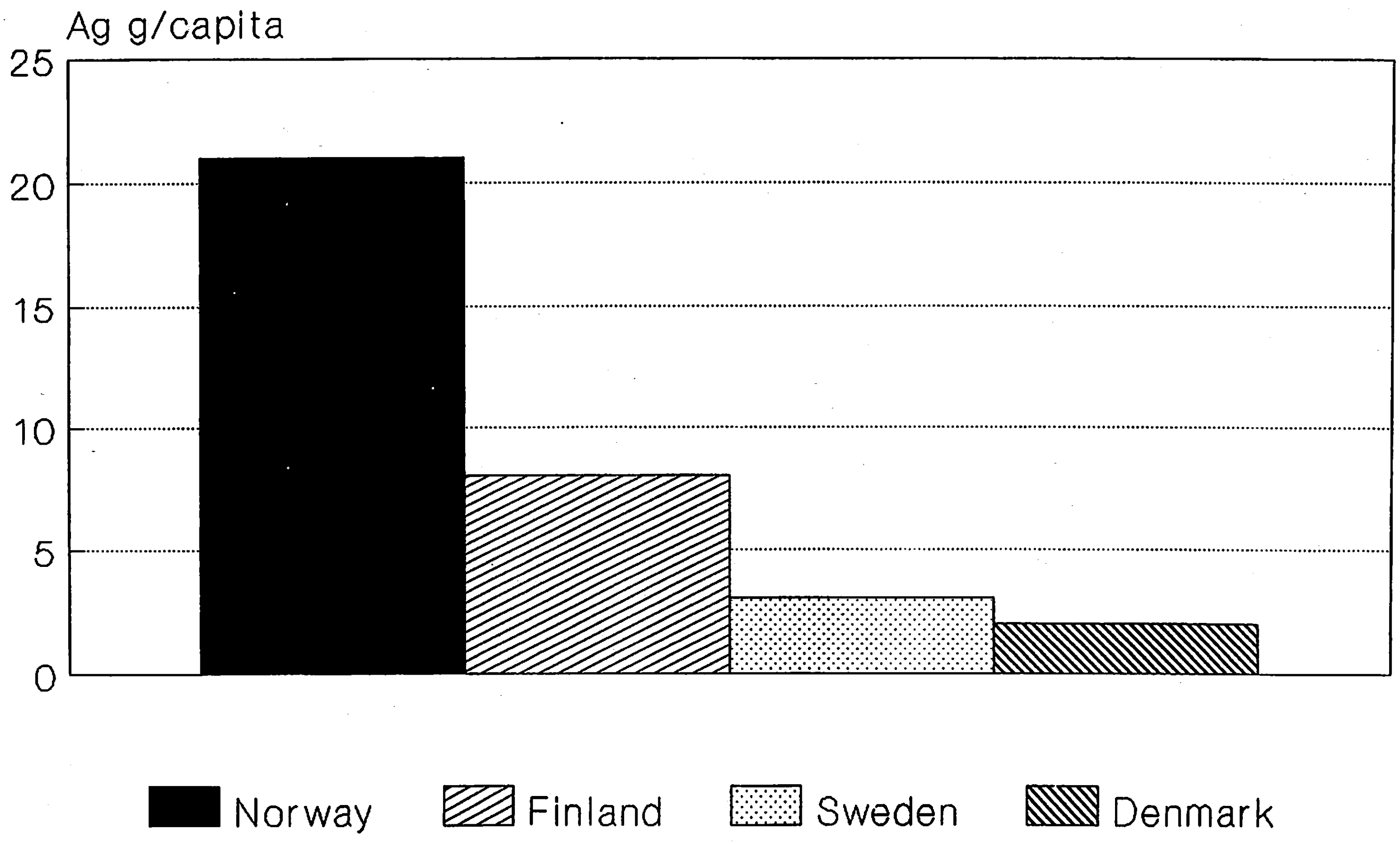


Silver Recovery
Non-ferrous Metallurgical Plant

Fig 2.

Silver use in Jewelry / Silverware

Per Capita in Nordic Countries



Silver discharge from anthropogenic sources

The chief sources of silver losses to the environment have been identified and their annual magnitude to the environment of Finland is shown in Table 2. It is believed that due to high boiling point of silver (2163 °C; 3925 °F), its emission to air is in the particulate form. Very little is known about possible vapor concentration of silver to the atmosphere (Bertine and Goldberg 1971). In this study, it is observed that maximum emission of silver occurs from utility boilers and forms of silver in the atmosphere are probably as silver sulphide, silver sulfate, silver carbonate, silver halide and also metallic silver (Smith and Carson 1977). Maximum aquatic discharge of silver occurs from photofinishing and silver recovery plants.

Table 2. **The Release of Silver (kg yr^{-1}) into the Finnish Environment, 1993.**

Source Category	Air	Water	Land
Mining & milling	0	0	0
Zinc plant	0	0	20,000[1]
Copper plant[2]	50 + ?	-	-
Cement industry	0	0	0
Power plants[3]			
- Coal	460	0	5,600
- Peat	50	0	600
- Crude oil	3,500	0	0
Secondary metal industry	-	-	-
Photo finishing & silver recover plant	10	500	0
Dental	0	0	520
Scrap	0	0	2,300
Waste water treatment plant	0	-	-
Total	**4,070**	**500**	**29,000**

Note: A dash indicates that the quantity discharged is not known

Note: 1. Silver as silver jerosite (Karlman, pers. commun.). 2. (Outokumpu Oy, pers commun.). 3. Air emission calculated on the basis: Ag content mg kg^{-1} (Coal: 1.7; Peat: 0.4 and oil: < 2.2); fuel burned: Coal: 5.39×10^6 t; Oil: 1.64×10^6 t; Peat: 5.2×10^6 t (containing 50% water).

The Finnish emission inventories and the best estimates have been applied to find out the total emission of silver to air and water in the other Nordic countries (Table 3).

Table 3. **The Tentative Estimation of Total Discharge of Silver to the Environment of the Other Nordic Countries, 1993 (Unit: kg yr^{-1}).**

Country	Air	Water
Sweden	6,100	1,700
Denmark	4,000	500
Norway	4,000	525

Conclusions

The present study indicates that the maximum recovery of silver occurs in Sweden and it was about 320 metric tons (10.28 Million Troy Oz) in 1993. The use pattern of silver varies from country to country and the maximum use (100.54 tons, i.e., 3.23 Million Troy Oz) was noted in Norway though complete information was not available.

This is the first attempt to estimate the emission of silver in the environment of the Nordic countries. Hence, there exists more latitude for future studies. However, it is observed that maximum silver emission to the atmosphere occurs from the energy producing industry whereas estimated maximum aquatic discharge of silver stemmed from photofinishing and silver recovery units.

It is necessary to study further discharge of silver from precious metal plant and photoprocessing industry. In addition, silver in drinking water, sludge, lake sediments should be measured. It is also necessary to find out fate and effects of silver in photoprocessing effluent.

Acknowledgement

I am grateful to the industry and government officials of the Nordic countries for supplying me valuable current information on silver. I am also grateful to Professor Anders W. Andren, Director, Sea Grant Institute, University of Wisconsin-Madison for the grants to present this paper to the 2nd International Conference on *Transport, Fate and Effects of Silver in the Environment* at Madison, USA. The assistance received in preparation of this manuscript from the staff member of the Department of Limnology and Environmental Protection, University of Helsinki is gratefully acknowledged.

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Questions & Answers: An Initial Assessment of the Production, Consumption and Emission of Silver in the Nordic Countries

No questions.

Nature and Fate of Silver, Part I

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Introduction:

This is a report on ongoing study of the geochemistry and fate of Ag in the environment. The study is classified as follows:

1. Ag binding mechanisms
    - Ag - S - (Fe)
    - Ag - carboxyl groups on organic matter
    - Ag - organo S coordination
2. Mobilization of Ag at Cobalt, Ontario camp
    - Ag mobilization in an inorganic setting
    - Ag mobilization in sewage outfall

Section 1. uses the existing literature on Ag association, mostly in minerals, and the crystal chemistry of Ag, to propose coordination in other media, especially with organic municipal wastes. Section 2 is an empirical assessment of the levels of Ag and its mobilization in a mining camp which has tailings with concentrations above crustal background levels.

The crystal chemistry and the coordination of Ag in "simple" inorganic crystalline solids is complicated. Ag, a group "B" element is somewhat similar to Cu, and binds very strongly with sulfur. Thus the solubility of Ag_2S is very low ($K_{so} = 10^{-49.7}$).
Argentite has been analyzed, and it has 2-fold, 3-fold and modified tetrahedral coordination of S about Ag. There are many unoccupied sites for these coordinations to exist (1). In a similar manner, Ag tends to form stable linear (2-fold) coordination bonds with S in organic substances. Ag also forms bonds with COO^- and O, but they are much weaker than coordination with S. Examination of stability constants for Ag with various compounds (2) confirms the binding strength. Stability constants (log k) range from 3.5 to 4.5 for carboxyl associations, 4.6 to 8.0 for S chelate associations and from 7-13 for S - Ag -S linear associations.

Control of Ag aqueous concentrations may be considered from a solubility or from an adsorption aspect. Little adsorption data exist for Ag for natural substrates, but one may estimate that binding strengths would be similar to those for Cu.

Solubility control of Ag concentrations may consider different minerals in the oxidizing and reducing environments. AgOH may be important in an oxidizing environment and for middle to high pHs. Thus Ag concentrations would be 1.6, 0.9 and 0.5 µg/L for pHs of 7.5, 8.0 and 8.5 respectively. Ag_2S solubility has been investigated for an inorganic system quite carefully (**3**). Ag forms a number of sulfur complexes, $AgHS^0$, $Ag(HS)_2^-$ and $Ag_2S_3H_2^{2-}$, which control the aqueous concentration of Ag. Figure 1 shows the relationship between total soluble Ag^+ and total sulfide for an assumed pH of 7 and 8. At low S_t near 10^{-3} m/L, $AgHS^0$ is the predominant species, but at values above 10^{-5} S_t, $AgHS^0$, $Ag(HS)_2^-$ and $Ag_2S_3H_2^{2-}$ are all significant aqueous species. This system predicts concentration levels of Ag^+ similar to those found in the environment.

In most systems, there is an excess of dissolved organic carbon which with/without S can bind Ag. Data are lacking at present on association with DOC, but one might estimate from stability constant, a distribution of solid to liquid (L/kg) of about 10^{-5}.

The association of Ag with S is, however, seldom simple. Ag_2S is commonly found with other metal sulfides. A summary of common mineral associations of Ag and other metals is:

Simple: Ag_2S (amorph.), Ag_2S (acanthite), Ag_2S (argentite)

Complex:
with Fe: Ag-Fe-S, from Ag-Fe_2S_3 to Ag_2Fe_5S
with Cu: Ag-Cu-S, from Cu/Ag of 0.29 to >1
with Pb: Ag-Pb-S, variable stoichiometry (viz PbS, galena)
with As: Ag-As-S, Ag_7AsS_6 to $AgAsS_2$

also with Sb, Ni (Fe), Cu-As and Pb-Sn
The more important multi-metal system is probably Ag-Fe-S.

Cobalt, Ontario Field Study

Silver was studied in the field at the mining camp of Cobalt, ON. This camp, in northern Ontario, was the major producer of Ag from the early 1900s through about 1935. The camp was rejuvenated again in the 1960s and 1980s. The Ag is commonly found in a $CaCO_3$ gangue and is associated with diabase emplacements. The aqueous geochemistry of the area is therefore buffered at a pH of 7.5 to 8.5 from equilibration of the $CaCO_3$.

The abundance of Ag in various environments is summarized in table 1. It is apparent that Ag is somewhat concentrated in fine grained organic sediments. Of course some of the black shales may contain sulfide minerals, accounting for the elevated Ag. A similar conclusion can be made for municipal sludges. Anthropogenic concentrations are commonly one order of magnitude above crustal backgrounds and in some cases more. In comparison, the ambient concentration of Ag in tailings from Cobalt are commonly nearer the highest levels found in the environment.

Two sites were studied. One was a partially filled lake (Cart Lake) with little or no vegetation. There is a stream draining the side of the tailings pond, and the tailings are above the water table except for a small dammed catchment at the downstream portion. Cart Lake then drains through a series of ponds and streams across another (older) tailings filled Lake Crosswise. Here there is a well developed vegetation growing on the tailings. This in turn drain through Farr Creek which connects with Mill Creek.

FIGURE 1.

Ag_2S solubility: Effect of Total Sulfide

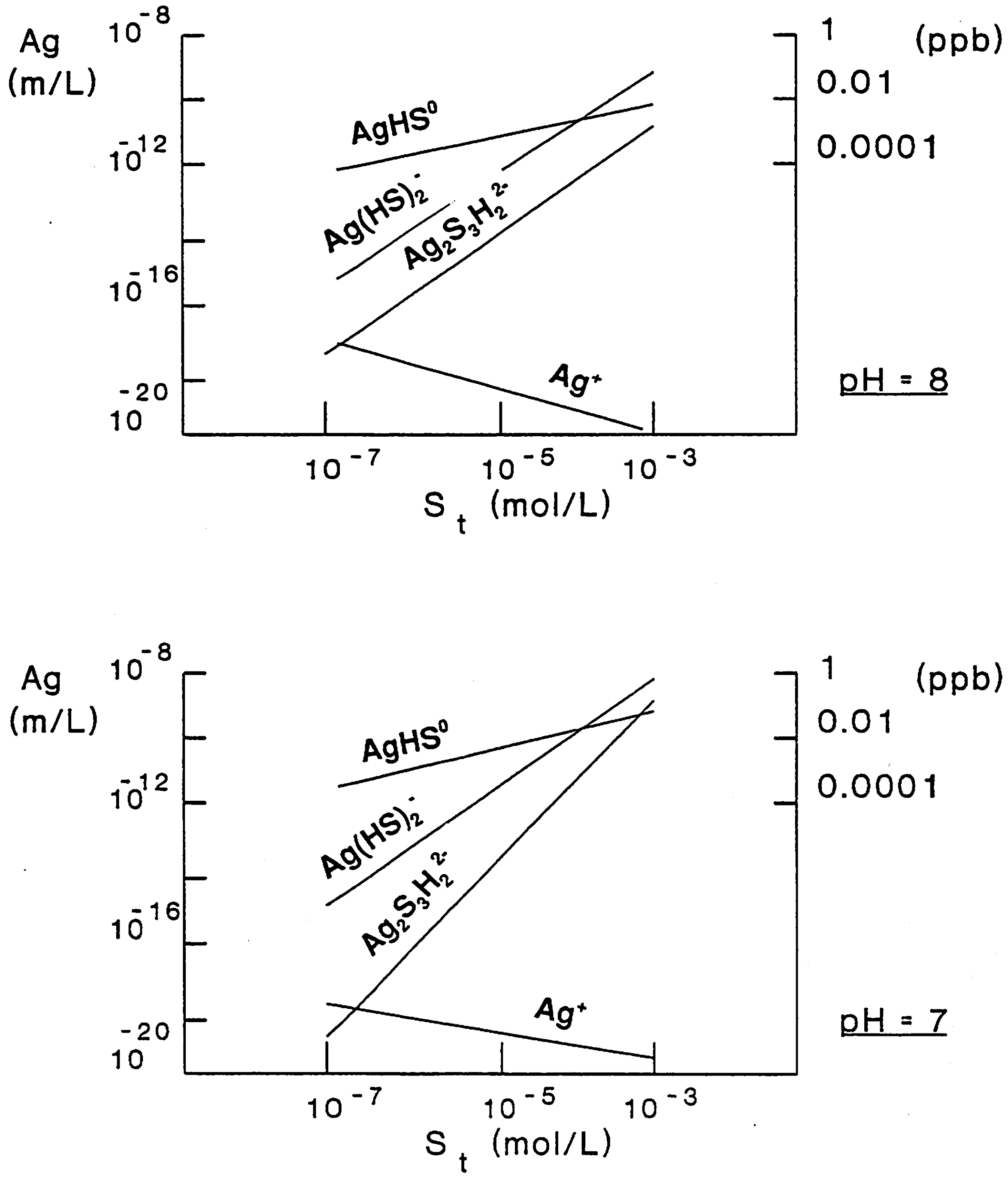

Table 1. **Concentration of Silver in various settings.** Data from (4) and this study. Values in mg/kg (ppm).

Crustal Backgrounds:	
granite	0.04
diabase	0.12
shales	0.10
black shale	0.2 - 5
deep sea	0.11
Suspended sediments in rivers	0.3 - 15 (urban)
Modified Solids:	
Soils 0.1 - 5 (0.3 = av.)	
near mines	10
Sewage sludge	0.5 - 4
Cobalt region:	
Cart Lake	3 - 23

Table 2. Cart Lake and downstream data for Ag. (FA) - field filtered (0.45 μm, acidified)

	Water (FA) (ppb)	*Soil/H_2O (log K_d)*	*Roots/Soil mass/mass*	*Grass/Roots mass/mass*
Cart Lake:				
S, upstream	< 0.01	--	0.77	0.16
Tail, SE	< 0.01	--	1.3	0.10
Tail, middle	< 0.01	--	NA	0.36
Tail, N end	< 0.01	--		
N, Lake end	1.2	2.8	NA	NA
(revegetated)	NA	--	1.0	0.14
Downstream:				
	< 0.01	--	0.38	0.33
Cross. L. Tails	0.73	3.4	**5.2**	0.017
up from Mill Ck	< 0.01	--	**6.0**	0.17
dn from Mill Creek reveg. tails	< 0.01	horsetail:	**26**	0.0023
		grass:	**4.3**	0.021

Mill Creek is the outlet of the sewage outfall from Cobalt. the Sewage outfall connects with Sasaginaga Creek and Mill Creek. Both of these creeks drain old tailings and mine outfalls. Hence they are elevated in metals and Ag. This system in turn connects over about 1 km to Farr Creek.

Thus study of these areas allowed the measurement on the retention of Ag in an "inorganic" oxidizing system and in an organic-reducing (in part) system.

Table 2 is a summary of the analytical data for Cart Lake (pH range for water data ranged from 7.9 to 8.6), whereas table 3 is a summary for the sewage outfall.

Table 3. Sewage outfall and downstream. (FA) - field filtered (0.45 µm, acidified)

Reference:		
Cobalt tap water (FA):	0.10 ppb	
Sewage outfall, size fractioned:		
< 0.45 µm:		0.63 ppb
< 100 000 MW	nd (< 0.01)	
< 10 000 MW		nd (< 0.01)
< 1 000 MW	nd (< 0.01)	

Downstream from sewage outlet:	*Water (FA) (ppb)*	*Soil/H_2O (log K_d)*	*Grass/H_2O L/kg*	*Roots/Soil mass/mass*	*Grass/Roots mass/mass*
Sewer outlet	0.1	5.1	3 100	--	--
downstream	0.4	4.3	3 000	0.03	--
input, Sass	0.05		2 100	--	0.11
below input	0.01	3.6	46 000	0.20	0.11
Mill Creek input (tailings):					
input	6.9	3.4	124 000	1.4	0.30
downstream	0.07	3.7	1 300	3.0	0.09

There are a number of points to be made from these data.

- Ag does not increase in solution when water passes through tailings with excess Ag. All of the FA values at Cart Lake were not detectable (using ICP-MS with a detection limit estimated at 0.01 µg/L). The measurable value at the outfall may be due to groundwater seepage.
- The nd level of < 0.01 µg/L is less than what is often found in ambient urban waters (i.e. about 0.1 µg/L). Is the higher Ag in other natural waters associated with colloidal organic matter?
- When water flows over tailings with vegetation, the Ag may increase, but goes to background levels again in a few meters distance.
- Ag is rapidly concentrated in vegetation in the roots and grass. Roots concentrate more Ag than the grassy parts.

Concluding Statement

From this study, one may propose that Ag is rapidly concentrated in the organic fraction. Furthermore much of the Ag in urban environments may exists as colloidal organic Ag bound material, rather than in true solution. This may also be the case for Ag and other trace metals found in organic wastes. How stable the metal-organic binding is over time must be ascertained.

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Questions & Answers: Nature and Fate of Silver - Part I

No questions.

Session II

Silver and Other Tracers of Sewage Particles in Coastal and Deep Sea Sediments Off the East Coast, USA

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Silver concentrations are often 1,000 times higher in sewage particles than in uncontaminated fine-grained marine sediments, making silver a useful tracer of sewage particles discharged into marine waters. Typically, the primary source of silver in municipal waste streams is from photographic uses, with some contribution from electronics and electroplating industries. We measured gradients in the concentration of silver in sediments with distance from sewage discharges at the mouth of Boston Harbor and from the sewage sludge dumpsite on the Continental Rise (water depth = 2,500 m) 106 miles (171 km) southeast of New York Harbor. At both locations, the assumption that silver was introduced with sewage particles is supported by a strong linear correlation between the concentrations of silver and spores from the bacterium Clostridium perfringens, a biological indicator of sewage (Hill and others, 1993; Keay and others, 1993; Bothner and others, 1993). At the 106-Mile Dumpsite, silver is also positively correlated with linear alkylbenzenes and coprostanol, additional markers of sewage contamination (Bothner and others, 1994).

Silver analyses are part of a comprehensive research and monitoring program in coastal Massachusetts designed to identify the possible environmental effects of a $4 billion sewage-treatment facility, that, in 1996, will discharge treated effluent 10 miles (16 km) seaward of the present sewage-effluent outfall at the harbor mouth. The distribution of silver in surface sediments (Fig. 1) and in sediment cores has contributed new information about the fate and transport of sewage particles

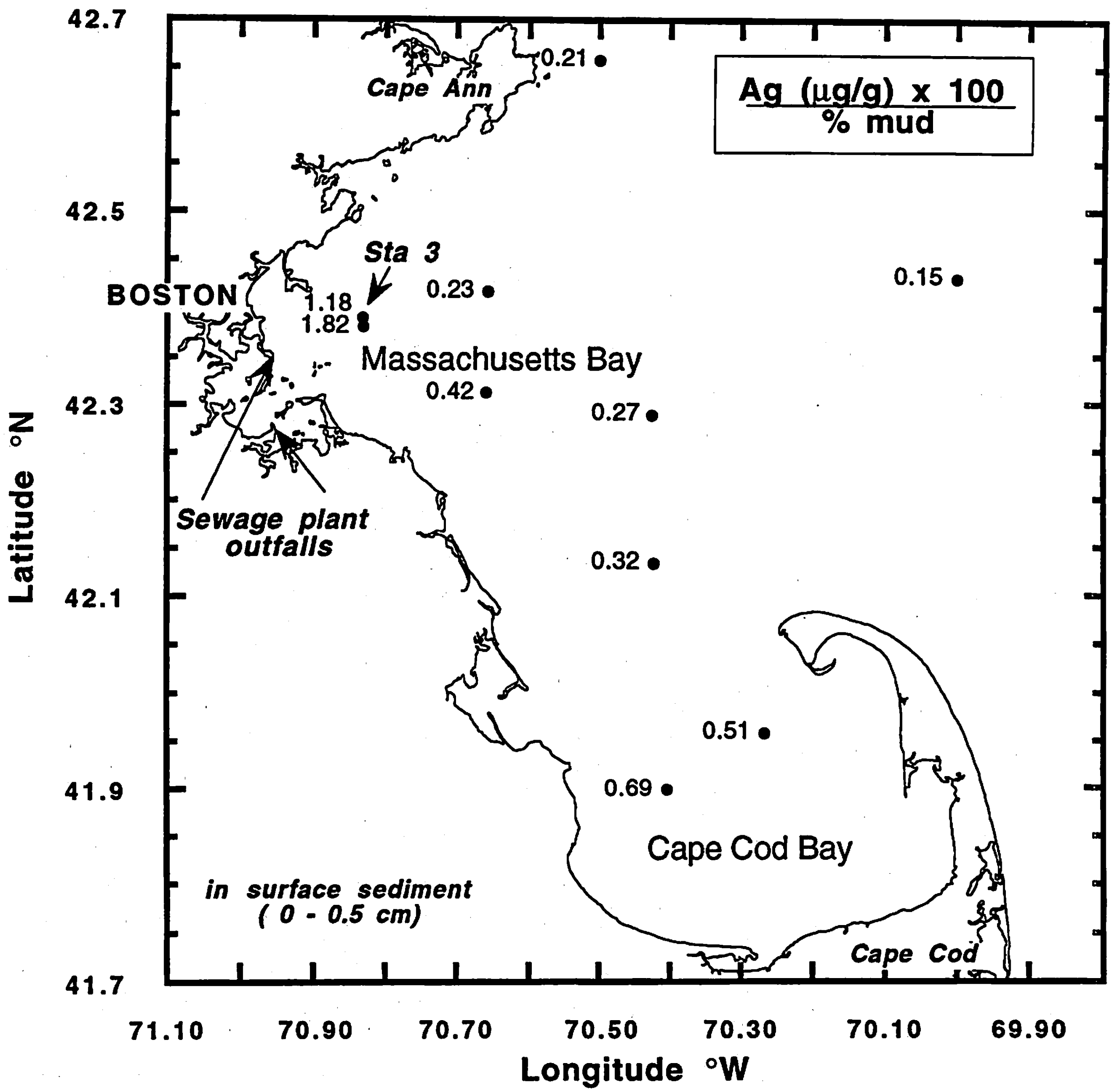

Figure 1. Concentration of silver (normalized by the %mud) in surface (0-0.5 cm) sediments collected at 10 locations with a hydraulically damped gravity corer (Bothner and others, 1993).

discharged from the present outfalls. Silver concentrations and inventories, as well as concentrations of Clostridium perfringens, are anomalously high in Cape Cod Bay. The Boston sewage-treatment plants are the only known major sources of these analytes. Thus, the silver distributions suggest that material introduced to Massachusetts Bay at the mouth of Boston Harbor can be preferentially deposited in Cape Cod Bay, 45 miles (72) km to the southeast. Transport and deposition from Boston to Cape Cod Bay is reasonable based on the average current pattern defined by Geyer and others (1992) who showed a southerly current flow along the western shore of Massachusetts Bay into Cape Cod Bay where slow current flow and protection from storm waves increases the probability of fine-grained particle deposition.

Silver in this system may be preferentially associated with fine-grained, organic-rich particles. Figure 2 shows the distribution of silver and organic carbon in mechanically separated size fractions (Barbanti and Bothner, 1993) in a sandy sediment from Massachusetts Bay. In this sample, the fraction finer than 16 microns (30% of the bulk sample) contained most (75%) of the silver. Silver concentrations in the <2 micron fraction were 1.7 ppm compared to 0.6 ppm for the bulk sample. Organisms living in sand and selectively feeding on the fine fraction may receive a larger dose of silver and other heavy metals than suggested by the concentrations in bulk sandy sediments.

We are determining the concentration and isotopic ratio of osmium in the same Massachusetts Bay sediments that have been analyzed for silver. Osmium is a platinum group metal that is used in medical research as a tissue stain for electron microscopy. The concentration and isotopic composition of osmium in municipal sewage containing medical wastes has been used as a potential tracer for medical wastes in the coastal environment (Esser and Turekian, 1993). Preliminary results show an osmium anomaly in Boston sewage particles and in harbor sediments and a measurable signal in offshore sediments having high silver concentrations. Because

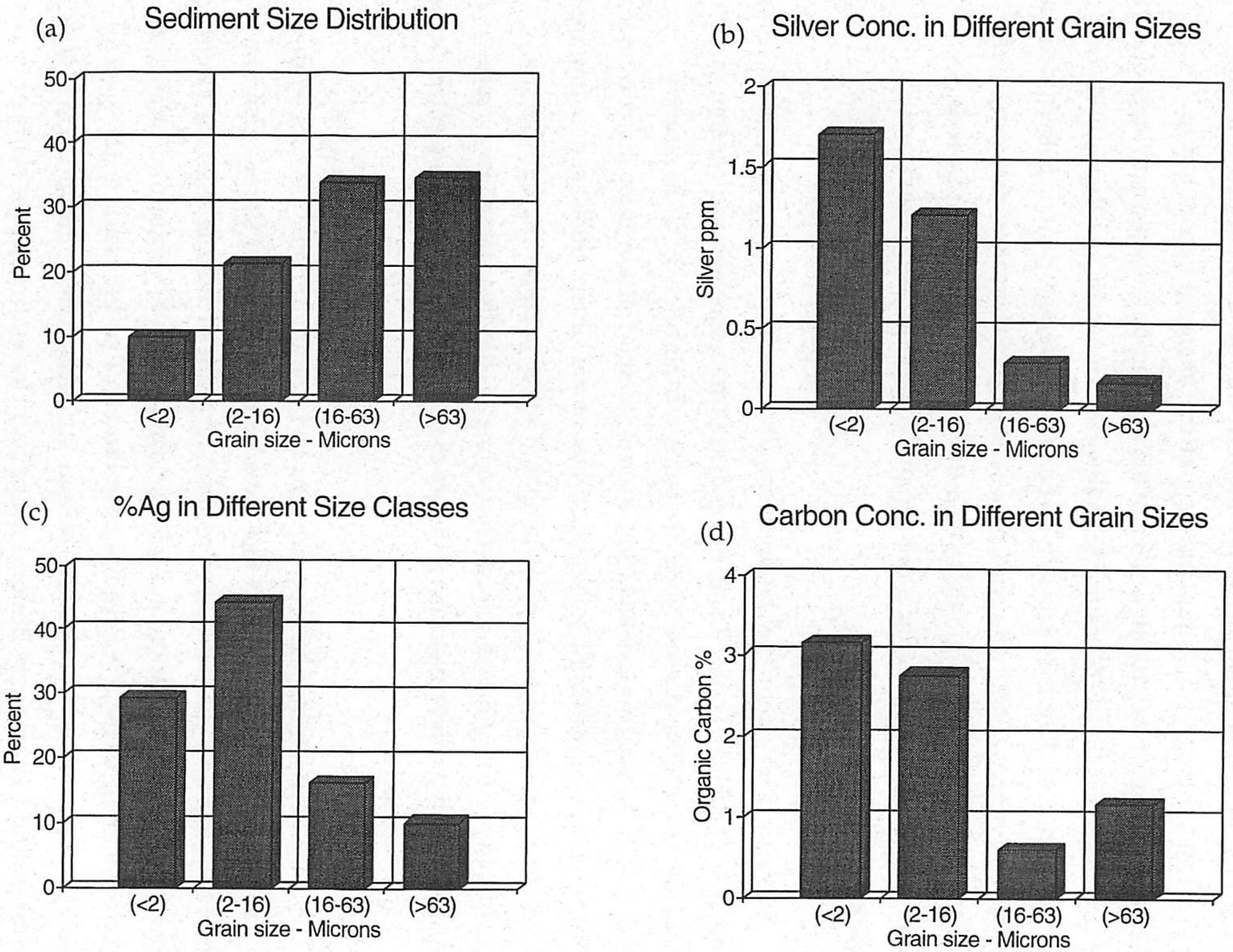

Figure 2 (a-d). Distribution of sediment texture (a), silver concentration (b), inventory of silver (c), and organic carbon concentration (d) within different size fractions of a sandy sediment in Massachusetts Bay (location immediately south of Station 3, Fig. 1). In this sample, the fraction finer than 16 microns (30%) of the sample contained most (75%) of the silver. Silver and organic carbon concentrations are similarly distributed with highest concentrations in the finest fraction of the liments. The bioavailability for organisms living in sands and selectively ingesting fine particles need be luated.

of the many medical research centers in Boston, osmium may be a unique tracer of the sewage wastes from Boston and may also help confirm the source of silver found offshore. We are conducting additional work to define the associations and chemical behavior of both silver and osmium in this region.

At the 106-Mile Dumpsite off New York, silver and the other chemical tracers of sewage sludge (linear alkylbenzenes, coprostanol, and Clostridium perfringens) were used to trace the deposition pattern of sludge. The silver distribution showed that a fraction of sludge discharged at the surface rapidly settled to the bottom (2,500 m) in a spatial pattern that agreed with the sludge deposition model of Fry and Butman, 1991. The highest concentrations of silver and all of the other sludge tracers were found along the western edge of the dumpsite (Fig. 3) and decreased gradually in the direction of mean currents to the southwest (Takada and others, 1994; Hill and others, 1993). The sludge tracers were found throughout the upper 6 cm of sediment following the 1989-1992 dumping period. This is much deeper than can be explained by rates of burial by sedimentation (0.5-1 mm/yr) and suggests that biological mixing of the sediments beneath the dumpsite is an active process.

The cessation of dumping in July 1992, has provided an unprecedented opportunity to document changes in silver and other sludge-derived contaminants with time by natural processes. The results of continuing monitoring in these coastal and deep-sea areas will increase our understanding of fundamental biogeochemical processes in the deep sea and will help assess whether or not the world's oceans should be used for the disposal of wastes.

SILVER CONCENTRATIONS IN SURFACE SEDIMENTS (0-1 CM)

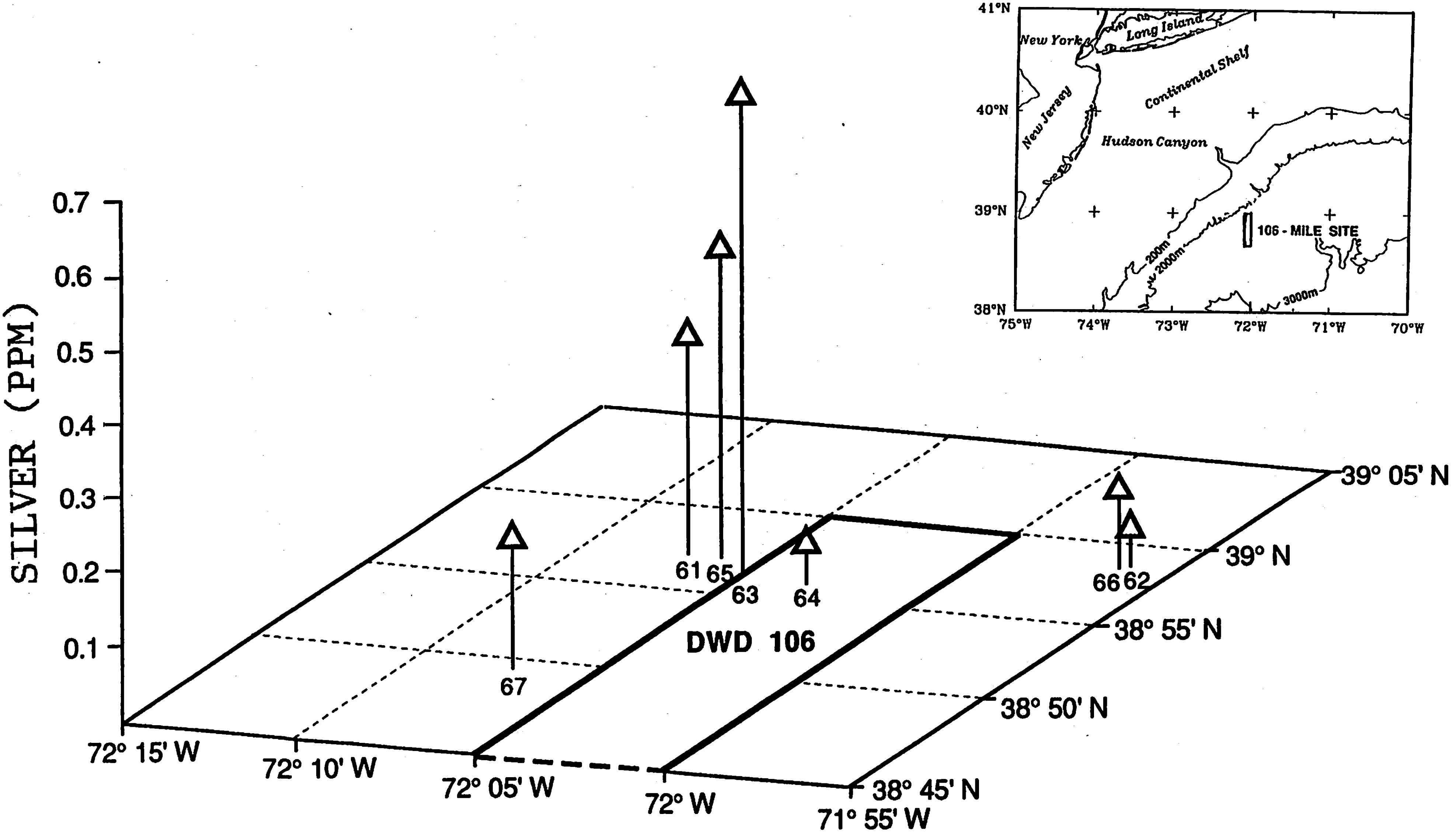

Figure 3. Three-dimensional plot showing the concentration of silver in surface sediments near the 106-Mile Dumpsite located 106 miles (171 km) southeast of New York, NY, U.S.A. (see inset). Sample locations are indicated by the last two digits of the Deep Submersible ALVIN dive numbers 2161-2167 (Bothner and others, 1994).

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Questions & Answers: Silver and Other Tracers of Sewage Particles in Coastal and Deep Sea Sediments Off the East Coast, USA

Q. GREGORY CUTTER (Old Dominion Univ.): You showed in the fluff material that the silver was decreasing in the dump site. Where's it going?

A. I'm glad you asked that. The answer's unclear at this time. If I had really definitive results — if I had more than one core that showed you that it was increasing downstream, I would have stood on that. But I'm really not — if you look at the fluff layer downstream, quite frankly you don't see any change whatsoever. But if you look at the sediment cores downstream, at one location there's a slight increase — in here between sludge stopping, and one year hence. And there are two other pieces of evidence that suggest there is southwestern transport, even of material that is initially hitting the bottom. That is that the current is increasing somewhat, and the consumption of oxygen by organic matter is changing with time. And it changes more downstream than it does upstream, suggesting that some of the organic matter, as it's being respired, is moving downstream. In another year I'll be able to really define that, when I've got more replication. So that's our suggestion.

Q. ARUN MUKHERJEE (Univ. of Helsinki): Actually, I could not understand. What is the source of silver to this sludge? Another thing, do you put this sludge in agricultural soil? And, if so, what is the concentration of silver in the agricultural soil per hectare, that means 1000 m by 1000 m? Do you have this type of information?

A. I think I have some of the first part of the information. Let's see, you asked me what was the source. From the work I've seen, the photographic wastes represent one very significant part of the silver in sewage sludge, in sewage particles. There's a small contribution from the electronic industries, but I think photographic represents the largest source. The other answer — the concentration in New York sewage sludge averages about 57 parts per million. What that translates into, moving the sludge off to agricultural uses — I don't know what limits they have, but it is a significant issue. And it's one of the reasons why silver is being reduced in sewage sludge, because there is some regulation preventing sewage sludge with high metals to be put into an agricultural arena.

Proposal to Develop a Probabilistic Wasteload Allocation Model for Silver Discharges to Surface Waters

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The objective of this effort is to develop a probabilistic model to evaluate effluent permit limits and demonstrate the advantage of a probabilistic approach over traditional steady-state wasteload allocation techniques. Wasteload allocations for silver will become more complicated as USEPA revises water quality criteria for metals. USEPA is considering expressing silver criteria as a function of temperature, pH, and hardness, as well as expressing criteria in terms of dissolved metal concentration. These changes would mean that wasteload allocations would require specification of at least 6 variables: temperature, pH, and hardness (to set the criterion concentration) effluent flow and river flow to define dilution, and additional parameters associated with defining the partition coefficient (suspended solids, and possibly organic carbon). In traditional steady-state wasteload allocations, each variable in the calculation is typically assigned at a fairly extreme value. As the number of variables in the calculation increases, the cumulative effect of each successive conservative assumption may result in effluent limits far more stringent than necessary. Probabilistic wasteload allocations avoid this problem by directly evaluating frequency of compliance with water quality criteria.

The probabilistic analysis involves repetitive calculations using randomly generated values for all the variables in the mass balance calculation. The values for each variable are randomly generated based on a mean, coefficient of variation, and distribution type (normal or log-normal). The monte carlo program has the capability to modify the order of the randomly generated values to build in cross correlation between variables, which can sometimes be very important. This option is based on spearman rank cross correlation coefficients. The output of the analysis is a frequency distribution of the ratio of receiving water concentrations to criteria. Acceptability is judged by achieving compliance with the criteria at the required frequency, usually not more than, on average, one exceedence in three years. Adjustments can be made to the effluent characteristics in order to make the calculated frequency of compliance consistent with the target frequency.

Comparisons between probabilistic and steady-state wasteload allocations will be evaluated through sensitivity analyses covering ranges in variability of effluent loading and receiving water dilution flows. It is anticipated that inclusion of partitioning, which requires specification of additional variables, will amplify the difference between effluent limits derived through probabilistic and steady-state approaches. In previous experiences with un-ionized ammonia (criteria are a function of pH and temperature) and total metals (criteria are a function of hardness) effluent limits derived from steady state techniques produced more stringent results than those from a probabilistic analysis. Figure 1 shows comparisons from several studies, and indicates that under some circumstances, the differences between the two approaches can be relatively small. In other cases the differences between the two approaches can be dramatic.

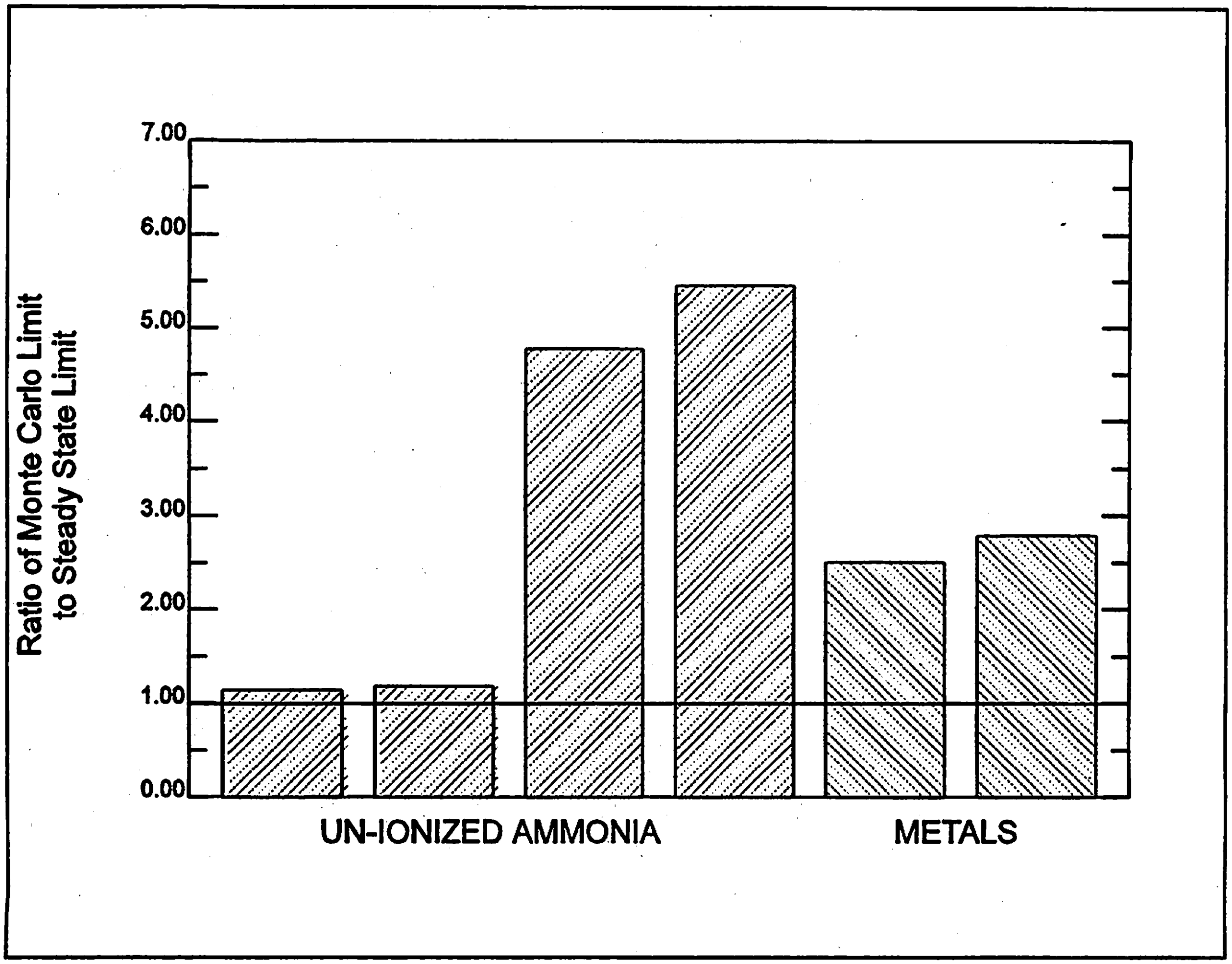

Figure 1.

Questions & Answers: Proposal to Develop a Probabilistic Wasteload Allocation Model for Silver Discharges to Surface Waters

Tape malfunction (Question and Answer session not recorded.)

Sources and Biogeochemistry of Silver in the Nearshore Waters of the Russian Far East

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Because silver has, not only a long history of varied uses in society but a long geological history also, and yet relatively little information of environment concentration, mineralogical, chemical forms, and biological effects are available, this review shows some Russian research results on sources, biogeochemistry, environmental distribution and biological effects of silver in the Russian Far East and in the nearshore waters of the Sea of Japan. The analyses was performed with a Perkin-Elmer atomic absorption spectrophotometrical method (model 303) at the Far Eastern Geological Institute, Vladivostok, (for hydrothermal minerals) and with a quantitative spectrometry PGS-2 at the Azerbaijanian State University (for biocarbonate minerals).

Silver hydrothermal deposits were formed in the Russian Far East between the Cretaceous and Paleogene periods and confined in East Asia (including China, Korea, Thailand, Vietnam, Malaysia) with big volcanogenous belts of basalts and similar deposits. The localization of silver areas is controlled by different tectonic structures including plicative and disruptive formations.

Most of Ag deposits are confined to fold geological systems, which are characterized by the simultaneous development of extensive volcanogenic belts.

The continental marginal belts contain Ag, Ag-Zn-Pb and Zn-Ag deposits while volcanic belts of island arcs contain Ag-Au pyrite and Au-Ag-Se deposits. The localization of Ag deposits is controlled mainly by complex isometric volcano-tectonic depressions as well as riftogenic structures. These are zones of active volcanic-plutonic magmatism, areas of release of magmatogenic-hydrothermal solutions, and the media which underwent hydrothermal metamorphism and now host the mineralization. The conjugated-consequent formation of volcanoplutonic associations and hydrothermal products and their spatial co-occurrence are due to the development of peripheral magmatic chambers.

In the hydrothermas of predominantly calc-alkaline magmatism, Ag was separated from belts during emplacement of subvolcanic bodies while Au was separated during the crystallization of granitoids which terminated the evolution of pericheral chambers (Kotlyar 1983). In riftogenic zones of thrachybasalt-trachyliparite magmatism, Ag seems to be derived from the mantle basaltic magma. Mineralogically, the Ag deposits are very diverse and contain native Ag, thiosalts, sulphides and Ag selenides. The deposits were formed at shallow depths and in complicated thermodynamic environments and evolved in a stage-by-stage manner. As indicated by experimental data, the Ag transportation in hydrothermas is possible as Cl^-, S^{-2}-, HS^-, OH^- complexes, perhaps as CO_3^{-2} and HCO_3^- complexes as well as in the form of Ag^{o} (aq.). The identified peculiarities of the development are typical, not only of Ag, but also of Au-Ag, some Sn, Sn-Ag, Ag-Pb-Zn, Au-Cu-Mo and perhaps Sb-Hg deposits distributed in the volcanic belts (Shilo and Goncharov 1984).

The concentration of Ag in hydrothermal minerals changed from 13.0% to 59.25%. The ratio Ag:Pb in raw material (mineral matter) show that concentration of Ag in the nearshore waters are connected, not only with lead industry production, but also with direct solution from volcanogenic deposits.

Bioaccumulation of the Ag in nearshore waters of the Sea of Japan (4-6 m depts) first was determined for the plants *Ulva fenestrata* (0.00001%), and *Phyllospadix iwatensis* (0.00004%) (Christoforova et al. 1979).

But more informative results after this were found for skeletal parts of bivalve molluscs. Our data for carbonate calcite show the following:

a) Trace of Ag was detected for the shell of *Chlamys farreri nipponensis, Modiolus difficilus, Mizuhopecten yessoensis, Mactra sulcataria, Mya arenaria japonica, Crassostrea gigas, Clinocardium californiensis,* and *Crenomytilus grayanus*;

b) Concentration about 0.0001% was determined for the calcite external layers of *Prototaca luglipta* and very common in world ocean species *Mytilus edulis*;

c) Comparatively high level of silver concentration near from 0.001% was detected only for external prismatic layer of calcite in the shell of bivalve mollusc *Mercenaria stimpsoni* (correlated with more high concentration of nickel 0.003% and middle level of copper - 0.002%).

The similarity of Ag bioconcentration led to preliminary conclusion that this result may be connected with nonspecific reactions to silver distribution in nearshore waters of the sea (after rains, storms, etc.). Species-specific variations of silver concentration between different marine plants and molluscs perhaps correlated with geochemistry of native land and habitats of ancestor forms.

Questions & Answers: Sources and Biogeochemistry of Silver in the Nearshore Waters of the Russian Far East

Q. JEROME NRIAGU (Univ. of Michigan): First of all, I must say that I'm not a biologist. I would like to point out that sometimes it is very expensive to measure some emissions of the metals. But I can take some plant species or animals from the water sources and analyze and estimate what is the emission of the metals from the anthropogenic sources. Now, could you suggest a couple of biological species which I can select to — would be proper — to find out silver emissions? What type of species would I take? Suppose if I want to find mercury, I take maybe a moss or lichen. What do you suggest for silver?

A. Not separately for silver, but for many, many anthropogenic pollutants, anything involving pollution, I suggest animals with successive layers of growth. Because only when one puts time and space scales together is it possible to understand more clear interactions between water and pollution, for example, silver pollution. This is a way for calculations, for estimations, for some probabilistic modeling, and for standards: for quality of water, quality of both animal and plant, and for man. And, for example, in environmental monitoring, only if we have some bio-models, living models, it is possible to change our approach from hard biological experiments in labs, change to natural experiments by organisms, without man, and show some indicator biomarkers of these processes. Processes of interaction, but not only chemical data separated from animals, some data about pathology or some diseases, separated from chemistry in seawater. This is integrative biomarker. And for successive layers of growth, it is very clear for me.

ESTIMATION OF SILVER LOADINGS, PHOTOCHEMICAL USAGE AND WASTE DISPOSAL PRACTICES BY PHOTOCHEMICAL USERS IN MASSACHUSETTS

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The Massachusetts Environmental Trust (the Trust) is a philanthropy that uses funds from compliance settlement agreements and other sources for environmental research and pollution prevention projects. It engaged Goldman Environmental Consultants, Inc. (GEC) in 1993 to conduct the initial research phase of its Photographic Chemical Waste Project. This project estimated photochemical use in Massachusetts by user group, waste disposal and silver recovery practices of each group, and loadings of silver recovered or disposed to sewer and groundwater. It also assessed regulatory and other barriers to better waste management, and designed an outreach program to reduce waste discharges through education or more cost-effective disposal. In subsequent project phases, the Trust will carry out and evaluate the outreach program.

GEC devised an innovative "mass balance" method to estimate photochemical use and waste generation. We estimated the number of photochemical users in each group from industry data. The average volume of processing activity for each common photographic process by a typical user in each group, and the group's percentage distribution of disposal practices, were estimated using interviews and original surveys of photographers, photolabs, and printers. We used data from manufacturers on chemical replenishment rates and film and paper silver content to estimate chemical use and silver generated in solution by user group. The silver loadings discharged to sewer and groundwater, recovered onsite, and hauled offsite were estimated using the percentage distribution of disposal to each pathway and typical silver recovery efficiency for onsite treatment.

To obtain the needed estimates of the number of photochemical users in each group, several existing sources provided useful data, but additional research was required. United States Census data on the number of business establishments directly engaged in photoprocessing or related activities (printing) were obtained as a starting point. However, we determined through discussions with experts in the industry that these data were incomplete and if directly used would have underestimated the amount of photochemical use. GEC consequently obtained permission to use estimates made by Eastman Kodak Company from its Draft Silver Regulatory Impact Assessment (November 1993) for several user groups of interest which indicated many more individual establishments than suggested by Census data.

No industry estimate was available of the number of amateur and professional photographers regularly doing their own photoprocessing (an important user group), or of their typical patterns of photochemical use and waste discharge. It was unclear to what extent photographers were using any form of silver recovery. Since most photoprocessors covered by local sewer discharge regulations do employ silver recovery, it was possible that photographers and other small operations actually discharged a large percentage of the total silver discharged to sewers or to onsite disposal systems.

Consequently, GEC roughly estimated the number of this group (7,500) by determining the membership of groups to which photographers belong and the size of mailing lists in Massachusetts of photographic equipment and chemical suppliers. We also prepared a written survey for photographers on photochemical use and disposal practices. The survey was distributed by mail and in person at a major camera equipment show. GEC obtained a total of 91 responses, an estimated sample of about 1% of the population.

The survey responses provided a revealing indication of how photographers dispose of photochemicals. Most photographers responding to our survey (76% of 89 responses to this question) do not employ any form of silver recovery. This result was suspected by knowledgeable industry informants, but has not previously been confirmed by survey to the best of our knowledge. 62% of respondents stated that they were unaware of proper disposal methods. 59% of respondents discharged rinsewater or spent photochemicals to a municipal sewer system, 14% used containers or tanks for offsite disposal, and a surprisingly high 19% used onsite sewage disposal (septic systems). Photographers indicated a willingness to participate in an educational program about proper disposal methods (85%). However, only 14% were willing to pay over $1.50 per gallon for offsite disposal of spent fixer, while the current market price is approximately $2.00 per gallon. These results suggest that if silver loadings to the environment from this group are to be reduced, effort needs to be devoted to both finding a more cost-effective disposal method and to changing the attitudes of photographers about the importance of silver recovery.

GEC also conducted mail surveys to collect information on waste disposal practices of photoprocessing and printing operations. A much smaller number of responses was received (approximately 40). The responses suggested that most respondents do employ on or offsite silver recovery, but wanted more information about the applicable regulations affecting them. GEC employed information it derived from the survey and telephone interviews with representatives of each photochemical user group to estimate an approximate percentage of photochemical wastewater containing silver discharged to municipal sewers, onsite disposal systems, or shipped for offsite treatment. These sources and available sampling data were used to estimate the percentage silver recovery efficiency for onsite treatment.

GEC estimated that a total of approximately 72,400 pounds per year of silver were generated in solution in Massachusetts in 1993, with the largest sources minilabs and photofinishing labs (30,700 pounds), large prepress operations (28,400 pounds), small X-ray processors (4,400 pounds), medium to large X-ray processors (3,200 pounds), small prepress operations (2,300 pounds), and medium-sized prepress operations (1,800 pounds). Amateur and professional photographers generated only approximately 700 pounds per year of silver in solution. However, photographers discharge 3.7% of the 10,000 pounds of silver discharged to sewer and 17% of the 1,000 pounds discharged to onsite systems. Our results suggested that smaller establishments in each user group generated less total silver in solution, but were less efficient at silver recovery than larger users.

GEC also assessed current waste management regulations affecting photochemical users, and the availability of effective pollution prevention methods and silver recovery technology. We found a complex set of regulations, varying locally according to the requirements of each local sewage treatment authority. State permits were also required for industrial wastewater discharge that covered dischargers with very low disposal volume. In many cases, photochemical users were not aware of the regulations. Often, the silver discharge limits were below 1 milligram per Liter (mg/L), a level that was difficult for small dischargers to consistently meet with commonly-used silver recovery equipment, electrolytic recovery combined with metallic replacement (steel woo) cartridges. Meeting limits below 1 mg/L would require use of ion exchange resin units or offsite shipment of silver-bearing wastes, both expensive for small operations.

GEC recommended regulatory reform by use of group permits, rather than permits issued individually to each user, and use of silver limits that can be met more easily with commonly-used electrolytic units and metallic replacement cartridges. We found that a wide variety of effective pollution prevention and silver recovery options exist for photochemical users. Many of these options are most economical for large dischargers, which process enough film to make investments in improved silver recovery and photoprocessing equipment worthwhile. However, other methods, such as proper maintenance of silver recovery systems, are applicable even to small dischargers.

GEC recommended an extensive educational outreach program to increase use of silver recovery and pollution prevention methods. We recommended methods that will maximize personal contact with photochemical users by people they know and trust, such as trade association representatives. Among the recommended options were a "train-the-trainer" workshop to teach a core group of user organization representatives and government outreach staff to make a standard presentation on photochemical waste management; preparation of brochures and other outreach materials targeted to specific groups, with distribution by their organizations; changing the way photographers and other photochemical users are taught to include curriculum materials on proper photochemical waste management; and presentations at meetings of user group organizations. Beginning in fall 1994, the Trust will carry out the outreach program and evaluate its effectiveness.

Questions & Answers: Estimation of Silver Loadings, Photochemical Usage and Waste Disposal Practices by Photochemical Users in Massachusetts

Q. SAM LUOMA (USGS, Menlo Park): Although a lot of what you said sounds like it would be difficult to do, in fact, I think there's an example of such a program you describe as might be ideal in Palo Alto, California, where the person who runs the sewage treatment plant and is responsible for that part of the city, has done many of the things that you've talked about in terms of communication. And the other thing that I think he facilitated was this question of transporting the silver waste — if you calculate how much it costs for everybody to call and get their own transport, it's one cost. But if the city subsidizes a common pick-up point, and take it to a silver recycler, much as you do recycling, which is what they've done, they've been quite effective. We did some monitoring around their sewage treatment plant, and you could see the beneficial effects of that source reduction. So what you've described, really, is something that can be accomplished with a city government that cares about communicating, and uses the mechanisms you say, and cares about facilitating the recycling of this material.

A. I've seen some of that data. It does look good.

Q. MICHAEL BOTHNER (USGS, Woods Hole): You heard that we were interested in Boston Harbor and Massachusetts Bay, from one of the previous talks. I'm just curious to know if your database could be separated geographically so that you might be able to identify the source and magnitude of silver entering the Boston sewage treatment system. That would be a really great piece of information for us, to be able to assess what's coming out of the pipe right now. And, of course, the other wrinkle is what happened in the past. So two parts to the question. Can you separate your database geographically, and would you have any [idea of the magnitude]?

A. There are ways in which that could be done, but it would take some work. The sewage treatment authority, especially the MWRA, has done a much better job of data management recently — it has an automated information system that has SIC codes, and so forth in it, for different users. So with some work with that database, it probably would be possible to separate out different categories within this group. But we did not separately break that out geographically. So our study in Massachusetts aggregates to a particular level, and that was it. But [what you suggest] could probably be done. There is also more information coming out now on the actual sampling information that eventually will be in some kind of usable form. Historically, again, you could probably go back to some of the public information from the MWRA and look at the number of users in each category, in the past, over time. It wouldn't be an easy paper exercise, though. It would take some work. But there should be ways of getting at it. Our results took our graduate student a couple of months.

Q. EUGENE KRASNOV (Kaliningrad State Univ.): What would you say about pollution prevention strategies in the near future?

A. Well, there are some things that, especially for the larger users, seem to work pretty well. Many of the printers are able to recycle, recirculate fixer through electrolytic means. And the economics of that look increasingly better, as the amount of production increases. The papers that are used now have less silver in them than they did in the past. So I think the industry as a whole is doing a lot of this on a manufacturing level. I'm not sure how the silver content in the basic material that you are using varies in the Soviet Union, but I would imagine that there's room for improvement, especially on the chloride content. And just maintenance is a very important thing, and replacing the cartridges when it's necessary. Many of these treatment systems are put on and forgotten about, never used, just simply monitored, for the silver that goes through them.

ARGENTUM
AN INTERNATIONAL CONFERENCE

Session III

Silver in the San Francisco Bay Estuary

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Recent analyses of the distribution of silver in San Francisco Bay will be presented. These include measurements of total (unfiltered) and total dissolved (< 0.45 µm) silver concentrations in surface waters of the estuary, which have been collected in seasonal transects over recent years, and the initial measurements of colloidal silver concentrations in those waters. They also include measurements of particulate and total dissolved silver concentrations in sediment cores from four sites in San Francisco Bay and two control sites in adjacent embayments. All of these data have been incorporated in benthic flux calculations to quantify the role of sediments as sources and sinks for silver in the water column. The flux calculations have, in turn, been incorporated in mass balance calculations to model the biogeochemical cycle of silver in the estuary.

Q. ROY CRYSTAL (GEC): Two questions for you. How did you calculate the anthropogenic inputs to the system? And second, have you done any toxicological studies of the real importance of the silver discharges there, in terms of adverse effects to the invertebrates or other parts of the system? How important, relatively speaking, are the silver levels out there, biologically?

A. I can answer the second question easily. No, that's not what we are involved with, and that's why we're very interested in the people who are doing the bioassays in this group, for silver. Certainly the porewater concentrations of 9000 pM exceed the EPA criteria for silver. And Sam Luoma's old professor, Brian from England, pointed out that silver is the second most toxic element for some marine invertebrates. And Sam has proposed that the elevated levels of silver in San Francisco Bay may account for its relatively low primary productivity and benthic diversity. So there's some indication that silver is having an adverse effect in the bay, and Sam is going to correct me in a minute. But, in terms of the first, the values for silver from POTW's are extremely questionable, and the state Water Resource Control Board collates those data from the dischargers, and that's the data that we use. The literature — or the reported values — range by at least one order of magnitude for every element measured by these dischargers. We're in the process now of going and looking at making our own measurements of the POTW discharges, but we can't go back and recreate history, so we don't know what they were before.

The other important thing for history is, we don't know where the silver in the South Bay came from. I understand there was a very large film processing plant there, and NASA has a big facility there, and the Navy has big facilities in certain parts of the bay. So there'd be good evidence that large amounts of silver are being put in by the film processing industry. But that plant was closed down eight years ago. But if the metal cycles through the sediments like our data indicates, you know, that's unfortunate. Because it's still there. In fact, we see the same thing for copper and nickel. Because the copper discharges, POTW discharges have decreased by 90 percent, and the levels of copper that we see there now are actually higher than they were a decade ago because the flow has been reduced, and so the copper concentrations have gone up.

But the other possibility — artifact, you know, the thing that messes it up — is that, what Jerome was talking about, using mercury to extract gold. And so, Dave McCullen and his associates with the Survey showed, probably three decades ago, that in the fine sediments of the northern reach of the Sacramento/ San Joachim Bay delta, there are really high levels of mercury. And they associate those with the use of mercury in mining. And the thing is, in the South Bay, you get these fines that come down. You not only get hydraulic flushing, but you get the fines carried down by hydraulic flushing, and it may be that some of the high levels of mercury that they see in the South Bay, and the silver that goes with it, may be due to transport of silver associated with gold mining. There other problem, though, is at the South Bay. There's the New Almaden Mine, which was the largest mercury mine in North America. So you have these natural cinnabar deposits draining into the South Bay. So we're trying to resolve — and Sam, this has been a collaboration with Sam — the historic record, to see if we can distinguish these different inputs.

Q. MICHAEL BOTHNER (USGS, Woods Hole): I'm just curious to know if you ever considered the atmospheric input, from incineration, or a source like that. I'm sure it's trivial compared to the ones you've got.

A. No, it's not. In Southern California, it's not. If you use Galloway's data — and they're old — but the atmospheric inputs of silver in the Southern California Bight, we certainly include in our particular mass balance calculations. And in the study that Sergio did, he demonstrated that essentially all of the elevated silver levels in the Southern California Bight above baseline levels could be attributed to point source discharges. In fact, the Point Wilbur discharge, by itself, could account for all of the elevated silver levels in the Southern California Bight. In San Francisco Bay, because the surface area is so small, the amount of silver being put in by atmospheric deposition is essentially negligible, but you do have a problem of surface runoff. And, in fact, they're trying to decrease the amounts of copper and nickel put into this part [of the bay] — and our data showed that they exceed the EPA criteria. And what they find is that the major sources of those are now surface runoff, rather than point source discharges. So it could be that you've deposited these other things. I don't think that's the case for silver, in the bay.

Silver in the Southern Ocean

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No abstract supplied by authors.

Questions & Answers: Silver in the Southern Ocean

Q. GARY GILL (Texas A&M Univ.): Two questions. First of all, have you any estimates of the residence time of silver in the open ocean? And secondly, you showed us from your data that there's sort of two different regimes, if you think about this for the oceans. One is the Eastern Atlantic data, and then there's the rest. Is it possible to speculate about the difference in the Eastern Atlantic data due to an anthropogenic silver source?

A. Yes. Actually, I didn't calculate the residence time here. But Jon Martin did: one year in surface waters, and about 1,000 years in deep water. The reason, in the Eastern Atlantic, is mainly caused by aeolian inputs from the African deserts.

Q. Anthropogenic?

A. Well, not anthropogenic. It's just, like aluminum, with aeolian inputs, it's enough. The concentration in the surface waters in the Eastern Atlantic is very low, sometimes near the detection limit, below 0.25 picomolar.

Q. I guess my question then would be, would you be able to explain that even if you normalize it against copper? That's why I think that — I mean copper should be delivered by aeolian sources as well.

A. Yes, and the thing is. You see here, the Eastern Atlantic. If you compare the Eastern Atlantic, for copper, with the rest, it's about the same. You see, the Eastern Atlantic, at least here, has about three nanomolar. And you see the others have about the same. So I think talking about changes in silver — it's not copper, it's silver.

Q. JIM KRAMER (McMaster Univ.): My question is sort of similar. On the Eastern Atlantic, do your data include the Mediterranean intermediate waters, or is it independent of them? Because that would be a very specific source.

A. Yes. This data, actually it's Russ' and mine. Yes, the station that I show here with silver, with salinity, is a station located north of the Mediterranean. We have also at other stations the effect of the Mediterranean.

Q. GREG CUTTER (Old Dominion Univ.): Is your hypothesis that most of the deep water in the Pacific comes from the Weddell?

A. No.

Q. I mean, because the Weddell Sea is only recycled water. So it's not a source, it's just recycling that. You can't reconcile that with C-14 ages of the water mass. The other problem is that the Eastern Atlantic is a dead end. I mean, you need the Western Atlantic to compare to Pacific.

A. Yes, you're right. We need the Western Atlantic to compare to the Pacific. We don't have Western Atlantic data.

Q. That's next time.

A. Yes, right. But, yes, these are the currents. The thing that happens is, in the west, the current from the Weddell Sea, and the current from the Ross Sea, and all the [currents] combine here. And the thing about it is not the deep water from the Weddell Sea. The Weddell Sea takes the Antarctic intermediate water. The thing that was affecting this profile from the (?) Sea is the Antarctic intermediate water, and it is the other reason I put 34.4 salinity and higher. All of these sources mix around the area, the circumpolar current. That is significant for Antarctica.

Desorption Behavior of Silver From Natural Sediments Under Freshwater and Marine Conditions

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Last year we reported on the adsorption of silver to various sediment materials [1], where we were able to obtain estimates of the conditional adsorption coefficients for environmental levels of silver. Upon adsorption, silver can remain attached for long periods, the time being a function of the surrounding conditions. Residence times in the order of 104 to 105 years [2] have been reported for estuarine and oceanic sediments. High binding capacity for silver correlates with the combined influences of sediment composition (amount of organic matter; iron and manganese oxides, clay, redox conditions, etc.) and other properties like texture, water content and weathering effects (e.g. [3]). For further predictions of silver reservoirs in the environment, additional knowledge about postdepositional migration, including kinetics of desorption, is necessary. Therefore, we investigated the desorption kinetics of silver to several types of particles as a function of a variety of variables, including chloride concentration and pH. The experiments were designed to simulate conditions encountered in both fresh and estuarine conditions. Silver speciation in the desorption solutions was modeled with the help of MINTEQA2, as the distribution over the individual species is of interest for evaluating silver mobility, bioavailability, and toxicity. At this time, we want to present results for two different sediment materials: Bentonite, a montmorillonite-type clay with a relatively homogeneous composition, whose silver adsorption capacity we previously investigated [1], and a standardized estuarine sediment (NBS #1646) from Chesapeake Bay.

Important aspects for the desorption of surface-bound silver are the surface charge of the sediment particle when suspended in the aqueous medium, characterized by the zero point of charge, pH-zpc, and the sediment's ion exchange properties. Additional reactions like surface catalyzed reduction, coprecipitation may occur during the adsorption process, leaving silver adsorbed not only as a cation, but in the form of Ag°, complexes or neutral compounds (see e.g. [4], [5]). Surfaced catalyzed reduction also may influence adsorption as well as desorption. Changes in the surrounding medium — for instance pH, redox potential, salinity, other ion concentrations (especially of those capable of forming strong silver complexes), anoxic effects — should affect the bond between silver and adsorption site. In this work, we studied the influence of the following solution parameters:

**** Salinity, or (more precisely) concentration of NaCl in the desorption solution***
An increase in salinity simulates the transport of silver-loaded particles from rivers into estuaries, where the surroundings gradually change from fresh to sea water conditions (simulated here with solutions containing 2.8 E-4 to 2.8·10-1 mol/l NaCl). Silver-chloro-complexes have high binding constants, so the formation of chloro-species at the particle surface can be expected. As the sediment materials we studied are assumed to have a negatively charged surface at our experimental pH of 8, the newly formed chloro-compounds should consequently be repelled, enabling more Cl- ligands to access the sediment surface.

**** pH of fresh water and higher salinity solutions (studied for bentonite)***
Lowering the pH should decrease the negative charge of the sediment surface and, therefore, enhance the desorption. This type of experiment can simulate the influence of local pH differences in natural waters or — especially in rivers, shallow lakes — effects of acid rain on suspended particles.

**** Sediment drying time***
Settling and burying of suspended particles and subsequent aging of sediments lead to a stronger bonding and better enclosure of silver (diffusion and incorporation into sediment lattice, shrinking of interlayer

distances, etc., see, e.g., [6]). We attempted to simulate these effects by drying the silver-loaded sediments for a defined time period prior to desorption.

* Desorption duration
In general, a two-day period was used, but we studied both shorter and longer times to learn more about the kinetics of the desorption process (within the given experimental restrictions).

* Initial silver concentration (studied for bentonite)
The influence of increasing silver concentration on the desorption was examined for several desorption solutions. Concentrations of 1-100 nmol/l were chosen to represent a range between background and slightly elevated levels [7].

For both sediment materials, desorption was negligible under freshwater conditions. Desorption under simulated estuarine conditions was also limited, but measurable. We found silver desorption for bentonite and estuarine sediment to be greatly influenced by the chloride concentration and the pH of the solution, the treatment of the silver-loaded sediment prior to desorption, and the length of the desorption period.

In the case of bentonite, silver desorption was highest in the solution of highest chloride concentration (≈12%), about 5% were desorbed in lake water at pH 5. The following table gives an overview of the results obtained in solutions of different salinity.

Table 1. Amount of Desorbed Silver in Solutions of Increasing [NaCl]

des. solution	[Ag+] in des. solution	% Ag des. of Ag ads.
LW 1	4.9·10-10 M	0.6±0.1
LW 10	6.6·10-10 M	0.8±0.1
LW 100	3.7·10-9 M	4.5±0.6
LW 1000	9.5·10-9 M	11.6±0.1

We refrained from investigating desorption in solutions of even higher [Cl-], in order to avoid the possibility of AgCl precipitation — calculations with MINTEQA2 [8] predicted AgCl(s) formation for our silver concentration range when [Cl-] exceeded 0.5 M.

Changes in the initial silver concentration during the adsorption process did not have any unexpected or unusual effects on the desorption (desorbed amount increases slightly with rising silver concentration).

During longtime desorption studies, bentonite was suspected to partly dissolve in solutions of high salinity after about three weeks, and, therefore, contribute to an increase in released silver (from 10% to 14% for the highest NaCl concentration). No such effect was observed during longtime studies in the pH 5 freshwater type solution, or for the estuarine sediment.

Independent of the adsorbing material, drying the silver-loaded sediment decreased the desorption. The effect was greater for short desorption periods. One example for bentonite: 24 h drying reduced the amount of desorbed silver to about 80% for the 2 d desorption period and to about 50% for 1 h desorption. Practically no silver was desorbed when the drying period exceeded 5 d. Similar dependence of ion-exchange capacity from water content has been observed for bentonite, zeolites and other materials elsewhere [6].

Kinetic studies with sediment that was not dried showed the desorption process to be very fast. Equilibrium was usually reached within one hour for both materials.

Under the same conditions, the amounts of both adsorbed and desorbed silver were higher for the estuarine sediment, where silver can be bound to a variety of sites (clay fraction, iron and manganese oxides, organic matter, etc.), than for the relatively homogeneously composed bentonite. In lake water with [NaCl] = 2.8·10-1 mol/l, the highest amount of released silver was 23%. Additionally, sediment drying influenced the desorption to a greater extent than for bentonite (drying the sediment for 1 day decreased the desorbed amount to about 41% of the one obtained without drying).

Calculations with MINTEQA2 for the silver speciation in the desorption solutions in most cases predicted silver to be present in the form of higher chloro complexes for both sediment materials. The method for deriving the required Langmuir modeling parameters for the adsorption process from the experimental data has been discussed previously in detail [1]. As a desorption process cannot be directly included in the MINTEQA2 program, we used the experimentally determined values for the remaining amount of solid-bound silver, and only calculated the silver speciation over the dissolved species for the various desorption solutions.

Table 2. MINTEQA2 Results for Bentonite

	Ag +f	SO-Ag	$AgCl^{\circ}$	AgCl2-	AgCl3-2	AgCl4-3
LW 1 (ads.)	12.2%	81.5%c	6.3%			
LW 1 (des.)	12.4%	81.2%e	6.4%			
LW 1 @ pH 5	18.8%	73.3%e	7.5%			
LW 10	2.8%	81.9%e	11.9%	3.4%		
LW 100		75.8%e	6.1%	17.2%	0.7%	
LW 1000		71.1%e	0.4%	11.1%	6.3%	11.1%

SO-Ag = silver bound to a surface site
c = calculated value
e = exp. determined value
LW 1 = sim, lake water with [NaCl] = 2.8·10-4 mol/l
LW 10 = sim, lake water with [NaCl] = 2.8·10-3 mol/l
LW 100 = sim, lake water with [NaCl] = 2.8·10-2 mol/l
LW 1000 = sim, lake water with [NaCl] = 2.8·10-1 mol/

Because of the similar adsorption behavior observed for both materials, the modeling parameters formerly derived for lake sediment [1] were applied to the estuarine sediment here.

Table 3. MINTEQA2 Results for Estuarine Sediment

	Ag +f	SO-Ag	AgCl°	AgCl-2	AgCl3-2	AgCl4-3
LW 1 (ads.)	1.9%	97.2%c	1.0%			
LW 1000		73.4%e	0.4%	10.2%	5.8%	10.2%

In addition to the results presented here, silver speciation was calculated for a variety of other solution compositions. Under oxygenated conditions, the amount of adsorbing material and the chloride concentration were determined to be the most influential parameters, which is consistent with our experimental results.

The observed characteristics of the desorption process seem to indicate that the relevant steps take place directly at the sediment surface. Naturally, the exact details of the reaction cannot be derived from the kind of experimental data obtained here. But, as a simple picture, the basic desorption reaction can be thought to consist of an exchange of an adsorbed silver ion against a solution proton, with subsequent complexing of the released silver by chloride ligands.

The total amount of desorbed silver is relatively small for both sediment types studied. Several reasons may be responsible for this: As was mentioned in the introduction, a certain fraction of the silver may have diffused *into* the sediment and become bonded to interlayer functional groups. Also, some of the silver may not have been adsorbed in the Ag^+ form in the first place, as reactions like coprecipitation of, e.g., AgCl and reduction to Ag (0) can occur ([4], [5]). On the other hand, the silver amount released at the very start of the desorption might have been higher than the one measured, but immediately decreased again by processes like readsorption of either Ag+ or newly formed neutral compounds like AgCl°.

Further investigations will be needed to clarify the details of the desorption process. But for a start, the experimentally observed influences of pH and chloride concentration agree well with the simple surface-desorption mechanism introduced here.

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Questions & Answers: Desorption Behavior of Silver From Natural Sediments Under Freshwater and Marine Conditions

Q. JIM KRAMER (McMaster Univ.): Anders, I'm not familiar with this MDS lake sediment. Maybe you could just briefly tell me about it. Also, in context to your comment earlier when you said, "But this does not include organic matter," I didn't quite understand. You mean soluble organic complexing?

A. Yes, that's what I meant, correct. The MDS standard, the estuarine sediment, is well-defined, well characterized. We had all kinds of measurements of total organic carbon in that part. Well, I meant the dissolved, DOM, right. But, perhaps, in estuarine sediment, as it ages, probably gives some [organic carbon] off. We didn't determine DOC in the suspension. But we used only about five, six milligrams at most in 60 ml bottles. By the way, all these experiments were done in dark, high density polyethylene bottles because of the problem that David talked about yesterday. Otherwise we could not reproduce our results very well. As we looked in the literature, actually, we called up some of the work by Jim Leckie a couple years ago, and they were saying they sort of gave up on silver adsorption experiments because, at the time, they couldn't really explain the data very well. We think the major reason for that is that they did it sometimes in light, and sometimes in the dark. And silver is very photoreactive.

Q. JEROME NRIAGU (Univ. of Michigan): Do I get it from your studies that silver should not be mobile in sediments, then?

A. No. I think that our data should be applied to oxygenated conditions, to nonliving materials. But when you do have redox conditions, of course our data are different. And [also] if the surface site changes with time, in the laboratory, and I think this is probably more directed at suspended sediments, nonliving suspended sediments.

Q. Yes, but if you were to reduce the silver, it should become less mobile.

A. To reduce the silver? It seems to indicate, from our data, that that's correct.

Silver Measurements in Texas Watersheds

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Introduction

Surface river water and estuarine water samples were collected using ultra-clean sampling protocols at nine sites in Texas for characterization of their silver content and basic water chemistry parameters. Riverine collections were obtained in seven watersheds (Red River, Hawkins Creek, Black Fork River, Trinity River, Brazos River, Colorado River, and San Antonio River), upstream and downstream of wastewater discharge points. Estuarine samples were obtained at three sites within the Houston Ship Channel (Galveston Bay) and at two sites in Corpus Christi Bay. Estuarine sampling sites were also located nearby and at some distance from discharge outfalls. These sites were chosen to represent diverse environmental settings, ranging from pristine waters with no known silver inputs to waters impacted by discharges from major urban areas. The main purpose of this study was to provide reliable silver measurements in conjunction with water chemistry parameters for regulatory purposes in Texas watersheds.

Methods

Samples were collected in the field using a peristaltic pump equipped with Teflon tubing inlets and outlets (Flegal et al., 1991). For sample collection, the tubing was attached to a non-metallic pole and the tubing inlet was oriented into the current to obtain water untouched by the sampling apparatus. Unfiltered samples were drawn directly into acid-cleaned Teflon bottles using ultra-clean sample handling protocols. Filtered samples were obtained by attaching an acid-cleaned polyethylene membrane cartridge to the pump outlet and dispensing the water directly into the Teflon sample bottle. Samples for silver determination were acidified with triply-distilled 6N HCl to a final pH of approximately 1.5.

Samples were preconcentration under class-100 clean laboratory conditions for total, dissolved (0.1 and 0.4 µm), and colloidal (1,000 Dalton cut-off) silver using APDC/DDC organic extraction methods. Prior to preconcentration, all samples were irradiated by a bank of ultra-violet lamps (100 W) to photo-oxidize organic matter present in the sample which may complex silver and interfere with the extraction. Silver measurements were conducted using graphite furnace atomic absorption spectrometry equipped with Zeeman background correction utilizing the method of standard additions to further correct for sample matrix interferences. Sample blanks and spiked samples were run with each set of samples extracted to determine yield correction factors and detection limit capabilities. We estimate our detection limit for silver measurements, based on three times the standard deviation of a blank signal combined with a sample preconcentration factor of fifty-fold, at 0.1 ng/L (0.93 pM). Separate samples were also collected for the determination of pH by *in situ* measurement with an electrode, alkalinity by standard titration methods, total suspended solids by gravimetry, major ions by ion chromatography and flame atomic absorption spectrometry, and dissolved organic carbon by high temperature catalytic combustion methods.

Results and Discussion

Total and dissolved (0.1 and 0.4 µm pore size) silver concentrations spanned more than two orders of magnitude. Total silver ranged from below detection (≤0.1 ng/L) at the Red River sites to 148 ng/L at the upriver Trinity River sites. Dissolved silver (0.4 µm fraction) ranged from below detection at the Red River and upstream San Antonio sites to 52 ng/L at the upstream Trinity River site. The 0.1 µm filtered samples ranged from below detection to 16 ng/L and had less silver than the 0.4 µm filtered samples at all sites. The silver concentration in suspended particulates ranged from a low of 14 ppb at the downstream Colorado River site to a high of 5,320 ppb at the upstream Trinity River site. Selected samples were also analyzed for colloidal silver content and significant amounts of colloidal silver (>20% of the dissolved fraction) were found. Generalizations about this silver fraction is hindered by a paucity of samples, method detection limits, reproducibility, and perhaps contamination problems.

Silver has a fairly high affinity for adsorption onto suspended particulates as evidenced by a mean particle-water partition coefficient (based on filtration through a 0.4 µm filter) of log $K_d = 5.0 \pm 0.6$ (n=13). This value agrees quite well with recent observations obtained in the San Francisco Bay and Galveston Bay estuarine systems where ultra-clean sampling and analytical protocols were followed (Smith and Flegal 1993; Benoit et al., 1994). The particle-water partition coefficient, based on filtration through a 0.1 µm filter, had a higher mean log K_d (5.4 ± 0.5) than for samples filtered through the 0.4 µm filter. Moreover, the particle-water partition coefficient exhibited a "particle concentration effect" for both filter pore size fractions; as suspended load increased, the partition coefficient decreased (Figure 1). Both the particle concentration effect and the difference in particle-water partition coefficients based on filter pore size can be readily

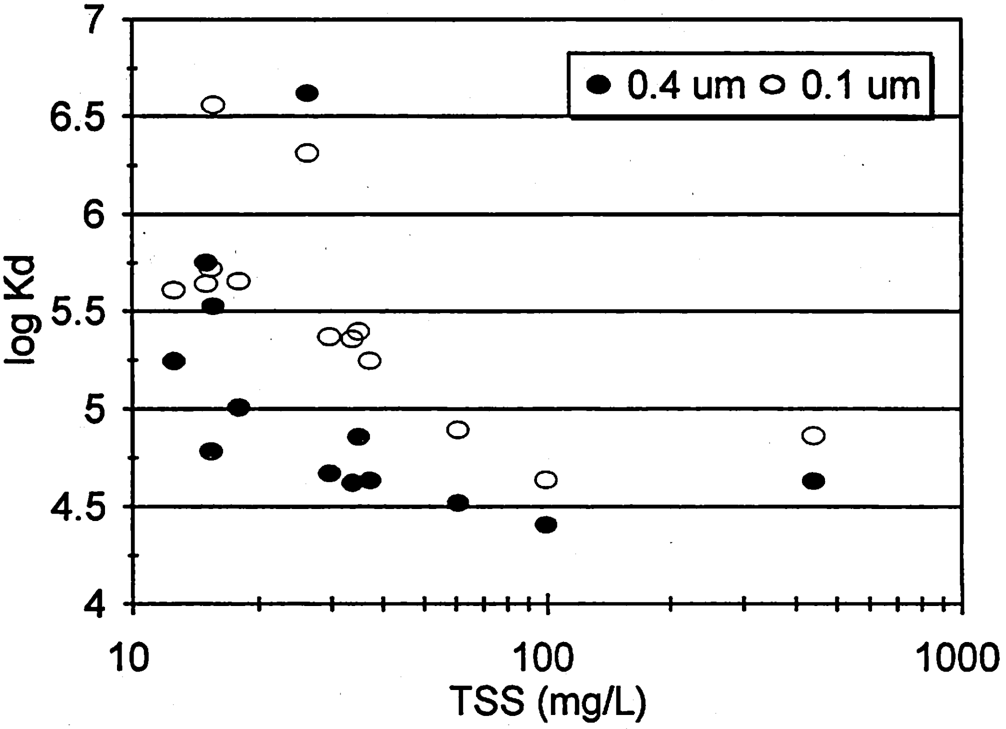

Figure 1. Particle-water partition coefficient expressed as log K_d for silver in Texas rivers and estuaries. Partition coefficients were determined based on filtration through two different filter pore sizes, 0.4 and 0.1 um.

explained by the presence of a colloidal silver fraction. The relative importance of colloidal silver can be assessed by determining how much silver was removed from the operationally defined dissolved fraction (i.e., a 0.4 μm filter) when samples were filtered through the smaller pore size membranes. Based on this comparison, 33-89% of the operationally defined dissolved silver fraction could be due to a colloidal silver component.

The partitioning of inorganic silver between free ion and chloro-complexes was conducted using thermodynamic equilibrium modeling. Free silver ion concentrations varied from 47% of the dissolved silver present, when total suspended solids and chloride ion content are low (Black Fork River), to less than 0.01% in marine systems.

Conclusions

1. Background total silver concentration levels in Texas surface waters are typically less than 2 ng/L (18 pM).
2. Downstream of major urban areas or discharges silver concentrations can increase over background levels by as much as 100-fold.
3. The mean particle-water partition coefficient for silver (based on filtration through a 0.4 μm filter) was log $K_d = 5.0 \pm 0.6$ (n=13).
4. Free silver ion concentrations can vary from 47% of the dissolved silver present when total suspended solids and chloride ion content are low, to less than 0.01% in marine systems.
5. Colloidal silver accounts for a major percentage (33-89%) of the dissolved silver present, based on the silver concentration differences observed between samples filtered with 0.4 μm and 0.1 μm pore size membranes.

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Questions & Answers: Silver Measurements in Texas Watersheds

Q. EUGENE KRASNOV (Kaliningrad State Univ.): These shrimp were from river or estuarine basin?

A. It's a marine shrimp.

Q. Salinity of what?

A. Oh, the reason we chose this particular species is it has part of its life cycle where it comes and spends in the estuary — as juvenile shrimp, it migrates into estuaries, and spends a fair amount of time in the Bay of Galveston. Galveston Bay is, like many estuaries, very impacted, as you've heard from Russ. And so that's why we chose this particular organism. Because it does have part of its life cycle that involves extended time in the brackish, estuarine waters in the bay.

Q. Did you feed them?

A. That's one of the mistakes we made. We fed them just before the experiment, which we shouldn't have done. So that's one of the complications that we're learning as we do this. I'm certain that you're familiar with these kinds of things.

Q. JIM KRAMER (McMaster Univ.): Regarding your lowest silver data from stream studies — below detection — and your highest, can you briefly summarize for us what the differences are in the environment — more suspended particles, more organic carbon. Is there any correlation in terms of environmental parameters?

A. Let me show you one thing — the only correlation that we found. I'm going to show this in terms of K_d. Here's K_d vs. dissolved organic carbon, as one of the parameters that we have indicated we needed to look at. You can draw your own conclusions, if you see anything there. But this is the one that surprised me most. If you look at dissolved silver — and again, I don't know if this is a real correlation — but it does look like that at very low chloride levels, you get a fair amount of dissolved silver. I don't know if this trend will hold true once we get more data points — there are very few here. But that's the one piece of relationship between silver and one of the water quality parameters that, perhaps, could be a significant relationship. We need a lot more data to find that out.

Partitioning and Fate of Silver in Background Streams and Effluent-Receiving Streams

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I. Background Streams

Using "clean" techniques and modern analytical methods we conducted an exploratory study of Ag levels in 49 Wisconsin, Upper Michigan, and Minnesota rivers during March and April of 1993. Nineteen of the 49 rivers are tributary to Lake Superior and were sampled near the mouths to estimate total loading to Lake Superior. Six sites represent the major river systems of Wisconsin, and were sampled at locations that integrate influences from many sub-basins. The remaining 24 sites were selected from a larger study group of 28 watersheds distributed throughout the state of Wisconsin that reflect homogeneous characteristics of land-use and principal geological variables. These streams were sampled at headwater sites where metal concentrations are not influenced by point source discharges. The 24 watersheds are used to establish "background" concentrations, fluxes, and yields of Ag and other trace elements from rivers draining characteristic homogeneous land units. In addition geochemical controls on metal levels are examined by evaluating relationships between metal signatures and the geochemistry and hydrology of these watersheds. Additional sampling for silver at a matrix of 9 Wisconsin river sites is being conducted at regular intervals throughout 1994 to examine seasonal influences on Ag levels and yields.

A statistical summary of Ag levels is presented in Table 1. Concentrations of total (acid leachable) Ag in the 49 rivers showed considerable variance, ranging from 0.9 to 75 ng L^{-1}. This variance is attributable to both large variations in SPM levels among the river sites (Ag partitions strongly to particles), and inclusion of sites in urbanized basins and near municipal wastewater treatment facility discharges. The lowest Ag levels are found in remote watersheds in streams with shallow hydrographs. Levels of total Ag in low SPM "background" sites are in the range of 1-5 ng L^{-1}. Filtrable (0.4 μm) silver distribution means are in the range of 1 - 2 ng L^{-1}, with over 80% of sample values below 2 ng L^{-1}. High filtrable Ag levels in non-impacted systems are associated with high DOC concentrations. Particle partitioning statistics are particularly valuable in interpreting anthropogenic influences and are also a sensitive indicator of watershed geochemistry. For instance; at "background" sites, the amount of Ag on particles (μg g^{-1}) was invariably less than 0.4, whereas impacted rivers show levels 2 - 3 times background. Low (<0.1 μg g^{-1}) levels of particle association were observed at sites characterized by either high DOC, high SPM, or categorized as wetlands. Partition coefficients (K_d's) averaged 230,000 L Kg^{-1} ($\log K_p$ = 5.4). Sites with low DOC and relatively low SPM show higher K_d's.

TABLE 1. Silver Level Summary - Spring 1993 River Sites
n=49

	Total ng L^{-1}	Filtrable ng L^{-1}	Particles $\mu g\ g^{-1}$	K_d L Kg^{-1}
Mean	11.3	2.1	0.37	230000
Median	5.5	1.7	0.26	183000
Mode	5.5	1.3	0.24	162000

Table 2 presents a summary of the Ag data from the homogeneous unit and major river sites in Wisconsin sorted into major Land Use classes. Total Ag levels are an order-of-magnitude higher in urban watersheds when compared with low-SPM non-urban sites. Similarly, the amount of Ag on particles in urban sites is 3 times higher than "background". Levels of Ag in the major river class are significantly elevated, reflecting the myriad of point source discharges to these systems. Total Ag levels in the driftless class are high as a result of the high sediment yields of this hilly, unglaciated area. The ensuing high SPM levels effectively "dilute" the mass weighted association of Ag with particles (0.12 $\mu g\ g^{-1}$ vs. 0.3 $\mu g\ g^{-1}$). In contrast to many other trace elements which show significant increases in stream concentrations in moving from cropland to forest to wetland dominated watersheds, Ag does not display a significant trend.

TABLE 2. Silver Level Summary - Category Means
Spring 1993 River Sites

Class	Total Ag ng L^{-1}	Particulate Ag $\mu g\ g^{-1}$
Urban	29.1 ± 26.4	0.88 ± 0.33
Major Rivers	12.2 ± 6.8	0.58 ± 0.24
Driftless	18.2 ± 8.6	0.12 ± 0.06
Forest	2.7 ± 1.2	0.34 ± 0.14
Wetland	2.5 ± 0.6	0.26 ± 0.22
Cropland	2.1 ± 0.9	0.089 ± 0.06

II. Treatment Plants - Effluent Receiving Streams

To examine the fate of Ag through wastewater facilities which are collecting waste from major silver end-users and the impact of the effluent on receiving streams, sampling was conducted at three treatment facilities in 1993 and in more detail at one plant in 1994. Results from the 1993 studies showed that in-plant removal was greater that 98% at all three plants. Ag leaving the plant was rapidly reduced to near background levels by dilution and incorporation into stream sediments. Very high levels of partitioning of Ag to suspended solids in the plant effluents was observed (450,000 - 870,000 L Kg^{-1}), suggesting an important role for particles in regulating Ag concentrations. Work in 1994 focussed on the Jackson, WI facility, a 0.5 MGD tertiary treatment plant, using RBC's, Alum/Polymer flocculation, and sand filtration. Table 3 summarizes the in-plant removal of Ag observed on three sampling dates. Total removal efficiencies were in the range of 92 to 99%, though levels of 1-5 μg L-1 Ag in the effluent are approaching 3 orders-of-magnitude higher than in the receiving stream.

TABLE 3. Silver Fate Through Jackson WWTF
Ag Levels In μg L^{-1}

Sample	May 1993	June 1994	August 1994
Inflow Grab	105	73.2	49.9
Inflow 24 hr	101	41.2	42.9
Effluent Grab	0.85	5.56	2.58
Effluent 24 hr	0.90	2.60	1.28
% Removal	99.2	92/94	95/97

The particle association of Ag was characterized in more detail in the 1994 sampling by examining the size-distribution of particle-bound Ag in the effluents and receiving stream. Table 4 outlines the distribution of silver in the effluent between four size classes on two sampling dates. It is apparent that the "dissolved" fraction, here defined as less than 50 nm, represents less than 11% of total Ag, and that a large (25 - 35%) portion of the total Ag is found in the colloidal fractions (50-400, and 400-1000 nm). Considering silver's extreme particle affinity, it is probable that a significant fraction of the "dissolved" phase is associated with <50 nm colloids. A large fraction of the total Ag in the receiving stream is similarly associated with colloids: e.g. 30m downstream from the discharge, 44% of total Ag was found in colloidal size fractions.

TABLE 4. Silver Size-Fractionation in Effluents
Levels of Total Silver

Size-Fraction	June 1994 $\mu g\ L^{-1}$ (percent)	August 1994 $\mu g\ L^{-1}$ (percent)
Particulate >1000 nm	4.073 (73.3)	1.407 (54.6)
Large Colloid 1000-400 nm	0.561 (10.1)	0.179 (6.9)
Small Colloid 400-50 nm	0.707 (12.7)	0.709 (27.5)
Dissolved <50 nm	0.214 (3.9)	0.283 (11.0)

Data on Ag levels in discrete size-fractions (above) were coupled with particle/colloid mass concentrations in identical size-fractions to evaluate the Ag content of colloidal- sized particles, and develop partition coefficients which reflect the colloidal association of Ag. Table 5 presents the results of these analyses. Levels of Ag in all particle classes are very high, typically 350-450 $\mu g\ g^{-1}$ (compare these values with background levels of 0.3 $\mu g\ g^{-1}$), but consistent with the nearly 1000 fold higher total silver levels in the effluent compared with receiving stream. Enrichment of Ag in the small colloids was seen in the August samples (approx. 50% elevation), however no enrichment was evident in large colloids or small colloids sampled in June. The partition coefficients shown in Table 5 are all calculated using the Ag levels in the 50 nm filtrate (except >0.4 μm) as the best estimate of the "dissolved" component. The K_d's developed in this manner show little variation with particle size, but are 2 -3 fold higher (1,500,000 vrs 500,000) than K_d's calculated using the typical 0.4 μm cutoff because of the large small colloid component.

If one develops the K_d's as simply the particle-bound component ratioed with the concentration of Ag passing any given filter (size), then the small colloids do show an apparent elevation because of the large mass fraction associated with the small colloid component. The magnitude of the effluent K_d's, calculated at the 0.4 μm level, are within a factor of two of mean K_d of background streams.

TABLE 5. Silver Size-Fractionation in Effluents Silver Levels in Particles and Partitioning

Size Fraction	June 1994		August 1994	
	$\mu g\ g^{-1}$	K_d ($L\ Kg^{-1}$)	$\mu g\ g^{-1}$	K_d ($L\ Kg^{-1}$)
Particulate >1000 nm	1120	5,240,000	420	1,470,000
Large Colloid 1000-400 nm	290	1,360,000	370	1,290,000
Small Colloid 400-50 nm	290	1,360,000	600	2,110,000
>50 nm	670	3,130,000	450	1,600,000
>400 nm	830	910,000	410	410,000

Results from the June 1994 sampling agree with 1993 work in showing rapid return of silver levels to near background levels in the receiving stream within 100m downstream of discharge. Table 6 summarizes the observed levels of Ag in the receiving stream in June. At a distance of 30m from discharge, Ag levels are elevated significantly above background. However, at 60m, total Ag levels have returned to within a factor of two of upstream concentrations. Complete, instantaneous mixing of effluent and stream flows would produce an in-stream Ag level of 97 ng L^{-1}. The difference between this value and the observed total Ag concentrations is calculated as the non-conservative fraction. As shown in Table 6, this fraction can represent upwards of 90% of calculated loss of Ag in the stream system.

TABLE 6. Silver Levels in Receiving Stream - June 1994

Location	Total Ag (ng L^{-1}) Particulate/Dissolved	Non-Conservative Fraction (%)
Upstream	2.0 (1.1 / 0.9)	
30m Downstream	57.7 (36.6 / 21.1)	41
60m Downstream	3.7 (2.6 / 1.1)	96
90m Downstream	10.1 (7.9 / 2.2)	89

Future work will focus on better defining the in-stream dynamics of effluent-derived Ag at the Jackson site, and a similar study in a high DOC river system.

Questions & Answers: Partitioning and Fate of Silver in Background Streams and Effluent-Receiving Streams

Q. KENNETH ROBILLARD (Eastman Kodak): You showed the loss of silver from downstream of the treatment plant was very quick — within 60 m, you lost the majority of it, in both the particulate and the dissolved form. It would seem like that was probably going to take a couple of minutes. Did it surprise you that lost so much of it, not only the particulates, but especially the dissolved?

A. I guess, initially — you know we started this a year or so ago — it surprised us. But there's a fairly large dilution effect here, too. A lot of that change is due strictly to dilution, and it's not beyond the possibility that the particle reaction and sedimentation can take care of the rest.

Q. ARUN MUKHERJEE (Univ. of Helsinki): Actually, it appears that in the data you've taken from the forest sample, that's 2.7 +/- 1.2 mg/l. What type of samples are you taking: some kind of dilytical species, or soils, or what?

A. These are all whole water river samples.

Q. River samples. But why are you mentioning the forest?

A. Well, our watershed designation is for the forest. I mean, greater than 90 percent of the wetland, of the watershed, is classified as a forest.

Q. NICK FISHER (SUNY-Stony Brook): Have you attempted to characterize the particles in your system? To what extent are they living, or biogenic, as opposed to totally abiotic? And if you have characterized, do you see a difference in K_d values between the living and nonliving particles?

A. We have looked at the filters directly in terms of major elements, and we're in the process of determining the POC on them. But other than those indicators, we haven't done any specific characterizations. The only indicators for living/nonliving is organic carbon content, which is very rough at the best. We wouldn't have any chlorophyll, any specific pigment information on the nature of the particles themselves. So I guess it would be difficult to say whether they were living or not.

Q. So then, where you see differences in K_d values under different scenarios, regardless of what the particle load was — is it possible that the differences are attributable to the fact that you just have different kinds of particles?

A. Oh, undoubtedly. I think our data from the other metals show that when we move into a region of ancient lake sediments that have a lot of red clay, we'll get extremely high partition coefficients. In other areas, where we're dealing with somewhat organic materials, our partition coefficients are much, much lower. So, obviously, the nature of the particle is as important as the nature of the solution medium.

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Session C

Toxicity of Metals to Aquatic Organisms

J.H. Rodgers
Session Chair

The Physiology of Silver Toxicity in Freshwater Fish

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Seven day LC50 tests performed with juvenile rainbow trout (*Oncorhynchus mykiss; approximately 4 g*) in dechlorinated Hamilton tapwater (Lake Ontario: $[Na^+] = 0.6$, $[Cl^-] = 0.7$, $[K^+] = 0.05$, $[Ca^{2+}] = 2.0$, $[Mg^{2+}] = 0.4$, [titratable alkalinity] = 1.9 mequiv.l^{-1}, hardness = 140 ppm as $CaCO_3$, pH = 8.0, 15 ± 1°C) have indicated that the acute toxicity of Ag varies dramatically according to the chemical form which is tested, and correlates with the availability of free ionic Ag^+ (Wood *et al.*, 1993). Thus $AgNO_3$, which is strongly dissociated, was extremely toxic, while $Ag(S_2O_3)_n$ and $Ag(Cl)_n$ were relatively benign, presumably due to the abilities of the anions to remove ionic Ag^+ from solution. The 7 day LC50 for $Ag(S_2O_3)_n$ (137,000 ug.l^{-1}, 95% C.L. = 118,000 - 159,000) was more than 4 orders of magnitude greater than that for $AgNO_3$ (9.1 ug.l^{-1}, 7.3 - 11.3), whereas no toxicity at all was observed with $Ag(Cl)_n$ concentrations up to 100,000 ug.l^{-1}, a level far above the solubility limit. These results were in broad agreement with earlier toxicity data of LeBlanc *et al.* (1984) on fathead minnow (*Pimephales promelas*).

The objective of the present series of experiments was to compare the physiological responses of rainbow trout to $AgNO_3$ and $Ag(S_2O_3)_n$ in order to understand the toxic mechanism(s) (or lack thereof) of these two very different forms of Ag. Adult rainbow trout (200 - 400g) were fitted with chronic indwelling dorsal aortic catheters for repetitive blood sampling without disturbance, allowed to recover for 48-72h, then exposed to the test conditions for 6 days. $AgNO_3$ was tested at 10 ug.l^{-1} and $Ag(S_2O_3)_n$ at 30,000 ug.l^{-1} in dechlorinated Hamilton tapwater (composition as above) where the predominant natural ligand for Ag^+ is Cl^-. $Ag(S_2O_3)_n$ was synthesized by dissolving AgCl in $Na_2S_2O_3$ (1:4 molar ratio). The same concentration of $Na_2S_2O_3$ alone (1.11 mmol.l^{-1}) was used for control exposures which were performed concurrently with experimental exposures. Although the absolute Ag concentration was 3000 times greater in the $Ag(S_2O_3)_n$ exposure than in the $AgNO_3$ exposure, geochemical speciation calculations with MINEQL+2.1 (Schecher, 1991) indicated that free Ag^+ was less than 0.003 ug.l^{-1} in the former *versus* 3.7 ug.l^{-1} in the latter. One-pass flow through exposures were employed in these physiological experiments to avoid changes in speciation or complexation, and comparably sampled control fish were run to check for non-specific effects due to the experimental procedures. For most parameters, there were negligible changes in the control fish.

Responses to the two different forms of Ag were dramatically different. Whereas $AgNO_3$ (10 ug.l^{-1}) induced severe physiological disturbances, there was a complete absence of these toxic symptoms during exposure to $Ag(S_2O_3)_n$ (30,000 ug.l^{-1}). Plasma glucose elevation is considered a highly sensitive indicator of stress in fish (Pickering, 1981). Plasma glucose increased approximately 5-fold during exposure to $AgNO_3$, but actually fell slightly during exposure to $Ag(S_2O_3)_n$, an effect also seen in the $Na_2S_2O_3$ controls (Fig. 1).

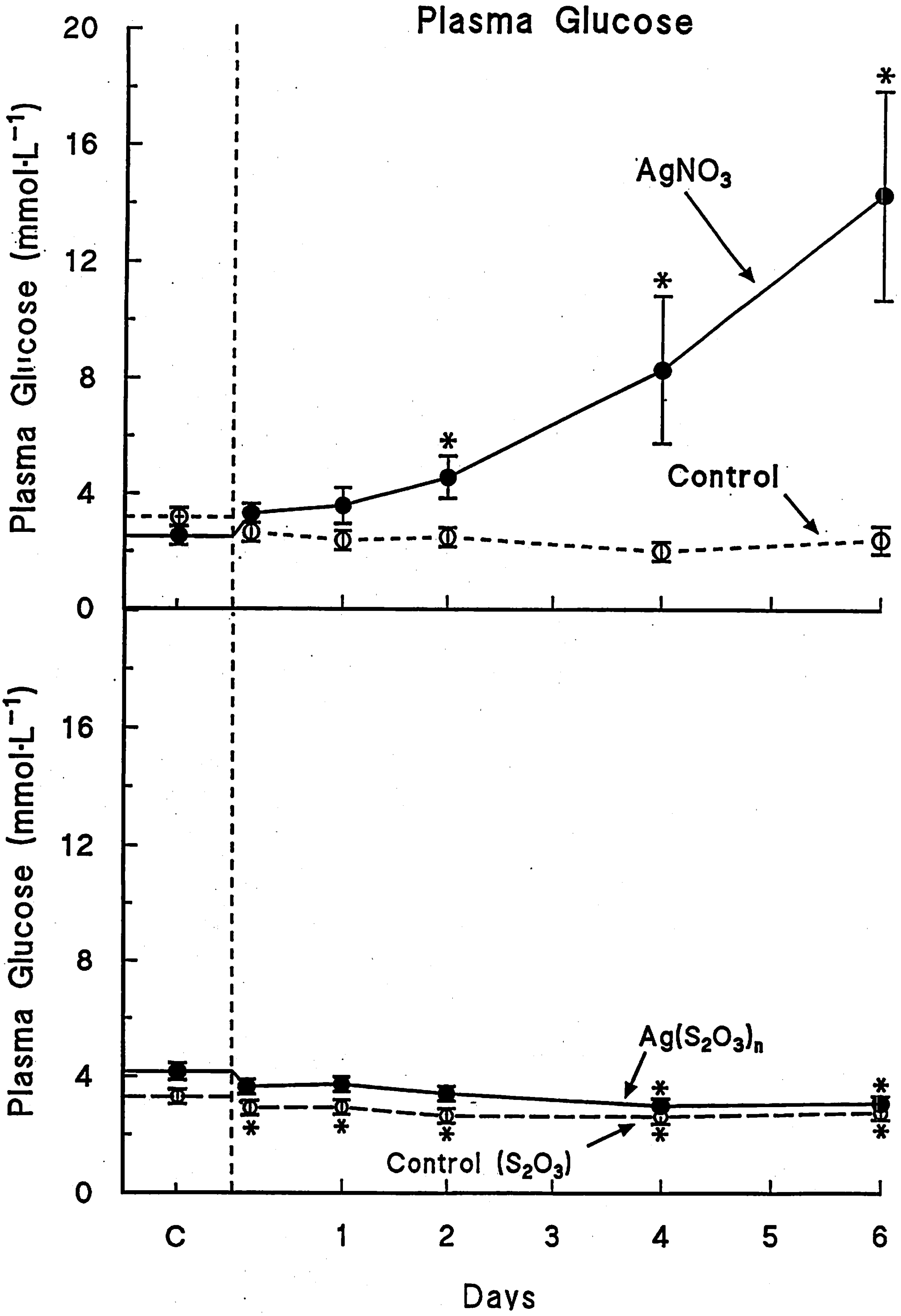

Figure 1. The influence of 6 days exposure to either 10 ug.l^{-1} Ag as AgNO$_3$ (top panel; N = 8 - 12) or 30,000 ug.l^{-1} Ag as Ag(S$_2$O$_3$)$_n$ (bottom panel; N = 15 - 18) on plasma glucose concentrations in adult rainbow trout. Means ± 1 SEM. Control treatments were either continued exposure to control water (top panel) or exposure to 1.11 mmol.l^{-1} Na$_2$S$_2$O$_3$ (bottom panel). * indicates mean significantly different ($P < 0.05$) from pre-exposure value (C).

While many metals at high levels induce a suffocation response in fish via gill swelling and mucification (McDonald and Wood, 1993), the source of the stress during $AgNO_3$ exposure was not inhibition of respiratory gas exchange. Indeed arterial blood P_{O2} increased and P_{CO2} decreased, an effect likely due to noticeable hyperventilation. In contrast, arterial P_{O2} and P_{CO2} were stable during $Ag(S_2O_3)_n$ exposure, and ventilation remained unchanged. The probable cause of hyperventilation during $AgNO_3$ exposure was a severe metabolic acidosis (Wood and Munger, 1994), manifested in decreased arterial plasma pH and HCO_3^- levels. This effect was not due to lactic acid production; blood lactate levels remained low and unchanged. Arterial blood acid-base status exhibited negligible alteration during $Ag(S_2O_3)_n$ exposure. The most striking effect of $AgNO_3$ was on ionoregulation. Plasma Ca^{2+} and K^+ levels exhibited only minor fluctuations, but plasma Na^+ and Cl^- levels fell progressively to 70% of control values after 6 days. In contrast, $Ag(S_2O_3)_n$ had negligible influence on the plasma levels of all four ions. The precipitous loss of plasma Na^+ and Cl^- and the occurrence of metabolic acidosis during $AgNO_3$ exposure were almost identical to the symptoms which we had documented earlier in rainbow trout exposed to environmental acidity (pH = 4.0 - 4.5) in the same water quality (reviewed by Wood, 1989).

In the latter circumstance, we have demonstrated that these effects result from an inhibition of active Na^+ and Cl^- uptake mechanisms at the gills, a stimulation of passive diffusive losses at the gills, and associated alterations in net H^+ balance (Wood, 1989, 1992). The loss of Na^+ and Cl^- entrains an osmotic shift of fluid out of the blood plasma and extracellular space into the intracellular compartment of muscle and red blood cells. This hemoconcentration is made worse by the discharge of stored red blood cells from the spleen which further increases blood viscosity and blood pressure at a time when the blood volume is severely reduced. An eventual circulatory collapse appears to be the proximate cause of death during low pH exposure, but one which is originally induced by the loss of Na^+ and Cl^- through the gills via the "surface effects" of H^+.

Several lines of evidence indicate that a similar toxic syndrome occurred in response to $AgNO_3$. Firstly, pilot experiments using radioisotopes indicated that ^{22}Na uptake at the gills was severely inhibited, while ^{45}Ca uptake was unaffected. Secondly, measurements of hematocrit, hemoglobin, and plasma protein revealed a similar intense hemoconcentration such that plasma volume had decreased to about 60% of control levels. Thirdly, measurements of spleen weight and hemoglobin concentration indicated that the spleen had discharged more than 50% of its stored red blood cells by this time. None of these effects were apparent during $Ag(S_2O_3)_n$ exposure. While radioisotopic fluxes have not been measured, the stability of plasma Na^+ and Cl^- argues against any disturbance of ion exchange at the gills. Hemoconcentration did not occur and the spleen did not contract.

The above results might suggest that Ag entered the fish with resultant internal toxic effects during $AgNO_3$ exposure, but did not during $Ag(S_2O_3)_n$. However, this was not the case. During both exposures, Ag accumulated in the blood, reaching a plateau by 2 - 4 days; however this plateau concentration was approximately 4-fold higher in the $Ag(S_2O_3)_n$ exposed fish (Fig. 2). We therefore conclude that the toxic syndrome caused by $AgNO_3$, and not by $Ag(S_2O_3)_n$, is likely due to the "surface effects" of ionic Ag^+ at the gills, and not due to internal toxicity. Ionic

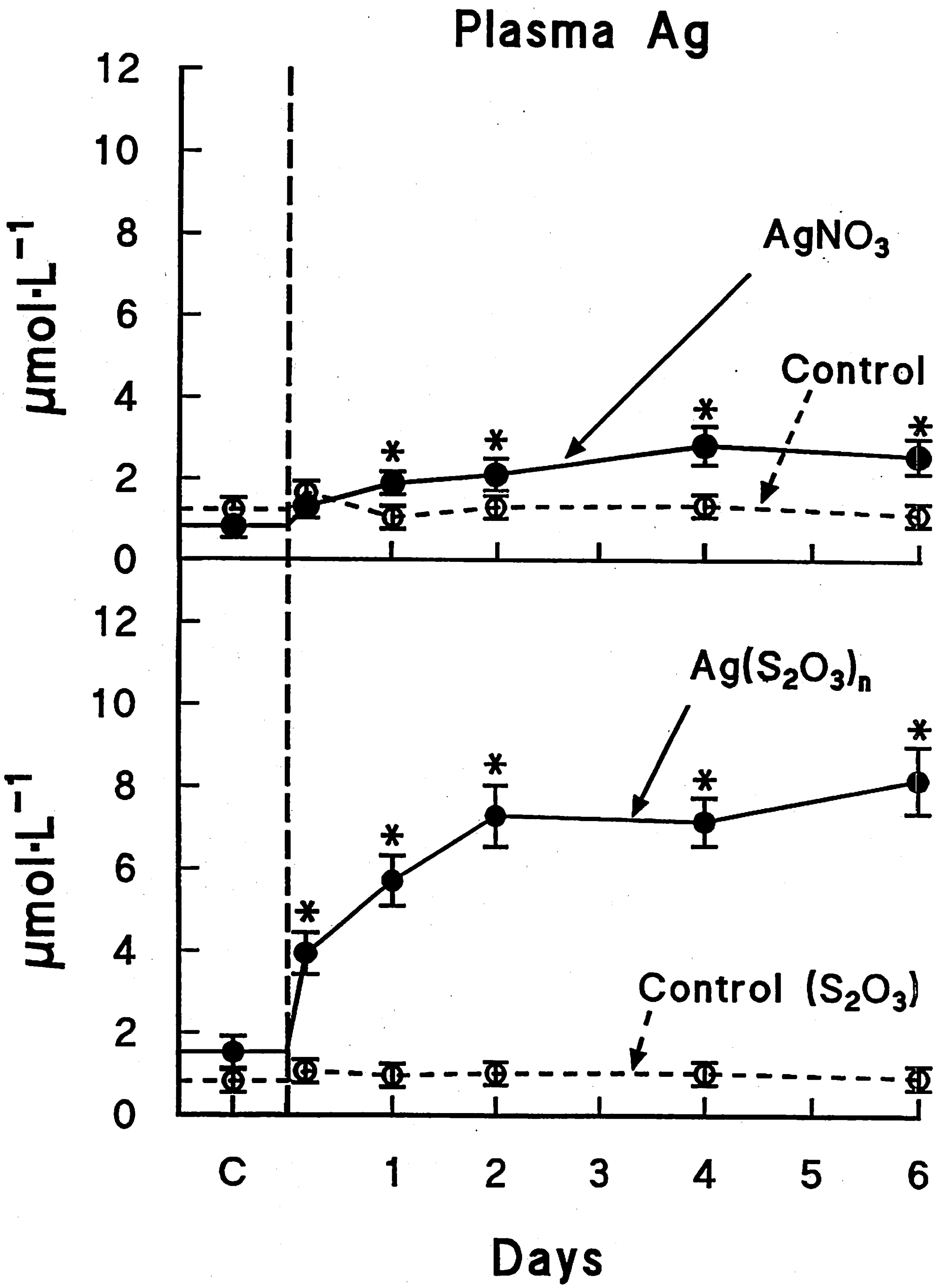

Figure 2. The influence of 6 days exposure to either 10 ug.l^{-1} Ag as $AgNO_3$ (top panel; N = 8 - 12) or 30,000 ug.l^{-1} Ag as $Ag(S_2O_3)_n$ (bottom panel; N = 15 - 18) on plasma total Ag concentrations in adult rainbow trout. Means ± 1 SEM. Control treatments were either continued exposure to control water (top panel) or exposure to 1.11 mmol.l^{-1} $Na_2S_2O_3$ (bottom panel). * indicates mean significantly different ($P < 0.05$) from pre-exposure value (C).

Ag^+ appears to be the toxic moiety. We hypothesize that Ag^+ disrupts Na^+, Cl^-, and H^+ exchanges at the gills, which initiates a complex chain of events culminating in cardiovascular collapse. Internal toxic effects of Ag entry may be avoided because Ag is a potent inducer of metallothionein synthesis in the rainbow trout (Hogstrand *et al.*, 1993).

(Supported by a grant from the National Association of Photographic Manufacturers/Silver Coalition)

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Questions & Answers: The Physiology of Silver Toxicity in Freshwater Fish

Q. NICHOLAS FISHER (SUNY-Stony Brook): I was wondering whether or not the silver could be causing any effect on the action of the carbonic anhydrase. Carbonic anhydrase has zinc as a co-factor and regulates the bicarbonate-CO_2 balance in your system. And the silver may possibly displace the zinc, or in other ways affect the behavior of the carbonic anhydrase, producing the acidosis effects that you observe. Could you comment on that?

A. I think that's a good suggestion. Because if you remember the model — perhaps some people do — the carbonic anhydrase feeds the acid and base to run the sodium and chloride uptake process. So if you would knock out that enzyme, you'd affect both the acid/base balance and the sodium/chloride uptake, which, in fact, appears to be the problem in fish. We haven't looked at that yet, but that's obviously something that we do have to look at in this next year. What I would say is, that with another metal, zinc — we found that with zinc in the water, you knock out that enzyme. Unrealistic levels, but certainly you can hit that enzyme. So it's a good suggestion.

Q. You might look at different exposure ratios of silver to zinc to see whether or not higher ambient zinc concentrations decreases the effect of the silver.

A. Good idea. I like that.

Q. JIM KRAMER (McMaster Univ.): Chris, the last part of your discussion on silver and the effect of chloride [described] very high silver levels, compared to what we would find. So, I mean, the equation you gave was really a sort of overkill. Do you have a feeling that we can factor these down so, if we talk more like silver exposures at one ppb or less than one ppb, that we can just use this simple silver-chloride binding model? Or what else can you come up with?

A. I don't think I would say that we can definitely do that. I think we would have to do the test before we can do that. But what we have done — and that's illustrated on Fern's (Fernando Galvez') poster, which is just outside here — is that when we have gone to lower levels of silver by titrating with chloride, you can get exactly the same LC_{50} as if, in fact, we titrate standard Hamilton Lake Ontario water with silver nitrate. So while we're working with 100 μg/l there, we can certainly get down to ionic levels of silver, on the order of seven or eight micrograms per liter, and still make the model work. But whether, in fact, we can take that down to say, half a microgram or one microgram per liter, I think [that] needs to be tested experimentally. I would actually think that maybe Rick Playle could comment on that in some of the work that he's going to present today.

Silver Interactions at Fish Gills

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Our approach is to experimentally determine metal-gill equilibrium binding constants (*K*) and the number of metal-gill binding sites. These values are then inserted into an aquatic chemistry program (MINEQL$^+$; Schecher and McAvoy 1992) to predict metal-gill interactions and therefore toxicity to fish. This method has been used before to model Cu and Cd interactions at fish gills (Playle et al. 1993a, b).

Small rainbow trout (Oncorhynchus mykiss, 1-3 g) were acclimated to synthetic soft water (Ca, Na ~300 μM, pH 6.5-7.5), then were exposed in soft water for 2-3 h or 1 week to about 0.1 μM Ag (~11 $\mu g \cdot L^{-1}$). Water chemistry of the soft water was varied by adding Ca, Na, or H^+ (for competition experiments), or thiosulphate ($S_2O_3^{2-}$), dissolved organic carbon (DOC), or Cl (for complexation experiments). Fish gills were removed at the end of the experiments, and gill Ag was measured by graphite furnace atomic absorption spectrophotometry. Silver concentrations of 0.1 μM were used because this concentration yields measurable Ag accumulation on the gills, yet was not toxic in our experiments. The 96 h LC50 for Ag in soft water is between 0.06 and 0.15 μM (Davies et al. 1978; LeBlanc et al. 1984).

About 30X more thiosulphate than Ag was needed to prevent Ag deposition on trout gills. This protective effect of Ag persisted for 6 d. From the thiosulphate data, the conditional equilibrium constant of Ag-gill interactions must be greater than that for Ag-thiosulphate. That is, $\log K_{Ag\text{-}gillAg} > \log K_{Ag\text{-}S2O3} = 8.8$. We calculated that $\log K_{Ag\text{-}gillAg} = 10.0$, with approximately 1.3 nmole Ag binding sites per fish. Inserting these values into the MINEQL$^+$ program gave a good fit between observed and predicted gill Ag concentrations ($r = 0.924$ (6); $p < 0.01$). In contrast, gill Ag concentrations predicted on the basis of free Ag^+ concentrations calculated by MINEQL$^+$ gave a bad fit between observed and predicted gill Ag ($r = 0.525$ (6); $p > 0.05$).

At high enough concentrations (11.3 mM), Cl was able to keep 0.1 μM Ag off trout gills by complexing the Ag as AgCl and $AgCl_2^-$. Similarly, 24 mg $C \cdot L^{-1}$ DOC kept Ag off the gills. From these data, the binding constant between Ag and DOC can be calculated at $\log K_{Ag\text{-}DOC} = 9.0\text{-}9.2$, and $\log K_{Ag\text{-}Cl(n)} = 4.8\text{-}5.7$. There are no values in MINEQL$^+$ for Ag-DOC interactions, but $\log K_{Ag\text{-}Cl(2)} = 5.3$, right in the middle of the range calculated from our experimental data.

As for competition for Ag binding sites on the gills, 16 mM Na kept Ag off the gills, pH as low as pH 4.5 did not, and concentrations of Ca up to 10.6 mM also did not keep Ag off the gills. From these results, log $K_{\text{Na-gillAg}}=4.7\text{-}5.7$, log $K_{\text{H-gillAg}}<7.1$, and log $K_{\text{Ca-gillAg}}<4.5$.

Calculated log K values were optimized to the experimental data, and the final log K values were inserted into the MINEQL$^+$ program. The model was tested using fish exposed to Ag in natural waters. Observed and model predicted gill Ag concentrations agreed remarkably well, except for one case. This exception was City of Waterloo tapwater, for which the model predicted background gill Ag concentrations but we observed high gill Ag. Waterloo tapwater has very high Ca concentrations (~3,000 μM); the model predicted low gill Ag mostly on the basis of these high Ca concentrations. This exception to the otherwise good predictive capabilities of the model may indicate a kinetic constraint on the thermodynamic basis of the model.

Silver accumulation on fish gills is exceptionally fast, so that cold trout (with low metabolic rate; 4°C) end up with as much Ag on their gills in 2.5 h as do warm trout (with higher metabolic rate; 20°C), even though warm trout initially accumulated much more Ag on the gills. Warm fish (18°C) given twice as much oxygen need to ventilate half as much water to satisfy their doubled oxygen demand, so accumulated only as much Ag on their gills as did fish held at 8°C. Finally, cold trout (8°C) given half as much oxygen need to breathe twice as much water to satisfy their oxygen demand, so accumulated as much Ag on the gills as trout held at 18°C. These results indicate, at least for initial accumulation of Ag on the gills, that gill Ag concentrations are dependent on the "dose" of Ag reaching the gills.

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Questions & Answers: Silver Interactions at Fish Gills

Q. RUSSELL ERICKSON (EPA-Duluth): Your data on the chloride addition suggests that there was no real effect, no competition for uptake — the way you were measuring gill uptake for silver, at 0.3 and 0.4 millimolar — were your concentrations correct?

A. Right.

Q. OK, it was taking up as much silver as in the absence of chloride. Yet Chris' data show a major effect on toxicity at 0.1. Would you comment on what implication that has to do with how your uptake at the gill is, in fact, correlating to the toxic mechanism, or if it isn't?

A. It's kind of difficult to compare studies in that way. Those were our baseline conditions of 0.3, 0.4. If in Chris' lab they could get chloride down much lower, then that's great. I would predict that if we had run our experiment at lower chloride concentrations, we would have ended up with more silver on the gills. So, I guess that's the answer — sort of a different starting point.

Q. JIM KRAMER (McMaster Univ.): I want to go back to your model and emphasize, or look at, the silver/DOC stability constant, which you gave a log value of nine, which, to me, would be very high unless you had some sulfur binding there. Can you tell me a little bit about your black box DOC?

A. I can tell you a little bit, not a lot about it. I got my dissolved organic carbon from Ken Burnison. Ken's at the Centre for Inland Waters and he gets it from Luther Marsh, up near Orangeville. He's done some characterization of it, but I really can't comment on that.

Q. (From Audience): How do you get your stability constant?

A. Oh, yes, it's a bit of a guesstimate. We make an estimate of the number of binding sites per milligram of carbon per liter, and then make an estimate of the strength of binding. You can have more binding sites and lower binding constant, or fewer binding sites and a higher constant.

Q. (Audience): What you know is the concentration.

A. Yes. I don't think it's particularly out of line for anything I've seen.

Q. KRAMER: Well the only thing we find in the literature is . . .

A. . . . is for copper.

Q. . . . is sulfur driven. That's what I'm saying.

A. On the organic carbon?

Q. Yes, on the organic carbon.

A. Sure.

Q. We can use DOS.

A. Yes, DOS. We're working on it.

Q. GREGORY CUTTER (Old Dominion Univ.): You had a number for the apparent stability constant for the gill site. Do you want to speculate on what it is, then?

A. Well, based on Chris Wood's data, I'd say it's some kind of protein involved in sodium or chloride uptake. But in my model, it doesn't really matter what it is. It's just a site. But, again, based on Chris' data, I'd say it's some kind of active ion uptake site.

Q. I guess I was thinking more of a chemical . . .

A. Oh, I see what you mean.

Q. I think you have to have a thiol.

A. Yes, well it would be — I think it would be a carboxyl group. Proteins have lots of carboxyl groups on there.

Q. KRAMER: We run them the same way though. We don't get numbers like nine for carboxyl. Not unless you've got some exotic chemical that nobody knows about.

A. Oh, okay. Yes, there's sulfhydryl groups, too. Sure.

Q. (Audience): All I'm saying is, if we get the exponent wrong, we won't get these.

A. No. Again, I'm not really speculating. Carboxyl groups could be sulfhydryl groups. I think the value is reasonable.

Q. (Audience): Yes, I don't have a question on the value. I just think, what do you speculate? Because that, mechanistically, is what you need to know.

A. Yes.

Effects of Laboratory Test Conditions on the Toxicity of Silver to Aquatic Organisms

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Like many other heavy metals, the toxicity of silver to aquatic organisms depends on various physicochemical properties of the test water. Uncertainties in how to extrapolate among different water conditions can produce considerable uncertainty in water quality standards. Current water quality criteria are referenced to water hardness, but this entails the combined effects of several factors that are incompletely understood. Preliminary toxicity tests have been conducted to identify test conditions important to silver toxicity and to support development of more definitive tests needed to improve application of silver toxicity data to water quality criteria.

Major water chemistry factors affecting silver toxicity were investigated in acute, renewal tests using 30-day-old fathead minnows. Hardness has been reported to affect the toxicity of silver and other heavy metals, but these effects are often confounded by several factors. In this study, the effects of hardness were determined by the addition of 2:1 $CaSO_4$:$MgSO_4$ to Lake Superior water, such that alkalinity, pH, and other ions were invariant. Increasing hardness in this fashion reduced toxicity, the reduction being approximately 2.5-fold when hardness was increased from about 50 mg/L to 250 mg/L as $CaCO_3$ (Figure 1). The effects of pH and alkalinity were determined by addition of sulfuric acid and sodium bicarbonate. Toxicity decreased with increasing pH and alkalinity, LC50s being nearly 3-fold higher at pH 8.6 than at pH 7.2 (Figure 2). Silver has a high affinity for various types of dissolved organic matter. The addition of humic acid resulted in a four-fold increase in LC50s, demonstrating that dissolved organic carbon should be a major consideration in interpreting and predicting toxicity (Figure 3). Studies with copper have shown that addition of >1 meq/L sodium can reduce toxicity. However, for silver, the addition of 2

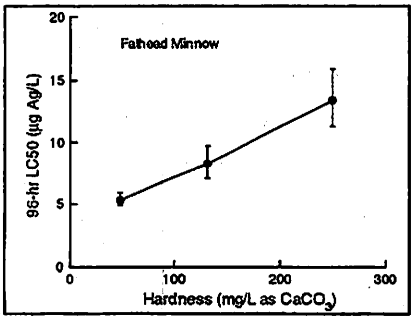
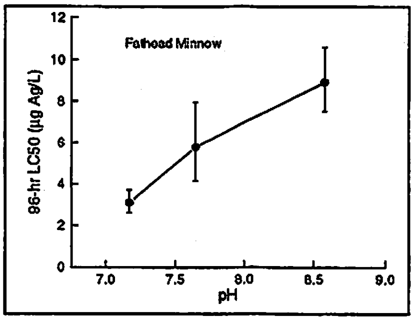


Figure 1



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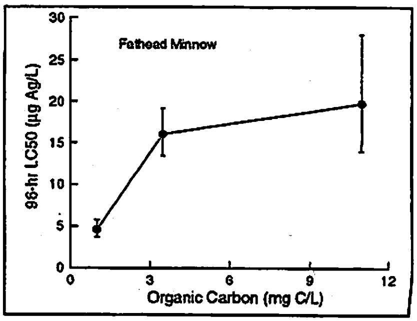

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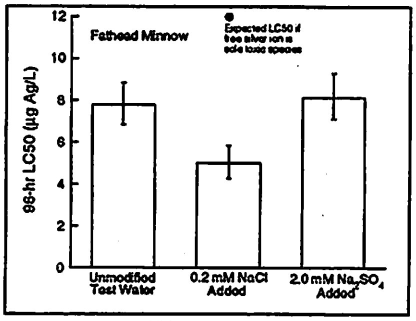

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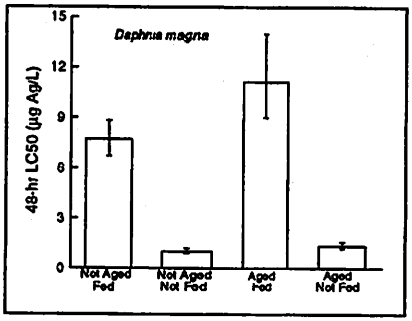

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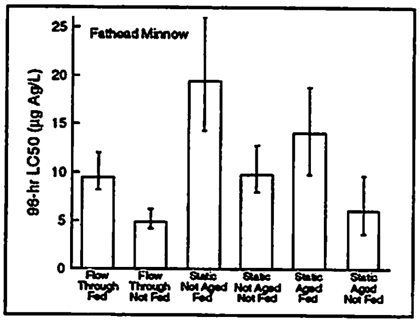

Figure 6

meq/L of Na_2SO_4 had no effect (Figure 4). Chloride can complex a significant fraction of silver and should decrease toxicity if free silver ion is substantially more toxic than silver chloride complexes. Addition of 0.2 meq/L chloride was expected to reduce free silver ion by about 25%, but resulted in a significant increase, rather than a decrease, in toxicity (Figure 4).

Because of the importance of organic matter in regulating silver toxicity, a major concern regarding extrapolation of laboratory toxicity test results is the extent to which feeding and water turnover affect the concentration of organic matter and alter toxicity. Another concern involves the kinetics of formation of silver complexes and to what extent slow kinetics might cause toxicity to depend on the time interval between the addition of silver and the exposure of the test organisms. To evaluate these concerns, simultaneous acute static tests with *Daphnia magna* were conducted to determine the effects of feeding and the effects of aging test solutions for 48 to 72 hours prior to adding test organisms. Feeding greatly reduced toxicity, while aging the test solutions had little effect (Figure 5). For fathead minnows, the effects of feeding, aging of static test solutions, and flow-through versus static conditions were evaluated. Again, feeding reduced toxicity and the prior aging of static test solutions had little effect (Figure 6). However, 96-hour LC50s were lower in flow-through tests than in static, non-aged tests (Figure 6). This result can be attributed to declines in total silver concentrations, declines in the fraction of silver that was dissolved, and increases in organic carbon during the static tests. Because of these changes, mortality ceased more quickly in the static tests. If compared based on 24-hour LC50s, flow-through and static tests were not significantly different.

The ultimate concern of these tests is how laboratory tests can best be used to interpret and predict toxicity under field conditions. Static, unfed acute tests were conducted using both Lake Superior water and water obtained from the nearby St. Louis River. For fathead minnows, 96-hr LC50s were approximately ten-fold higher in the river water. This shift was consistent with the higher dissolved organic carbon concentration in this water. For *Daphnia magna*, 48-hour LC50s were approximately sixty-fold higher in the river water. This extreme shift seems to reflect an even greater importance of organic matter at the lower effect concentrations for this organism and underscores the need for methods to extrapolate toxicity results to site conditions.

Questions & Answers: Effects of Laboratory Test Conditions on the Toxicity of Silver to Aquatic Organisms

Q. JEROME NRIAGU (Univ. of Michigan): I'm not really a toxicologist, so my question may be totally out of whack, but that's okay. My concern is the effect of sample contamination in your bioassay analysis. For example, if you show your last slide, which was Daphnia, you got 0.5 µg/l as the LC_{50}. And Jim Kramer showed some slides this morning where the concentration in the top water was about 0.1 (100 ng). I don't know what the concentrations in the various reagents that you use in your sample and stock solution are. The fact, really, is that sample contamination may, in fact, influence and affect the LC_{50} you are getting, especially at the low concentration. I was wondering how far you have gone to control sample contamination in your experiments.

A. All right. Good question. I think it's a really important aspect of this. I would say, particularly in those experiments, that it's probably not documented well enough. Larry could speak more about it, and maybe I'll turn it over to him. But, recently, we've been having University of Wisconsin-Superior run some more quality control on blanks over there. As I recall, their silver blank is less than 0.1. Is that right?

A. LARRY BROOKE (Univ. of Wisconsin-Superior): Yes.

A. ERICKSON: But this was an early experiment, and I think the detection limit, if I recall, referred to in reports was right around 0.1 at that time, in that experiment. Like I said, more recently, we've put their team through a set of quality control tests with both the dissolved and total analysis, and I think they've established it for that level. But I wouldn't completely dismiss your concern that it might even be a little inflated, that Daphnia number. I don't think there's any problem with the fathead minnow numbers. I mean, that's well above any level of contamination that we've been able to see. For the very early Daphnia numbers, yes, I think they could be perturbed by contamination. And that really is sometimes a problem, especially the historical toxicity tests. I think we're doing a better job of it now. But historically, there's a lot of uncertainty because of that problem. I don't know what more I can say about that.

Q. CHRIS WOOD (McMaster Univ.): I guess just a comment and a question also, Russ. I think that the disparity between your results and our results on rainbow trout could, perhaps, be explained by Rick Playle's work. If the binding constant were just a little bit higher in fathead minnow, at that sort of chloride level, then I think you would not get the protective effect of chloride.

A. Yes, I would agree. I mean, I didn't want to speculate. That's why I asked Rick the question, because I think — some people were talking about it earlier, and I think I was talking to Fernando last night — as you vary these test systems, it's not going to be surprising that you get slightly different results. And this wasn't a major decrease, it was just reflective of [the complexity of the problem]. It was the opposite of what we expected. The whole issue of the chemistry at the gills is so complicated, and I don't think any of us are yet addressing what is happening really in the chemistry at the gill surface. As you penetrate to that surface, you have at whole series of questions. The data itself shows that, well, at least the stable sodium thiosulfate obviously penetrates through the gills. Are there complexes which will penetrate into the gills but dissociate and provide you with higher silver ion concentrations than you would otherwise have? And that gets to Playle's work, in terms of what is the interaction with the binding sites at the gills? So, again, I don't see this as really disagreement. I mean, I think they're both real phenomena that have to be understood.

Q. Just a question. On your static tests, were they totally static, or static renewal?

A. The first ones I showed with hardness were renewal. Sorry I didn't mention it. The last ones we ran deliberately static, to really look at the time trends of dissolved and total concentrations during that time.

Q. ANDERS ANDREN (Univ. of Wisconsin): You ran the water quality parameter table kind of fast for my mind, but I couldn't see — did you have suspended solids when you compared St. Louis River water and your tapwater?

A. No, I didn't put suspended solids up.

Q. What was the difference?

A. In fact, in the river water our measured dissolved concentrations were still high. Larry, do you remember offhand? I'd have to go back to my room. What's the suspended solids in the St. Louis River water? It was rather low.

A. LARRY BROOK (Univ. of Wisconsin-Superior): Three or four.

A. ERICKSON: It was rather low.

Q. What about the lab water?

A. Less than a milligram of suspended solids.

Q. So did you measure the dissolved concentration for silver only?

A. Only the dissolved. That's the first thing we looked at in the river water. Again, I can't cite the particular number but the dissolved was certainly above 75 percent in the river water.

Q. And when you talk about dissolved, that's separated, filterable through 0.4 [micron filter]?

A. Yes, filterable.

ARGENTUM

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Session D

Food Chain Transfer of Metals in the Aquatic and Terrestrial Environment

S.N. Luoma
Session Chair

Bioindicators of Ag Availability in UK Estuaries

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Ag concentrations in sediments and indicator organisms in UK estuaries are presented. The principal indicator species analyzed included seaweed *Fucus vesiculosus* (reflecting dissolved Ag concentrations), winkles *Littorina littorea*, ragworms *Nereis diversicolor* and deposit feeding bivalves, e.g., *Scrobicularia plana:* most characterize regional variations in patterns of contamination satisfactorily. Examples of spatial and temporal trends for Ag in the above indicator species, from some of the 100(+) estuaries studied, are described. Some of the factors modifying silver accumulation and effects in these organisms are also discussed.

The data reviewed are the results of measurements of Ag concentrations in estuarine sediments and organisms carried out at the Plymouth Marine Laboratory over the past 20 years. In addition to Ag, other metals determined included As, Cd, Co, Cr, Cu, Fe Hg, Mn, Ni, Pb, Sn and Zn. Data were obtained for most estuaries in England and Wales. Principal objectives were:

(1) to assess the usefulness of benthic invertebrates and seaweeds as analytical indicators of metal contamination;

(2) to study factors goveming the availability of dissolved and sediment-bound metals to benthic organisms;

(3) to use indicators to identify heavily contaminated sites around the UK;

(4) to assess the potential for deleterious effects caused by Ag.

Monitoring was not the primary objective, although ultimately most estuaries in England and Wales were visited. A few estuaries were sampled only once while some of the more polluted received far more attention. Thus, rather than being a continuous record the results are a series of snapshots of a large number of estuaries.

Estuarine organisms as indicators of metal availability

Since most of the metals (including Ag) in estuaries lie in the sediments, analysis of these deposits is very useful for assessing the retention of inputs. Sediment data are also of use in determining whether or not biological effects might be expected. However, such measurements on sediments (or water) rarely take account of the existence of metals in different chemical forms having different biological availabilities. The best way of assessing the presence of bioavailable metals is by measuring their concentrations in indicator organisms. These are species in which the accumulation of metals in tissues reflects their availabilities in waters or sediments. Few organisms are ideal indicators for all metals. For example, some species are able to control their body concentrations of certain metals by excretion or exclusion; others are poor accumulators of some metals and are thus more difficult to analyze.

The species used in this study were: *Fucus vesiculosus* (brown seaweed; bladderwrack); *Littorina littorea* (herbivore; common winkle); *Nereis diversicolor* (sediment-dwelling worm; ragworm); *Scrobicularia plana* and *Macoma balthica* (both deposit-feeding clams). A summary of indicator properties of these organisms for Ag are described below, and concentration ranges are shown in Table 1. Species are divided into categories reflecting bioavailabilities of metals in water or sediment, though the relative importance of these vectors is sometimes uncertain and may differ between sites:

1. Water mainly: - directly, *Fucus,* and indirectly, via diet, *Littorina*

Experiments have shown that metal concentrations in *F. vesiculosus* reflect levels of dissolved metals in seawater. Direct proportionality is observed up to concentrations of 10 µg Ag/l. Concentration factors (dry tissue/water) of the order of 40,000 may be achieved. Application of these CFs to the field imply a range of dissolved concentrations up to 0.25 µg Ag/l - in agreement with water analyses. It is concluded that under field conditions concentrations in *Fucus* provide a useful indication of the bioavailability of dissolved Ag.

The gastropod *Littorina littorea* probably accumulates metals including Ag from *Fucus* upon which it grazes, and, therefore, directly or indirectly, reflects concentrations in the overlying water. Very significant relationships occur between concentrations of Ag in *Littorina* and *Fucus,* however, the slope is >1 and levels in *Littorina* usually exceed those in *Fucus* by a factor of 10 making it a good indicator for this metal. High levels of dietary copper (>25µg/g) may reduce the availability of Ag, a factor which may influence environmental assessments.

2. Sediment mainly: *Nereis, Scrobicularia, Macoma*

Much of the dissolved Ag entering estuaries is likely to be scavenged by particulates. Concentrations of Ag in sediments (<100µm fraction) from estuaries around the UK range over almost three orders of magnitude (0.055-28.4 µg/g, Table 1). However, support from biological data is important in determining what should or should not be regarded as a contaminated sediment. Under field conditions, identification of dominant processes influencing bioavailability of sediment-metal can be achieved by observing the goodness of fit between metal concentrations in ubiquitous deposit-feeding species and levels in various types of sediment extract over a wide spectrum of sediment types (Luoma and Bryan 1982; Langston 1982; Bryan and Langston 1992).

In multiestuary comparisons, significant relationships exist between Ag concentrations in *Nereis* and sediments (best fit with 1M HCl extracts, possibly modified by organics, confirming observations of Luoma and Bryan 1982). Of the estuarine species studied *Nereis diversicolor* usually penetrates furthest upstream, making it a valuable bioindicator in low salinity regions, though bioaccumulation potential may be low compared with molluscs (see ranges, Table 1). Thus, correlations between Ag in sediments (1M HCl extracts) and infaunal clams *Macoma balthica* and *Scrobicularia plana* are even more significant, and slopes of regression lines greater than for *Nereis*, properties which make these clams valuable in the detection of Ag contamination. Unexpectedly low levels of Ag have been found in *S. plana* from Cu-contaminated sediments in SW England, however, and it would seem that a high level of this metal in substrates may out-compete Ag for accumulation pathways/sites in clams, resembling observations of Ag-Cu interactions described for *Littorina*.

In all infaunal species studied, slopes of relationships (body burdens vs. sediments) are > 1 indicating that bioavailability increases disproportionately as contamination in sediment increases. Consequently, compared to other metals, tissue:sediment ratios for Ag are among the highest, confirming the importance of particulate Ag. Uptake of dissolved forms of Ag may, however, assume increasing significance where overlying water is contaminated and sediment levels are low (e.g., Severn Estuary).

Table 1. Summary: Ag Concentrations in Sediments and Indicators (µg/g dry wt.)

Sample	Source (Primary)	Low Mean (n=31-32)	Maximum	Site	Major Influence	Modifying Factors
Fucus vesiculosus	dissolved	0.066	7.4	Severn	industrial	
Littorina littorea	dissolved/diet	0.73	1.01	Thames	industrial	Cu in diet
Mytilus edulis	dissolved/ suspended s.	0.02	198	Whitehaven	industrial	sewage
Sediment ('total')		0.041	13.6	Gannel	Mining	
Scrobicularia plana	sediment	0.098	259	East Looe	industrial	sewage, Cu
Macoma balthica	sediment	0.460	301	East Looe	industrial	sewage
Nereis diversicolor	sediment	0.100	36.4	Gannel	Mining	

Mapping Ag contamination

A PC-based program has been developed to produce maps showing the distribution of metallic contaminants in estuaries around the UK and histograms displaying the relative levels of contamination in different estuaries. This has been used to demonstrate spatial and temporal trends for Ag in UK estuaries, determined using the above indicator species and sediments (see, for example, Figure 1).

Highest Ag levels in sediments occur in SW England (Gannel, Restronguet Creek) and have their origin in metalliferous mining. In the western arm of the Looe Estuary, waste from Pb-Ag mining has led to Ag contamination, but in the East Looe, sediment loadings (Ag) may have come from inputs of sewage contaminated with industrial (e.g., photographic) wastes. The latter category of input also explains elevated sediment-Ag levels elsewhere, including the Thames, Medway, Itchen and Clyde Estuaries and the coastline near Whitehaven, Cumbria.

Concentrations of Ag in *Nereis* reflect contamination from both types of source and are high in all the above-mentioned estuaries, particularly mining-impacted sites. Trends exhibited by clams *S. plana* and *M. balthica* are somewhat different in that despite the high Ag levels in deposits from mining impacted parts of SW England, Ag bioavailability to these species is generally most evident where combinations of sewage and industrial waste prevail (Severn, Whitehaven, E.Looe). One reason for this apparent discrepancy may be that the uptake of Ag is suppressed by the high levels of sediment Cu that also occur in some of the southwest 'mining' estuaries: Alternatively, the disproportionately high levels of Ag in clams at sewage impacted sites might be explained by a similar phenomenon to that described by Harvey and Luoma (1985), who found in experiments with *M. balthica* that bacterial extracellular polymers enhance particulate Ag bioavailability.

Fucus and, indirectly perhaps, *Littorina*, are both indicators of dissolved Ag and reflect, locally, metal-mining inputs in this form. On a country-wide basis, however, sewage/industrial sources are more significant, e.g., in the Severn and Thames Estuaries and at Whitehaven.

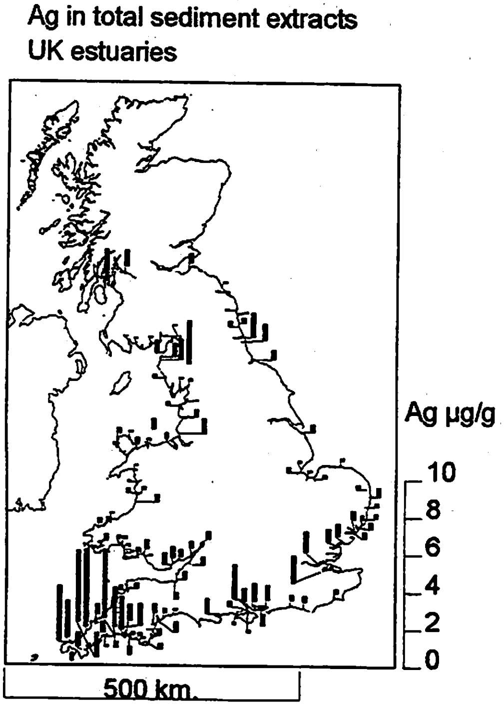

Figure 1 Map showing Ag in total sediment extracts (mean values each estuary).

Environmental impact

In view of the wide ranges of Ag concentrations measured in the field (Table 1), there is, undoubtedly, impact in terms of bioavailability, though a review of effects studies suggests that concentrations of dissolved Ag commonly encountered in the environment are usually below harmful levels. Nevertheless, the potential for deleterious effects caused by Ag in the environment is a realistic concern, particularly with respect to enhanced Ag bioavailability encountered in sewage-enriched sediments. More research on this topic should be a priority.

Summary

Concentrations of Ag in sediments and indicator organisms vary by several orders of magnitude between the least and most contaminated localities. There is some evidence that Ag associated with sewage inputs is more readily available to molluscs than Ag originating from metal-mining. Areas where Ag contamination is widespread include the Thames and some neighboring estuaries in SE England, some estuaries in SW England (especially the Looe), the Severn, the Clyde Estuary and parts of the West Cumbrian coastline.

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Questions & Answers: Bioindicators of Ag Availability in UK Estuaries

Q. EUGENE KRASNOV (Kaliningrad State Univ.): You have very interesting data about pollutants. The Baltic region is absolutely [a prime study area] for bioconcentration. But this data is only connected with soft tissues, without skeleton parts. Have you any data about carbonate?

A. Very little. Our concern was really what was being accumulated in soft tissues. So we've done very little work on that.

Q. About seasonal deviation, or variability of concentration: Have you any?

A. In what particular component?

Q. Data for months, years.

A. Well, certainly for species like Mitro fabulus, there's a big seasonal variability associated with the development of gonadal tissue, which can cause big fluctuations in growth effects. But when we're using these things as indicators, we avoid that particular season. We choose times of the year when levels are more stable. But certainly there's variability between times of the year.

Q. NORMAN NEWMAN (3 M): You associated the toxicity with the soluble silver species. Have you any characterization of the speciation of the silver form?

A. No.

Q. JIM KRAMER (McMaster Univ.): I'd like to refer to the phosphate discharge-fertilizer discharge. You mention that all metals are concentrated there. How do you relate that? Is that increased productivity effect? Or what is the mechanism we should think about?

Q. Why are you getting elevated levels?

A. It's principally the source of the phosphate oil that they use to produce the fertilizers. And part of the process is you treat the ore with apatite.

Evaluations of the Bioavailability and Toxicity of Silver in Sediment

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In a series of laboratory experiments, several aspects of silver bioavailability and toxicity in aquatic systems were investigated. These experiments focussed on 1) the comparative toxicology of silver to aquatic toxicity testing species, 2) amendment of sediments with silver compounds, 3) sediment toxicity of silver compounds, and 4) a microcosm study of silver bioavailability. Silver compounds differ several orders of magnitude in their toxicity to aquatic species and aquatic organisms normally used for toxicity testing vary widely in their responses to silver. Amendment of sediments with silver compounds requires a different technique for each salt. Observed silver partitioning between particulates, pore water, and overlying water vary widely and this is reflected in sediment toxicity testing results. In experiments with silver in aquatic microcosms where the bioavailability and toxicity of silver were monitored for > 60 days, silver toxicity decreased through time. Manipulations of the microcosm sediments such as resuspension did not result in increased bioavailability as measured by survival of *Hyalella azteca* and *Chironomus tentans*.

INTRODUCTION:

As we transfer and transform metals such as silver around the globe, questions often arise concerning the consequences of local increases in concentrations. Although silver has a predominately lithic biogeochemical cycle, the use of water in silver mining and industrial processes serves to alter aqueous and sediment concentrations in receiving aquatic systems (Plansson and Cato 1980). Since "free" or bioavailable silver is relatively toxic to aquatic species (U.S.E.P.A. 1980), clear understanding of the fate and effects of silver is required to accurately characterize the potential risks of silver in aquatic systems. Like other metals with an affinity for particulates and sediments (Parkerton et al. 1989), only a fraction of the total silver that may be found in a sediment or its overlying water is bioavailable (Terhaar et al. 1977; LeBlanc et al. 1984). Thus, the purpose of this research was to obtain results that begin to provide answer to the question: when does the presence of silver in sediment become harmful in aquatic environments?

Numerous studies have illustrated that silver nitrate in laboratory tests is relatively toxic to fish and other aquatic organisms (U.S. E.P.A. 1980; LeBlanc et al. 1984). This toxicity is apparently strongly correlated with the concentration of ionic silver. Ionic silver is rapidly complexed in natural aquatic systems and sorbed by dissolved and suspended materials that are usually present. Several studies have also shown that the complexed and sorbed silver species in waters are an order of magnitude less toxic to aquatic organisms than the free silver ion (e.g. Terhaar et al. 1977). For example, silver sulfide and silver thiosulfate are at least fifteen thousand times less acutely toxic to some aquatic species than free, ionic silver. Longer term experiments have also illustrated similar patterns for free vs. complexed silver. Embryo-larval tests with fathead minnows have been conducted that identify significantly less toxic forms such as silver thiosulfate. However, silver in sediments has not been as extensively evaluated. This research was designed to add to currently available information regarding the bioavailability of sediment associated silver.

We initiated a multi-tiered research program to elucidate factors in aquatic environments that influence the bioavailability of silver. The initial focus was on freshwater sediments as sources or sinks for silver. As for other metals, it was clear that understanding silver speciation would be crucial for predicting bioavailability (Chudd 1983; Coley et al. 1988; Kramer and Allen 1988; LeBlanc et al. 1984; Lytle 1984; Sanders and Abbe 1989). This paper contains information that was gathered in the four phases of this research project: 1) the comparative toxicology of silver to aquatic toxicity testing species; 2) evaluation of sediment amendment procedures using silver compounds; 3) measurement of the bioavailability and potency of silver using typical freshwater sediment toxicity testing organisms; and 4) evaluation of silver speciation kinetics and bioavailability in laboratory microcosms. This paper summarizes the results of the first year's research efforts.

MATERIALS AND METHODS - SUMMARY:

The first phase of this research involved investigation of the comparative toxicology of silver sources (compounds). In the first phase, standard (96h and 10d) toxicity tests were performed with Ceriodaphnia dubia, Daphnia magna, Hyalella azteca, Chironomus tentans and Pimephales promelas. The second phase of the research was an evaluation of sediment amendment procedures using three silver compounds as sources of silver. Sediments representing a range of characteristics anticipated to influence silver speciation (e.g. pH, organic carbon, A.V.S.) were selected for evaluation of sediment amendment procedures, as well as some formulated sediments (Suedel and Rodgers 1991). Silver concentrations in interstitial water and sediment were measured to determine silver partitioning in these compartments of the selected sediments. Measurements of silver followed Standard Methods (1992) for atomic absorption spectrometry. The third research phase involved measurements of silver bioavailability by using routine sediment toxicity tests with *Hyalella azteca* and *Chironomus tentans* (A.S.T.M. 1992). These organisms were exposed to characteristically dissimilar sediments that were amended with silver from different compounds (salts of silver). *H. azteca* and *C.tentans* responses to silver in these sediments were used to further evaluate characteristics regulating silver bioavailability. Further, it was important to evaluate several sources of silver (silver nitrate, silver chloride, and silver thiosulfate complex) in this phase of the research since they may influence bioavailability.

The fourth phase of this research involved a time course study of silver bioavailability in laboratory microcosms in an attempt to verify information developed in sediment testing phase. A common thread throughout this laboratory based research has been to improve our understanding and predictive capabilities regarding the speciation and temporal fate and effects of silver in aquatic ecosystems.

RESULTS AND CONCLUSIONS:

Comparative Toxicology of Silver Compounds to Aquatic Species

1. The initial form of silver (i.e. the silver compound selected for study) strongly influences

thiosulfate complex is orders of magnitude less toxic than either silver chloride or silver nitrate.

2. Responses (sensitivity) of aquatic organisms to silver exposures vary widely. In general, micro-crustaceans (Daphnia magna and Ceriodaphnia dubia) are very sensitive to bioavailable silver. The amphipod, Hyalella azteca, is similarly sensitive. The fathead minnow (Pimephales promelas) is somewhat less sensitive. The midge, Chironomus tentans, is relatively insensitive to silver (10d EC50 = 259 mg Ag/L as $AgNO_3$).
3. Insoluble silver in some forms may be bioavailable through ingestion or direct contact. In experiments with AgCl, amphipods in contact with crystals of AgCl, died in 24h or 10d exposures. This needs further study, however.

Amendment of Sediments with Silver Compounds

1. The affinity of sediment particulates for silver varies by a factor of about two to three.
2. Concentrations of silver in overlying water of sediments amended in the same manner vary about two orders of magnitude. Bioavailability would be anticipated to vary widely also.
3. Concentrations of silver in interstitial (pore) water of sediments vary three orders of magnitude.
4. There was no relationship between overlying water and pore water silver concentrations.
5. Concentrations of silver are relatively stable after 24h of contact with the sediments.
6. The affinity of silver for the silt/clay fraction of the sediments was observed (~ 2 - 100 x).
7. The silver compounds studied ($AgNO_3$ and AgCl) differed greatly in their affinity for sediments.

Bioavailability of Silver in Laboratory Sediment Toxicity Experiments

1. Hyalella azteca is two orders of magnitude more sensitive to silver (as AgCl) in sediments than Chiromomus tentans.

2. Sediment characteristics strongly affect silver partitioning. However, no single sediment characteristic regulated apparent bioavailability.
3. Silver as AgCl and AgS_2O_3 complex is orders of magnitude less bioavailable (and toxic) in sediment as $AgNO_3$ amended sediments.

Microcosm Study of Silver Bioavailability

1. In laboratory aquatic microcosms with silver-amended sediments, suspension of sediments did not result in increased toxicity (bioavailability) of silver.
2. Toxicity of silver (as AgCl) decreased over time ($\leq$ 65 days) in these microcosms. The toxicity of silver as $AgNO_3$ was relatively unaffected.

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Questions & Answers: Evaluations of the Bioavailability and Toxicity of Silver in Sediment

Q. GREG CUTTER (Old Dominion Univ.): I think one of the problems with these toxicity tests is that when you amend sediments, the silver that's in the sediments may not represent what really is in the environment. Did you do any checks on the partitioning of silver after the amendment and compared it to, let's say, a contaminated sediment?

A. Actually, we didn't follow this up with a "contaminated" sediment because we're still pursuing the silver as a solo sediment contaminant out there in nature. Maybe we'll find that one day. The issue of time, and time-course bioavailability, was something we were trying to track in the microcosm study. That study went for over 60 days. That's time for microbial growth and other biological activities — bioturbation, and so on — that might take place and influence bioavailability. That's a tough problem, making that transition from laboratory to field site.

Bioaccumulation of Silver in Marine Bivalves

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The accumulation of silver in marine bivalves was studied in a series of laboratory experiments employing radiotracer methodology. To efficiently study the kinetics of accumulation and retention of Ag in individual organisms, an approach was adopted employing a gamma-emitting radioisotope (^{110}Ag), which allowed for rapid and nondestructive analyses using low Ag concentrations.

Silver uptake and depuration in clams, mussels and oysters were compared from diverse phytoplankton food sources. Additionally, silver uptake and depuration in mussels from dissolved sources were determined. The assimilation efficiency of ingested Ag in oysters was 44 percent, in clams assimilation efficiencies ranged from 22-35 percent from different phytoplankton food sources, and in mussels assimilation efficiencies ranged from 5-35 percent. No correlation was found between C and Ag assimilation in mussels from phytoplankton food. Generally, an inverse relationship was found between food quantity and assimilation efficiencies for Ag in mussels for the same algal food source. Ag assimilation efficiencies were higher than those of some other particle-reactive, nonessential metals but lower than assimilation efficiencies of other elements (e.g., Zn, Cd, Se).

Loss of Ag from bivalves typically followed a two-compartment loss curve, where the loss rate of the slowly exchanging pool of Ag in the animals reflected the physiological turnover of the Ag. The biological half-life of Ag in mussels was about 27 days, in clams it ranged from 44 to 80 days (depending on diet), and in oysters it approached infinity (i.e., there was no loss). The influx rate (I) of Ag from the dissolved phase in mussels was described by the equation $I = 0.386\ D^{0.967}$, where I is in units of $\mu g\ g^{-1}\ d^{-1}$ and D = dissolved Ag concentration in units of $\mu g\ l^{-1}$. Ag loss rates were found to be essentially equivalent in mussels maintained in the laboratory in flowing seawater and in mussels held in the field. Loss rates of Ag from mussels were lower following accumulation from the dissolved phase than following accumulation from food.

Both dissolved and particulate Ag appear to contribute to its accumulation in marine bivalves. The elevated Ag concentrations found in oysters may be attributable to their extremely long retention times for this metal.

Questions & Answers: Bioaccumulation of Silver in Marine Bivalves

Q. RUSSELL ERICKSON (EPA-Duluth): On the *edulis* data, the difference in the long-term loss rates, for the two food sources. Did your tissue distribution show any explanation for that, as far as different distribution among the organs, that would explain it? It seemed to be one of the oddest points of your data.

A. I'm not sure I follow the question.

Q. Okay. You had a much longer half-life for the diatom food source — in *edulis, Mytilus edulis*. The depuration rate you reported was much longer for the diatom than for the *Isochrysis*. Do you have any explanation for that? I'm asking whether there was any different distribution of the silver — internal distribution in the silver — that you saw, or do you have any other explanation?

Q. Yes, we were interested in that. That's why we got into the carbon assimilation studies, to see whether there was some relationship — carbon or protein assimilation. And we didn't find an answer there. The dissection data don't really allow us to explain the differences, they're not sufficiently fine. It may be that once the phytoplankton cells are in the gut of the animal, they will release silver into the dissolved phase of the animal at different rates. That is, the release of silver from ingested particle into the dissolved soup in the gut may be different for the diatom and for the *Isochrysis*. To address that point, because these were acidic guts with pH of about 5.5, we looked at release rates of metals from diatoms and *Isochrysis* at pH of 5.5, and we did see a difference there. So that may partially explain it. But it's not apparent. If you look at the distribution in the soft part, you don't see a big difference.

LUOMA: I think that's something we have to revisit the calculation of. So there are several things we need to do in those calculations. It's a work in progress.

A. Yes, very much.

Q. DALAND JUBERG (Eastman Kodak): Nick, your data suggest that silver uptake and assimilation may be a good biomarker of exposure, I would say. Do you have any evidence of adverse impacts, such that marine bivalves may become biomonitors, not only of exposure, but effect, or susceptibility?

A. It's entirely possible, but the concentrations we're using are so far below those which are going to elicit any toxic effects. We see no evidence. But again, we're working with high picomolar to low nanomolar concentrations, where the silver is added as the nitrate. And we see absolutely no evidence of toxicity. At higher concentrations, obviously, you can get to some point where there will be toxic effects, but whether or not those will be environmentally realistic levels, I rather doubt.

Q. EUGENE KRASNOV (Kaliningrad State Univ.): How about tissue defenses, in the context of bioaccumulation?

A. Yes, we have that data, and I can show that to you. I really am not going to have time to go into the details, but the main point is that, from the dissolved phase, it's primarily on the shell and a little bit in the gill tissue, and a very little bit in other tissue. No, we see almost nothing in the reproductive. Following food uptake, there's a little bit in the shell, but that comes from the silver, which was released during the feeding into the dissolved phase and got sorbed to the shell. And that is released more slowly than the silver that is in the soft parts of the animal. Predominantly, it is in the soft parts of the animal, primarily the digestive gland. Some of the assimilated metal ends up in the foot.

Bioaccumulation of Silver in Marine Bivalve Mollusks

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Experimental

Surface sediments (top 1 cm) and marine bivalve soft tissues have been collected from approximately 200 sites along the coastal US. For chemical analysis 20 oysters or 30 mussels of similar size were collected, shucked and the soft tissue pooled into a single sample. Crassostrea virginica (cv) have been collected from Delaware Bay south through Texas, Mytilus edulis (me) in the Northeast U.S. and several sites on the West Coast, and Mytilus californianus (mc) at the remaining West Coast sites. Analytical methods have been described in detail (NOAA, 1993). Both sediment and soft tissue samples were freeze-dried and homogenized prior to analysis. Sediment samples were digested with a HNO_3-HCl-HF mixture, and tissue samples were digested with HNO_3 or HNO_3-$HClO_4$. Total metal concentrations were determined by GFAAS or ICP-MS analysis. Data analysis was performed with SAS/PC version 6.08.

Spatial distribution of silver in sediments

Sedimentary Ag concentrations, in general, are greater along the Northeast and West Coasts than along the Gulf of Mexico and Southeast Atlantic Coasts. The geometric mean Ag concentration in sediments from the NS&T sites is 0.14 µg/g dry weight. Concentrations are greater in sites near large population centers, and concentrations above 0.2 µg/g are found almost exclusively near urban areas. Using data from the US Census Bureau, Ag was found to correlate strongly with the human population in a 50 km radius, with a Spearman ranked correlation coefficient of 0.596. This is in agreement with previous results that suggested that sewage discharge is the primary source of Ag in coastal waters.

Correlations between sediment and tissue concentrations

In addition to sediments, bivalve mollusk tissue samples have been analyzed by NS&T. Geometric mean tissue concentrations of Ag are: 1.71 (cv), 0.29 (mc), and 0.18 (me). Spearman ranked correlation coefficients between tissue and sediment Ag concentrations are shown in Table 1. Average tissue concentrations do not correlate with sediment Ag levels (r_s=-0.150), but when the correlations are calculated by species, the r_s values are greater. Correlation between sediment and tissue Ag concentrations are significant for all species (p=0.05); however, mussel Ag concentrations correlate more closely with sediment Ag concentrations than oysters do.

Surface sediments that have been analyzed by the NS&T program may represent average concentrations for time periods ranging from months to decades, depending on the rate of accumulation. Bivalve mollusks, on the other hand, accumulate contaminants only during their life span. Thus, sediment and bivalve tissue Ag concentrations represent different time frames and accumulation routes. The lower correlation of oyster Ag concentrations with sediments probably reflects the small degree of interaction between these two compartments.

Table 1

Spearman Ranked Correlation Coefficients (r) between Tissue and Sediment Ag concentrations

All	-0.150
Crassostrea virginica	0.252⊗
Mytilus californianus	0.561⊗
Mytilus edulis	0.463⊗

⊗ Significant at the 0.05 level.

As mentioned above, sewer discharge is the primary source of Ag to natural waters. The amount or volume of sewer discharge is expected to relate to human population in the vicinity of a site thus, population should be a good measure of total silver input. Correlations between sediment and population at a 50 km radius (P50), and tissue-P50 suggest that sediment Ag concentrations are directly related to input levels (Table 2). This correlation is very strong for all parts of the country, except the Gulf of Mexico Coast. The lack of correlation between sediment Ag concentrations and P50 in the Gulf of Mexico is not well understood. Similar types of correlations between P50 and tissue Ag concentrations are significant only for the Northeast and West Coasts, where mussels have been collected, but not for the Southeast and Gulf of Mexico Coasts, where oysters have been collected.

Table 2

Spearman Ranked Correlation Coefficients (r_s) for Silver

	Sediment-P50	Tissue-P50
All	0.596⊗	-0.131
Northeast	0.806⊗	0.337⊗
Southeast	0.571⊗	0.022
Gulf of Mexico	0.007	-0.005
West	0.673⊗	0.538⊗

⊗ Significant at the 0.05 level.

Pathways of silver bioaccumulation

The NS&T silver concentrations in oysters are always greater than those in mussels, an observation also made in a previous mussel watch project (Goldberg et al, 1983). Both oysters and mussels (me) have been collected at a few sites in Long Island Sound, with similarly high Ag concentrations in oysters. The greater concentration of silver in oysters may relate to the utilization of copper by these animals. Factor analysis of the data shows a strong association between silver and copper. The greater covariation of Ag with Cu is also seen in Table 3, where the correlation coefficients of Ag with some essential elements have been calculated. Statistical analysis of a database of elemental composition of several aquatic species revealed that Ag correlated strongly with Cu (Lobel et al., 1992). Oysters use Cu in their respiratory pigment (hemocyanin), while mussels use hemoglobin, an iron containing pigment. It is the chemical similarity of the two elements, and in particular, their affinity for sulfur, that promotes Ag bioaccumulation.

Table 3

Correlation Coefficients of Ag with Essential Elements in Mollusks

Species	Cu	Fe	Se	Zn
All	0.641	0.102	0.261	0.543
cv	0.537	0.204	0.287	0.350
mc	0.376	0.077	0.114	0.298
me	0.351	0.066	0.140	0.060

Although Ag is not an essential element, marine and estuarine organisms tend to accumulate large quantities of this metal. The apparent route of Ag entry into the oyster is through the gills (Martoja et al., 1988; Abbe and Sanders, 1990). This is followed by transport through the bloodstream to cells where Ag may be deposited in granules that remain at least partially non-bioavailable. These granules were both inorganic (Ag_2S) and organic in nature, as suggested by chemical and electron microprobe analyses (Martoja et al., 1988; Berthet et al., 1990). Martoja et al. (1988) found that granules in the amebocytes of oysters (C. gigas Thunberg) contained both Ag and Cu bound to sulfur. This is an additional indication that Ag may follow the same pathways as Cu in bioaccumulation.

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Questions & Answers: Bioaccumulation of Silver in Marine Bivalve Mollusks

Q. LUOMA (USGS, Menlo Park): Has anybody ever looked at amoebocytes in oysters? It's something I think that Jeff Bryan a long time ago explained, knowing this other effect. A lot of the copper bioaccumulation is due to the fact that they have amoebocytes that go in and out of their tissues, and can act as detectors for metals.

A. I think some French group has looked at these things. And they had certain explanations. But to look at silver, one would like to see if there is a need by the animal, and apparently there isn't. And it's getting confused, with the need for copper.

COMPARISON OF SILVER AND OTHER TRACE ELEMENT UPTAKE BY PHYTOPLANKTON

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The interactions of silver and other trace elements with phytoplankton are governed by a complex mixture of physical, chemical, and biological constraints. Many elements are extremely particle reactive and sorb readily to both living (phytoplankton) and nonliving particles (sediment). Phytoplankton are efficient scavengers of trace elements, accumulating high concentrations from the surrounding medium. Both active and passive mechanisms can be involved in trace element sorption; the relative importance of different sorption pathways varies with the element of interest.

Silver is similar to a number of transition elements (e.g., cadmium, mercury, zinc) present as cations. Silver sorbs rapidly, generally in proportion to silver concentration within the surrounding medium. Silver accumulation by phytoplankton varies between species, with cellular content strongly correlated with cell surface area or cell volume. Accumulation of silver in marine systems is inversely proportional to salinity, indicating (as has been demonstrated with other transition elements) that only some forms of silver are available for uptake (see below).

The incorporation of trace elements by phytoplankton can regulate trace element form and availability. Most simply, as is the case with silver, uptake by phytoplankton reduces the amount of dissolved metal, thereby reducing its likely availability to higher trophic levels. Once associated with a cell, silver is not easily removed. The binding of silver by algal cells is quite strong. Silver remained bound to cells when subjected to low pH, in the presence of strong buffer solutions, and even when the cells were subjected to digestive enzymes.

In addition to changes in trace element partitioning, phytoplankton incorporation can greatly affect the chemical speciation of some elements in the water column. For example, arsenic incorporation by phytoplankton and subsequent reduction and methylation can yield dramatically different forms of dissolved arsenic within the water column, and a corresponding shift in arsenic toxicity and availability. The release of dissolved organic compounds by cells can also affect the degree of organic complexation of some elements and can facilitate photoreduction reactions.

While many trace elements are accumulated in proportion to dissolved concentration, others are not. With elements that are present as anions, such as arsenic, selenium, or chromium, chemical similarity to necessary nutrients (As-P, Se, Cr-SO_4) can regulate cellular incorporation, controlling cellular content regardless of dissolved concentration.

In marine systems, silver accumulation is regulated by salinity. Silver speciation is controlled by chloride ion concentrations, with the free ion present in decreasing concentrations as salinity increases. While the accumulation of other transition elements has been shown to be controlled by the free ion, with silver the monochloro complex may also be available. In our studies, and those of others, variation in silver accumulation more closely follows the variations in $AgCl^0$ than the free ion. In addition, the uncharged species, AgHS, may be available for uptake. Further research will assess this potential uptake pathway.

Silver toxicity is also regulated by salinity. As with accumulation, silver toxicity to phytoplankton decreases with salinity, again in strong correlation with the concentration of the monochloro complex.

Phytoplankton incorporation of trace elements is an important regulating mechanism in their transport and availability. The interactions between biological and geochemical controls of silver and other trace element availability to phytoplankton in estuaries and other aquatic systems underscore the need to fully understand the biogeochemistry of reactive trace elements in order to make predictions of ecosystem impact and to allow for effective system management.

Questions & Answers: Comparison of Silver and Other Trace Element Uptake by Phytoplankton

Q. MICHAEL BOTHNER (USGS, Woods Hole): Jim, I just was curious to know if you could combine your results with what Nick told us about the uptake by bivalves. One graph which interested me was that silver stayed on the cellular wall, in spite of a pH range, EDTA, the treatment, and if you hit it with sonification, broke the cells. And Nick shows some significant uptake. The question I have is, does that imply that the bivalves have a tremendous digestive system that yanks the silver off the tests?

A. I don't know how to answer that question, Mike, because, as Nick will tell you, we have differing data on bivalve uptake. The work that we've done with cold silver has essentially shown that they are not able to take it out of phytoplankton cells. But the uptake of silver that we see by bivalves is essentially from dissolved pools. Nick is working at lower levels than we're able to with cold silver, and so, I'll defer somewhat to that. However, with other species we've looked at, most of what's in that tissue is going to pass right through, and very little is going to stay behind. And John Reinfelder's and Nick's data, again, if you look at it, silver is down there at the lower end of their curve. There's not a lot of silver in the cytoplasm, and relative to something like selenium or cadmium — what else is up at the upper end, zinc — they're going to take it all out of the cells, they're not going to get much of the silver. But Nick's suggesting that they're getting enough that you can see it.

LUOMA: I'd like to comment on that. And I'd also like to ask people to stay around for a few minutes because I have a couple of announcements when we're done. But in response to what you just said, I think adult bivalves — unlike copepods and less-developed enlarvae — have a two-phase digestive system. They have a lumen, a gut, in which the typical extracellular digestion goes on, kind of the way we think about digestion in a vertebrate, and they also have a digestive gland in which particles are engulfed by the equivalent of amoebocytes, and intense digestion occurs. And we've published, Alan Beckel and I, and, again, in conjunction with the kind of studies Nick talked about — we have pretty much in detail described that digestive process, and showed that for a lot of metals, if you run the experiments long enough, or if you do the experiments right, you can show that a lot of assimilation of metals occurs during that intense digestive gland phase of digestion. So indeed, adult bivalves do have this capability. And different bivalves differ in the amount of material they put through the digestive gland, and the kind of particle affects that. So again, different organisms are different, is kind of the lesson. And some bivalves, especially opportunistic bivalves, are really good at using this type of digestion. And so, I think we're getting contradictory results in some of these experiments. But part of it is that we haven't done this long enough or enough of it to really understand the total biology of what we're looking at.

A. And the [results are] not completely contradictory. I think that Nick would agree that most of the silver is passing through the gut, which is different than you would see for some of the other metals. So silver is really staying tightly [bound] onto particles, and they're getting some of it, but they're not getting a lot.

LUOMA: And if you look at different solution/solid ratios and different assimilation efficiencies from those solids, you can get different dominance by different vectors. But a model can tell you that, and I think that's where we should go.

A. But we're headed that way.

Q. NICHOLAS FISHER (SUNY-Stony Brook): If I could just add one more thing. We do see release of silver from phytoplankton, unlike what you're seeing. It's not rapid, but it's definitely there. In fact, one of my students, Byong Lee, who is now post-docing with Sam, wrote his whole thesis essentially on the release of metals from decomposing phytoplankton cells. But even in intact cells that are not yet decomposing, we don't see irreversible binding. Now, we did not work with *skeletonema*, and it may well be that there are differences between phytoplankton species. But with other diatoms, we see some release. It's not rapid. It's certainly far less than we would see for cadmium, for example. But it's more rapid than you would see for lead or some of the actinides or lanthanides.

A. Yes, now these are only after 24 hours. What we're looking for is if you can take a cell, if you can knock something off quickly, or whether or not it's going to stay with it. And obviously with time, yes, it's going to get released.

Q. GARY GILL (Texas A&M Univ.): I want to make sure I understood the last part of your talk when you were dealing with mutation and toxicity. If I understood it right, you were suggesting that the active parameter here is the chloro species, the monochloro species that would be the active parameter that you could normalize everything to, in terms of uptake. Is that correct?

A. Well, I won't be quite that strong, because, again, we're working with speciation models. But if you take what a chemical speciation model will do, ignoring sulfide — and if you assume that we've got nanomolar levels of sulfide there, sulfide would be a major player as well — and if you just look at best fit for the various forms that are around, that's what you get. That's what those data were showing, simply the best fit between toxicity results and the various chemical forms.

Q. Assuming that is indeed the mechanism, does it look like it is not an active transport across the cell membrane, but rather a diffusion-controlled process?

A. I would say. One of the other things we were talking about, Greg and I earlier, [that] as with many transition elements, you've got lots of passive processes that will bring that ion onto the cell surface. And at that point, then, there may be more active transport, using a thiol group or what have you, to get that stuff inside the cell. So it may be a two-coupled thing. And our simple-minded approach of saying, well, it fits well with a monochloro complex, may be extremely simple-minded, because we've got to be able to handle those two processes, and we're not doing that yet. It's nice and suggests the fact that the uncharged species may be playing a role, and, as we said so far throughout this conference, the levels of free ion are so vanishingly small, it's hard to believe that that's regulating uptake.

Fate, Bioavailability and Toxicity of Silver in Estuarine Environments

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The salinity of brackish and marine waters greatly affects the chemical behaviour of Ag. Thermodynamic models show that strong chloro complexes ($AgCl^{o}$, $AgCl_2^{-}$, $AgCl_3^{-2}$, $AgCl_4^{-3}$) dominate speciation in brackish and marine waters (Cowan et al, 1985). The speciation of Ag affects bioavailability and toxicity. All three contribute to a concern about this element as a pollutant in marine and estuarine waters. Natural concentrations of Ag in seawater are very low (1 - 3 pM; 0.1 - 0.3 ng/l) (Sanudo-Whilhelmy and Flegal, 1992). Instead of remaining in the form in which it is introduced, the Ag-chloro complexes favor the retention of at least some Ag in dissolved form. As a result, relatively small anthropogenic inputs result in substantial environmental enrichment. Anthropogenic contamination can result Ag concentrations in estuarine and marine waters that are 100 - 300 times higher than natural concentrations (Sanudo-Whilhelmy and Flegal, 1992). Such concentrations can be widely dispersed.

The chemistry of Ag in solution should affect its association with particulate materials, but the chloro complexation does not prevent association of Ag with natural particles. Sediments stripped of their coatings did not accumulate as much Ag as untreated sediments, even over a two week period. Pre-treatment with hydroxylamine in acetic acid resulted in removal of 99% of the weak acid-soluble Mn, 90% of the weak acid-soluble Fe from the sediments and nearly complete removal of bacteria. . It also resulted in a 25% increase in surface area (presumably because clay surfaces were exposed). Less Ag accumulated on these stripped sediments than on untreated sediments, despite a greater surface area. Thus, Ag in seawater reacts with natural particles and most readily with the removable aggravates that coat the surfaces of such sediments.

Silver also reacts with sediments in nature. This is evidenced by a net accumulation of Ag in the sediments of estuaries affected by human activities. Background concentrations of 0.1 µg/g Ag occur in San Francisco Bay and Tomales Bay. Silver can reach concentrations of 0.5 µg/g and in some cases >1.0 µg/g in cores taken in anoxic sediments from undisturbed environments (Koide et al, 1986). Surveys of a wide variety of English estuaries (Bryan, 1984; Bryan et al, 1985) also show Ag concentrations in surficial, oxidized sediments are 0.1 µg/g in the least contaminated environments. Concentrations of Ag associated with widespread anthropogenic disturbance range up to 5 µg/g (Figure 4). A few environments occur where Ag concentrations exceed 100 µg/g in sediment, but these are very exceptional (Bryan, 1984).

Cherry's (1983) broad review of Ag in mollusc tissue showed that Ag is the most strongly bioaccumulated of the elements in marine environments. This may occur because Ag is unusual for a trace element in that the dominant speciation reaction in seawater and processes important in sorbing Ag in sediments both favor enhanced bioavailability. The strong chloro complex not only enhances Ag mobilization, but is available to biota. The more amorphous aggregated coatings of sediments enhance Ag accumulation in sediments.

Laboratory studies demonstrate that Ag associated with oxidized sediments is available to detritus feeders. Association with sediment coatings enhances Ag uptake from sediments by deposit feeders. If coatings are stripped from sediments both accumulation of Ag on particle surfaces and bioavailability decline.

In nature, bioavailability also correlates with an easily extractable fraction of Ag that accumulates on contaminated particles. In estuaries, the bioaccumulation of Ag increases as a power function of Ag concentrations extracted from sediments by weak 0.5N hydrochloric acid (HCl) When data sets from English estuaries and San Francisco Bay for the clam *Macoma balthica* are combined, 80% of the variance in Ag concentrations in the clam is explained. The global nature of this relationship suggests it could be useful in predicting bioavailable sedimentary Ag. In this data set, one unit of Ag contamination in oxidized sediment results in 56 units of Ag bioaccumulation in the estuarine clam *Macoma balthica* over a wide range of estuaries. Thus a little Ag contamination in a marine and estuarine environment has great consequences for contamination of at least some organisms.

The toxicity of Ag is the primary source of concern in marine environments. Toxicity for sensitive marine species occurs at absolute concentrations as low as observed for any non-alkylated metal. The above lines of evidence may help explain toxicity and support concern. The chemistry of the element favors enrichment, dispersal and some environmental storage. Both the dispersed and stored form are bioavailable. As a result, bioaccumulation increases steeply with contamination, and low contaminant concentrations are toxic to sensitive species. Thus the environmental window of tolerance to Ag in marine and brackish water systems like estuaries may be more narrow than in freshwater. Only a few studies have considered Ag toxicity in natural systems. These have reached inconclusive results. It is clear that the effects of Ag in natural systems deserve considerably more careful study than have been assigned them to date.

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Footnote: A complete version of this paper has been submitted to *Marine Polllution Bulletin* for publication in a memorial issue for G. W. Bryan.

Q. ERIC CRECELIUS (Battelle): We've done just a little bit of the AVS work with silver in sediment, and we get some of the silver back.

A. Oh, do you?

Q. We spike silver in anoxic sediment and extract it soon afterwards. We get a little more silver back, and we get copper back. Copper is evidently very reversible.

A. So does that mean that some silver sulfide is available, or that silver associates with something other than sulfide in those sediments?

Q. We can't answer that. But I don't think you can make the statement that you can't get any silver.

A. That's probably too black and white. I don't know. I think that's an interesting thing to test.

Q. EUGENE KRASNOV (Kaliningrad State Univ.): Which tissues were used in your experiments about mollusks?

A. Soft tissue. Not shell. We don't think we're going to find much silver in the shell.

Q. Yes. What geological application do you see after your investigation? Geological application, to survey from?

A. I guess I don't understand. You mean looking for silver in deposits?

Q. No, no. But practical application to geology.

A. Oh, practical application. One of the things we can use soft tissues for organisms in — and I would continue on if there was more time — is as a monitor, as Bill says. Bill showed the other day — I think there are those kind of applications. The other big question is, is silver of concern in estuarine environments, in terms of its toxicity, and I think there are suggestions of that.

Q. CHRIS WOOD (McMaster Univ.): You made a comment at the beginning that geochemical considerations mean that you overestimate toxicity in tox tests, and biological considerations mean you underestimate toxicity. Can you elaborate a little bit on what you really mean by that?

A. The argument is made that toxicity tests geochemically are often done in waters of relatively low organic content, waters that would maximize free ion concentrations, and might maximize the bioavailability of the metal. This is the big argument toward moving toward standards that are more geochemically realistic. Especially when waters are not filtered. We know, of course, [that] particles influence and probably reduce availability, in a simplistic sense.

Biologically, however, if you think about the various conditions that are going on, and you look at field or even microcosm studies compared to results from single system bioassays, there are a number of factors — and I can send you the paper, but I'll list just a few of them. One is the lifespan of the organism that you're exposing the element to. We expose the organisms — and even the life stages of an organism — to a very short period, a high dose, for a very short period, because that's what is practical. That's not what happens in nature. The other has to do with the fact that testing a single life stage is not testing the life cycle of an organism. If you look at whole life cycle studies, you see greater sensitivity, oftentimes, than in single life stage studies. The other possibility is that in nature, organisms are not exposed to a stable environment and a dose of a metal. Organisms have critical stages in their life cycle, and they are exposed to different kinds of stresses at different times. It's a very complicated picture, and we just haven't been able to sort this out. But all these things would make the simplistic bioassay more insensitive, from a biological point of view. We're thinking a lot about the oversensitivity of it from a geochemical point of view. We're not thinking much at all about the insensitivity from a biological point of view. That's my point.

Q. GREGORY CUTTER (Old Dominion Univ.): Have you done any of the completed fractions for silver like you have done for copper? Because of the way you covered the HCl fraction. But what about doing careful carbonate, organic, you know, sequential leaching?

A. The problem is usually detection limits with those. About all we did — like in the English study where we did a lot of that — about all we did was just what you saw here, was ammonium hydroxide with HCl, and we don't see much, for example, in hydroxyl amine. But I don't know what that means.

Analysis of Silver in Mussels and Oysters by Inductively Coupled Plasma Mass Spectrometry (ICPMS)

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Common HNO_3 acid digestion procedures used in preparation of samples for the analysis of metals in marine tissue can cause low recovery of silver (D'Elia et al. 1989). Experiments conducted on marine mussel and oyster tissue indicate that silver recoveries from field samples containing high concentrations of silver are low and variable. Digestion of tissue (using a sealed microwave container) in nitric acid was not as effective as in a mixture of hydrochloric and nitric acids for dissolving silver or for recovering matrix spikes. Isotope dilution mass spectrometry (IDMS) using HNO_3 digestion was not as effective because digestion apparently does not completely solubilize the silver.

METHODS

Tissue samples were prepared for analysis by freeze-drying and grinding (Crecelius et al. 1993). For analysis by X-ray fluorescence spectroscopy (XRF), 0.5 g to 1.0 g of tissue powder was pressed into a pellet, then analyzed by the method of Zeisler et al. (1988). The detection limit was approximately 7 μg/g dry weight.

For ultrasonic GFAAS slurry analysis, 10 mg to 50 mg of tissue powder was weighed into a 1 mL Teflon autosampler cup. A slurry solution was prepared with 1 mL of 5% HNO_3 solution containing 0.005% (V/V) Triton X-100 (Sigma Chemicals). A model USS-100 ultrasonic slurry sampler (Perkin-Elmer) was used to automatically mix the slurry (Miller-Ihji 1993). The slurry was pipetted into the HGA-600 furnace of a Zeeman 5100-PC Perkin-Elmer spectrophotometer equipped with an AS-60 autosampler. The detection limit was generally lower than 0.02 μg/g.

For analysis by inductively coupled plasma mass spectrometry (ICPMS), 0.3 g of tissue was hot-acid digested by two methods. Either 0.3 g of tissue was digested with

5 mL concentrated HNO_3 or the tissue was digested with the combination of 5 mL HCl and 3.5 mL HNO_3 in a Teflon digestion vessel for 20 min at 90 psi in a microwave oven. After digestion, the digestate was diluted to 20 mL. In preparation for analysis by ICPMS, the digestate was further diluted 1:10 with 1% HNO_3 acid, and indium (In) was added as an internal standard. Additional details of the digestion and analysis methods are described in Crecelius et al. (1993). Quantification was done on a Perkin-Elmer Elan-5000 ICPMS. The detection limit for Ag by ICP-MS was about 0.03 μg/g. The (IDMS) analysis procedure used the HNO_3 sample digestion procedure. However, a known mass of isotopically enriched Ag-109 was added before the digestion step.

RESULTS

There was good agreement among results from HCl-HNO_3 digestates, slurry GFAAS and XRF. Matrix spike recoveries were also excellent for the HCl-HNO_3 procedure. The HCl-HNO_3 procedure also provides excellent results for Cd, Cu, Pb, Sn, and Zn in the National Institute for Standards and Technology (NIST) standard reference material (1566a) oyster tissue.

Comparison between two procedures (HNO_3 and HCl + HNO_3) for digestion of approximately 100 oyster and mussel tissue samples indicates that when the Ag concentration exceeds 3 μg/g, the HNO_3 procedure does not completely dissolve the Ag. For tissue samples that contain less than 3 μg/g, the two digestion procedures provide equivalent results. Probably during the HNO_3 digestion procedure, insoluble AgCl precipitates when the Ag concentration exceeds 3 μg/g in tissue or some Ag is insoluble in HNO_3. However, the HCl-HNO_3 digestion contains adequate chloride, which forms silver chloride complexes that keep the Ag in solution.

The IDMS method was used to quantify Ag in several samples analyzed by slurry and by HCl-HNO_3 digestion. The IDMS results were about 20% lower than the other methods for tissue samples containing about 10 μg/g Ag. These results indicate that the enriched Ag-109 isotope may not be equilibrated with the Ag in the tissue. Also, the recovery of the Ag-109 spike was lower for samples containing high Ag, indicating that part of the Ag-109 spike precipitated during the digestion with HNO_3.

CONCLUSIONS

Comparison of Ag concentrations determined by two different digestion procedures and two nondigestion methods (slurry GFAA and XRF) indicate that the HCl-HNO_3 digestion procedure is effective in solubilizing Ag in tissue containing up to 30 μg/g Ag. The HNO_3 digestion procedure is not satisfactory when Ag concentrations exceed 3 μg/g.

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Questions & Answers: Analysis of Silver in Mussels and Oysters by Inductively Coupled Plasma Mass Spectrometry (ICPMS)

Q. GREGORY CUTTER (Old Dominion Univ.): Eric, I was a little confused with your isotope dilution data. It suggested to me — and I think you need to do a lot more reps to get some error bars — but it seemed to me that it was instrumental and not digest. Because you're adding your isotope dilution spike, and it's not falling through the digest. And I think you were getting good recoveries on your isotope dilution using the old digest.

A. We used the nitric micro digest, and the concentrations that we ended up calculating were a little bit low.

Q. Well, a little, but they weren't half.

A. Oh, no, maybe they agreed within the 80 percent mark.

Q. LUOMA: What form was the silver in when you spiked the silver into the isotope dilution?

A. Probably silver nitrate solution.

Q. The same thing we've seen is that, somehow, getting chloride involved in the digestion or the reconstitution, you can eliminate a lot of it.

A. But do you use dilute hydrochloric acid?

Q. That's what we reconstitute the digest with. We dry the digest, and we reconstitute with HCl.

Bioaccumulation of Silver in the Oligochaete, *Lumbriculus variegatus* Following Exposure to Field-Collected Sediments Spiked with Silver Sulfide

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A 28-day bioaccumulation study was conducted to determine the potential of silver to bioaccumulate in the oligochaete, *Lumbriculus variegatus*. *Lumbriculus variegatus* were exposed to laboratory-spiked field-collected sediments containing approximately 444 mg Ag as Ag_2S/kg for up to 28 days. Fifteen test replicates were prepared by adding 300 adult oligochaetes to 4-L glass beakers containing 1 liter of silver sulfide-spiked sediment. An equal number of control replicates were also prepared. The exposure vessels were maintained at a constant temperature of 20°C in a water bath. After 1, 5, 13, 21 and 28 days of exposure to the sediments, three test and three control replicate vessels were removed from the water bath and the oligochaetes recovered from the sediments. The recovered organisms were enumerated and transferred to dilution water for 24 hours to allow the organisms to purge gut contents. By test end, the mean number of oligochaetes recovered from the control and test sediments increased 1.8- and 1.9-fold, respectively. The oligochaetes were then analyzed to determine tissue silver concentrations. The mean concentration of silver in the silver sulfide-exposed organisms was 34.7 µg/g. The biota-sediment accumulation factor (BSAF) was determined to be 0.078. The results of this study indicate that sediment exposure to silver sulfide at concentrations up to 444 mg Ag/kg does not adversely affect *Lumbriculus variegatus*, and silver, as silver sulfide, is not likely to bioaccumulate in the freshwater oligochaete.

Questions & Answers: Bioaccumulation of Silver in the Oligochaete, *Lumbriculus Variegatus*, Following Exposure to Field-Collected Sediments Spiked with Silver Sulfide

Q. ERIC CRECELIUS (Battelle): It looked to me like you had bioaccumulation, because your control was down to around a microgram and your exposed were 30 micrograms. You wouldn't consider that bioaccumulation?

A. A little bit. You might have a little bit, but I don't think it's significant. But I still think that some of that is contamination from the sample, compared to 400 milligrams.

Q. Is there any other element you could use to correct for that, such as aluminum or some other [element] which might be an indication that you're just looking at sediment contamination as opposed to [bioaccumulation]?

A. Yes, that's something, in hindsight, that we probably should have done.

Q. NICHOLAS FISHER (SUNY-Stony Brook): Related question. When you analyzed your worms, was there sediment in the worm when you analyzed it? In other words, is the silver that you're measuring in the worm really silver in the sediment which hasn't been excreted by the worm yet?

A. We aren't sure. They were purged overnight — and I forget the author of the other study that looked at the gut contents, and the time it takes. Pretty much most of it is purged within the first 12 hours, so we went until 24. But, like I said, we also had a heck of a time cleaning up what was on the outside. So although the guts may have been purged, they may not have purged completely. There was also, I think, a good chance that there was something on the exterior part of the worm. They tended to hang on to anything that was organic, like a leaf or a stick that was in the sediment. So my guess is that there might have been stuff that we didn't even see, as far as clean-up. So it could have been a little bit of both.

Q. JIM KRAMER (McMaster Univ.): I didn't quite catch the form of silver sulfide added, or did you add it as silver sulfide?

A. We added it as silver sulfide.

Q. What form of silver sulfide?

A. It was a crystalline acanthite. We had that checked. We would have liked to use an amorphous form, but we're not sure how to make it and confirm that it stays amorphous.

Q. Let me just throw in a comment, and this goes back to the talk yesterday from England. I think if you put a little copper in there, you'll stabilize silver dramatically. Interesting thing to look at, if you put a little copper in with it. And maybe your acanthite had some copper, I don't know, because often it does. I'm thinking back to the talk yesterday, remembering the copper and silver, because the acanthite will be stabilized very nicely with copper.

A. Maybe I'll recommend another one.

Q. LUOMA (USGS, Menlo Park): I'd like to make one comment too. We've done some work in streams around these mine wastes, looked at insect larvae where there's fairly high silver concentrations in the sediments. And the bioaccumulation factor like you see here is less than one, it's low. But then, again, to bring out this estuarine or marine/freshwater contrast, I think what Bill showed yesterday, and what I showed in the slide today: when you look in nature at clams vs. silver, the slope of that relationship is about 56, so, again, in estuarine environments there appears to be this much greater bioaccumulation factor in general than one sees in these freshwater systems, even when one looks at organism vs. sediment. So I think that's interesting. But what you see here, this low bioaccumulation factor, we've also seen in a natural system.

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Environmental Analytical Chemistry of Silver

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Strategies for Trace Metal Analysis in Natural Water Samples

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The detection power of analytical methodologies based on atomic spectroscopic instrumentation has improved with a new generation of equipment and the advent of hyphenated techniques. Inductively coupled plasma mass spectrometry (ICPMS) is one technique finding widespread acceptance as a powerful analytical tool due to its high sensitivity, the ability to perform multielement analysis as well as isotope ratio determinations for isotope dilution analysis. Using ICPMS the direct determination of a considerable number of trace elements in fresh water is feasible, and if required, detection.limits can be further decreased by the substitution of ultrasonic nebulization for the conventional pneumatic nebulization. However, the determination of many trace elements at "natural" levels found in seawater still require some form of sample preparation before introduction into the instrument due to interferences from concomitant elements and the high dissolved solid content.

In this laboratory concentration and/or separation schemes utilizing chelation/extraction, reductive precipitation, immobilized ligands and hydride generation have been successfully used off line to ICPMS and graphite furnace atomic absorption spectrometry (GFAAS). In this laboratory multielement extraction has been achieved using an ammonium pyrrolidine-N-carbodithioate-methyl isobutyl ketone (APDC-MIBK) extraction system(1). However, due to problems associated with manipulation of large sample volumes, high analytical blanks and incomplete recovery this technique was abandoned in favour of immobilized ligands. 8-Hydroxyquinoline immobilized on silica gel (I-8-HOQ) has been used for the preconcentration of Cd,Pb,Zn,Cu,Fe,Mn,Ni and Co from seawater prior to their determination by either GFAAS (2) or ICPMS (3). Following adjustment of the pH 8.0 the sample is passed through a 600 mg column of the resin at a flow rate of approximately 10 ml/min, the column is washed with high purity water and the chelated metals are eluted with an acid mixture of 10% HCl and 1% HNO_3. Blanks are generally lower than solvent extraction techniques and enrichment factors of 50 can be easily be achieved.

Table 1
Absolute Blank, ng

Element	APDC/MIBK	I-8-HOQ	Red. ppt.
Mn	<1	<1	4 ± 1
Fe	31 ± 4	75-100	--
Ni	<2	<3	<2
Cu	21 ± 5	<0.2	20 ± 12
Zn	62 ± 17	2 ± 1	8 ± 1
Cd	1 ± 1	<0.1	1.1 ± 0.3
Pb	7 ± 3	<0.8	1.7 ± 0.1

Irreproducible Fe blanks are due to the high Fe content in the silica substrate and can be alleviated by using the resin only at low pH or immobilizing the oxine on a plastic substrate(4). For the determination of Cr, an alternate ligand, diphenylcarbazone immobilized on silica was also successful(5).

An alternate concentration technique based on reductive precipitation by sodium borohydride has been used for the determination of 16 trace elements in seawater(6). A mixed solution of iron and palladium is added to the sample (typically 900 ml), the pH adjusted to 9 and $NaBH_4$ is added which forms a black granular precipitate. After aging the precipitate for 24 hours, the solution is filtered and the precipitate dissolved in aqua regia. Blanks are generally larger than the 8-I-OH procedure, however, detection limits are suitable for the determination of many trace metals in nearshore and open ocean water samples. Additional benefits of this technique are complete recoveries of As, Sb, Se, which cannot be concentrated using the previously described procedures.

In conjunction with flow injection techniques many of these procedures have been implemented on-line, resulting in additional benefits such as economy of sample and reagents throughput and the ease of replicating precise chemical manipulations. Miniaturization of a 8-I-OH column for on-line determinations with GFAAS(7) and ICPMS(8) has successfully been applied to the determination of trace elements in a variety of natural water certified reference materials(CRM). Results are shown below for the analysis of a coastal seawater CRM, CASS-2, using a miniaturized 8-I-0H column with flow injection techniques and two different detection systems. Results a acceptable with the exception of Fe using ICPMS due to contamination and poor sensitivity since ^{57}Fe was used for quantitation.

Table 2
Analytical Results for CASS-2

	GFAAS#	ICPMS*	Certified value
Mn	2.09 ± 0.10	2.22 ± 0.09	1.99 ± 0.15
Fe	1.15 ± 0.06	2.56 ± 0.06	1.20 ± 0.12
Ni	0.303 ± 0.011	0.305 ± 0.008	0.298 ± 0.036
Cu	0.664 ± 0.011	0.664 ± 0.004	0.675 ± 0.039
Zn	ND	2.22 ± 0.10	1.97 ± 0.12
Cd	0.017 ± 0.002	0.023 ± 0.003	0.019 ± 0.004
Pb	0.018 ± 0.005	0.021 ± 0.003	0.019 ± 0.006

\# - reference 7.
* - reference 8.
ND - not determined

Reduced interferences resulting from the separation of the analyte from the matrix is a benefit of hydride generation. For the determination of hydride forming elements in natural water samples large sample volumes are required when using conventional atomization techniques such as a quartz tube for atomic absorption or an ICP for atomic emission or mass spectrometry detection . A technique utilizing the graphite furnace as both the hydride trapping medium and atomization cell has been successfully applied for the determination of As, Se and Sb in waters, biological tissues and sediments(9). Utilizing this in-situ preconcentration procedure, high sensitivity and a substantial increase in the detection power can be realized. Coupled with flow injection procedures, complete automation of this procedure permits simple, rapid and relatively interference free determination of As, Se and Sb in these types of environmental samples.

Significant advances in instrumentation and analytical procedures have resulted in the generation of reliable analytical data for the total concentration of a suite of elements at "natural" levels. However, improved techniques must continue to be developed for many elements for which reliable environmental information is not yet available. Additionally, the study of trace element speciation presents the analytical chemist with the challenge to provide innovative solutions to environmental questions.

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Questions & Answers: Strategies for Trace Metal Analysis in Natural Water Samples

Q. ERIC CRECELIUS (Battelle): You said you've just begun to do a little bit of work on silver in your standard reference materials. Do you have anything to report at this time?

A. No. I think all our new biological CRM's will be certified for silver. We are in the process of replacing existing CRM's. And our new sediments will also be certified for silver, I expect. We're also in the process of replacing some of those. As far as the natural waters go, we haven't made any real effort to do that yet, although we've looked at it but haven't spent the time. I would think that it wouldn't be too difficult to do silver in Spurs, our river water. But seawater is another factor, because we need alternate procedures if we want to do a certification. You can't just rely on one procedure. And that's somewhat difficult to come by. Maybe we'll get some ideas today.

Q. JIM KRAMER (McMaster Univ.): At these ppt levels, many of us have many problems defining what the blank problem is, and determining what the level is, and subtracting, and so on. Can you give us any insights on how you approach the blank problem?

A. That is our problem too. Because whenever you do one of these procedures, you generally take through ultrapure water as your blank. And when you get very low, you begin to wonder if you're measuring the metal concentration in your ultrapure water, and whether subtracting that blank is appropriate. All I can say is that we try and preconcentrate large enough so that the blank is not a major factor. And in some cases where it is, we try to do alternate techniques, again to try to overcome that. With the reductive precipitation, those blanks are fairly large, but at those concentrations that we use it at, for a specific sample, it's not a severe problem. It becomes a problem with elements like tin, where the blank is fairly large, and the analyte concentration is extremely low. We've never been able to determine tin in seawater, and we've tried numerous times. Antimony can even be a problem, because of blank problems. I can't really give you any hints as to what we do, other than use alternate techniques. That's what we try to do most of to overcome that.

Q ANDERS ANDREN (Univ. of Wisconsin): In your bonded silica gel system, how sure are you that perhaps colloidally associated materials won't pass through?

A. Well, we're dealing with filtered seawater all the time, filtered through 0.45 [microns]. In fact, our river water is filtered through 0.2 microns. What happens after the filter, we can't really be certain. I don't think we have a problem, although it's hard to say. If we digest the sample and analyze again, which we do for numerous elements, we can still get the same result. Whether or not that answers your question, I'm not sure. Because we don't deal with real samples, as I'm sure none of you do. We try and get our CRM's to be at the natural level as much as possible, but we want to make certain that that concentration in that sample is accurate.

Q. Sure. Well, the reason I ask is that, for example, when we deal with hydrophobic organic compounds, some of which are colloidally associated, we know that if one uses resins, there is sometimes a problem with the colloidally associated material not being adsorbed.

A. On the silica gel.

Q. Whatever the resin is. In our case, we use XAD-2 resin.

A. That might be some of the problems we're having with the XE-305.

Q. Very briefly, in your crystal ball gazing, how do you consider polarographic techniques? We're especially interested in that to get more insight into total versus perhaps some idea about speciation.

A. Well, there are a few people doing that kind of work around the world. And especially the voltammetry technique is very sensitive. Using various ligands like EDTA to complex copper and measuring its selectivity is becoming quite popular too. I really can't say. I think we'll see new advances in that area, especially with the adsorptive accumulation technique and the complexation. What happens to the sample when you add your complexing agent is another factor that I just can't answer, and it throws everything out of whack. But I really think that adsorptive accumulation is a very powerful technique, with the limit of detection you can obtain, because you can work on the sample directly; you don't have to do any preconcentration, or any kind of evaporation to alter the sample. So it's a great technique for working directly with the sample.

Sampling, Processing, and Instrumental Techniques for the Analysis of Silver in Natural Waters

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A complete re-evaluation of trace element levels in freshwaters has occurred over the past 5 years as a succession of studies have demonstrated previously published data to be erroneous. Severe contamination during sampling and processing, and inadequate analytical sensitivity plague historic data. Recently, several published studies have applied "standard" oceanographic analytical techniques, developed over the past 10-15 years, with the latest in "clean" techniques to accurately determine natural metal levels. In general, these methods rely on a preconcentration step, either liquid phase chelation/extraction or a solid phase extraction to provide the necessary enrichment for standard instrumental methods. Our group has been developing and applying to natural waters, techniques that allow quantification of many metals at natural levels without a non-instrumental preconcentration step. This paper outlines our field and analytical methods for the quantification of Ag and a select group of other trace elements at low ng L^{-1} levels.

I. CONTAMINATION CONTROL - FIELD and LAB

The application of "clean" techniques to control contamination is an essential prerequisite for accurate quantification in all modern methods. Table 1 outlines some of the required steps and procedures followed in obtaining un-biased samples.

SAMPLERS

- Non-metallic, simple, isokinetic.
- Scrupulously acid-cleaned, blanked.

SAMPLE CONTAINERS

- Teflon bottles (FEP, PFA).
- Rigorously acid-cleaned (50% HCl, 50% HNO_3, 1% High Purity HNO_3).
- Double-bagged in clean-room.

FILTRATION - PHASE SEPARATION

- All Teflon holders, scrupulously acid-cleaned.
- Holders pre-loaded in clean-lab, double-bagged.
- Acid-leached polycarbonate track-etched filters.
- In-line or in field glove-box.
- Minimal surface contact - only filter holder/column - directly into Teflon filtrate bottle.

PRESERVATION

- Teflon vials, double-bagged in clean-room.
- Pre-dosed in clean-lab with 50% Ultrex HNO_3.

SAMPLE HANDLING

- Tyvek coveralls, poly gloves.
- "Clean-Hands" - "Dirty-Hands" Technique.
- Ultra-high purity reagents.

ENVIRONMENT

- Clean-lab processing, Class 100 benches for critical handling.

Scrupulously cleaned double-bagged Teflon sampling apparatus, gloved and garmeted personnel, and "clean-hands" - "dirty-hands" techniques are standard elements of clean field protocols. Particulate contamination in equipment preparation and sample processing is controlled by working under clean-room environments.

The ability to accurately determine trace metal fluxes and yields depends not only on the collection of un-contaminated samples but also on obtaining representative samples as well. We approach this complex issue through the use of various clean compositing techniques (large rivers), or with direct compositing iso-kinetic samplers (wadable systems).

A meaningful field quality assurance program is essential for the demonstration, maintenance and documentation of data quality. In addition to the measures described above, the following categories of samples are obtained to track performance.

TYPE	FREQUENCY OF COLLECTION
Bottle Blanks	20%
Filtration Blanks	20%
Analyte Spikes	15%
Complete Replicate	25%

II. ANALYTICAL METHODS

For analytical detection we have pursued two distinct approaches: Graphite Furnace Atomic Absorption (GFAA) methods for Ag levels >10 ng L^{-1}, and Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) for Ag levels down to 0.5 ng L^{-1}. Automated multiple-pipetting is applied to increase sensitivity in GFAA, and a simplified matrix modification protocol controls interferences. GFAA operating conditions are summarized below.

GFAA OPERATING CONDITIONS

PE 5100Z Spectrophotometer
AS400 Furnace
AS40 Autosampler

Source Lamp:	Hollow Cathode, 12 mA
Wavelength:	328.1 nm
Matrix Modifier:	$NH_4H_2PO_4$ (400 μg in 20 μL)
Char Temperature:	750 °C
Atom. Temperature:	1800 °C
Sample Volume:	320 μL (8 x 40 μL pipettings)
Furnace Tube:	L'vov platform in pyrolized tube
Purge Gas:	Argon, grade 5

Table 2 summarizes figures of merit for GFAA when operated under specified conditions.

TABLE 2. Silver: Multiple-Pipetting GFAA. Analytical Figures of Merit

Criterion	Value
Typical Sensitivity (A•s/ppb)	0.7
Typical "Noise" (A•s)	0.003
S/N	250
Typical Blank Standard Deviation ng L^{-1}	2.5
IDL ng L^{-1}	7.5 (5 - 10)

IDL = 3 σ of 7 blank replicates

Ultrasonic nebulization coupled with a high efficiency interface and modern mass spectrometer provide the necessary sensitivity in our ICP-MS methods. When Mo and Zr spectral interferences, and background noise, are monitored and controlled, the ICP-MS can accurately quantify Ag abundances and isotope ratios of natural water systems. ICP-MS operating conditions are summarized below:

ICP-MS OPERATING CONDITIONS

VG Plasmaquad II STE
Cetac Ultrasonic Nebulizer 5100AT

Analyte Masses:	107, 109
Other Masses:	90, 95, 98, 99, 101, 104, 105, 106, 108
Solid State RF:	27.12 MHz
Forward Power:	1350 W
Reflected Power:	<2 W
Argon Cool Gas:	13 L/min.
Argon Auxiliary Gas:	1.2 L/min.
Argon Nebulizer Gas:	0.8 L/min.
Sample Uptake:	1.5 - 2.5 mL/min.
Operating Vacuum:	1.2 x 10^{-6} mbar
Quad Mode:	Peak Jump
Peak Dwell Time:	200 msec.
Points per Peak:	3
Acquisition Time:	90 sec., 5 cycles
Rinse Time:	360 sec.
Cones:	1 mm Nickel
USN:	140 °C heat, 2 °C cool

Table 3 summarizes figures of merit for ICP-MS when operated under specified conditions.

TABLE 3. Silver: ICP-MS. Analytical Figures of Merit (mass 107 or 109).

Criterium	Ultrasonic Nebulization	Pneumatic Nebulization
Sensitivity (cps/ppb)	250,000 - 300,000	25,000 - 35,000
"Noise" (cps)	150 - 250	40 - 60
S/N	1400	600
Blank STD ng L^{-1}	0.15	0.4
IDL ng L^{-1}	0.45 (0.2 - 0.8)	1.2 (1 - 2)

IDL = 3 σ of 7 blank replicates

In both analytical techniques, filtrate samples are introduced to the instrument with no pre-treatment or pre-concentration. Total samples are taken through an in-bottle (original Teflon sample bottle) digestion at 60 °C for 12 hours with added Ultrex HNO_3 (1.6%), before instrumental analysis. This approach eliminates the contamination and recovery problems inherent in most pre-concentration schemes. The only surfaces the sample contacts prior to uptake into the instrument are the original Teflon sample bottle and polypropylene autosampler vial/tube.

Table 4 outlines the performance of the ICP-MS technique and associated field methods on a set of 49 river samples collected in Spring of 1993.

TABLE 4. ICP-MS Performance Evalulation: Silver

Sample Type	Value
Field Method Blanks (ng L^{-1})	mean = 0.74, STD = 0.26, n = 31
Replicate Precision (Relative % Difference)	mean = 10.1, STD = 9.8, n = 52
Analyte Matrix Spike Recovery (%)	mean = 88.7, STD = 8.3, n = 16
Silver 107/109 Isotope Ratio	mean = 1.059, STD = 0.081, n = 166 accepted = 1.056

No aqueous, environmental matrix, Standard Reference Material is certified for Ag at low ng L^{-1} levels. Accuracy of the Ag analyses is evaluated with dilutions of higher level certified SRM's, and with other internal checks. The Canadian NRC/IERT SRM SLRS-3 is run three times during a typical batch sequence of 20 samples, and serves well for most trace elements, however, Ag is not certified.

Questions & Answers: Sampling, Processing and Instrumental Techniques for the Analysis of Silver in Natural Waters

Q. DENISE SCHILDKRAUT (Eastman Kodak): I just wanted to make a comment. There is an NIST trace element freshwater sample that has certified silver concentration at 2.2 ppb. Would that be suitable for your purposes?

A. No, that's totally out of the realm of natural concentrations. We've obviously measured every CRM there is available for aqueous silver. You know, there's no problem measuring it. But you're a thousand times higher than natural concentrations. You have to dilute it down to get there, so the question becomes moot.

Q. GABOURY BENOIT (Yale Univ.): Martin, I think a lot of us clean-technique chemists have done what you've done here, which is assume contamination at every single step along the process, and then try to eliminate it in all those steps. Have you done any work to try to identify where the major sources of contamination are? Because if we always have to do all of these steps, as you know, it's very costly and difficult work. It would be nice if we could narrow it down to some key spots in the procedure, perhaps.

A. We've done some intercomparison exercises with USGS and other groups, comparing different methods. And the filtration step is usually the biggest source of error here, as well as the acidification step, which is another real big potential problem. Once you get beyond those two steps, and assuming everyone's using a relatively decent sampler, then it becomes more difficult to trace the nature of the contamination. It seems to me like some kind of stochastic, random contamination, which you [might] have to go to extremes to eliminate. So it's hard to say don't do some of this stuff, because you could then get a couple of samples where you don't know whether they're real or contaminated. I don't think what we do is really that out of line. Most of it seems necessary.

Q. JIM KRAMER (McMaster Univ.): You certainly showed us the very eloquent needs that you have to have if you're going to get those kinds of detection levels, from an analytical point of view. I'd like to concentrate, though, a little bit upon what you showed us in context with the field side, and the variability there. Given that one does what you do, what would be the percent variability in an analysis — and maybe you've done this — such as, if you go to a particular site and get a particular sample, then go back and repeat the whole thing say, in another ten minutes, or within a time interval of whatever you want to use the data for. What is the variability, compared to the kinds of variability in the analytical part?

A. We've done a fair amount of that. The overall analytical precision depends on the metal, but most of it's analytical. It's a little more difficult to do for silver. For low level [elements] like cadmium and silver, overall, if we go out and sample half an hour, half an hour again, half an hour again, getting triplicates, it's on the order of 10 percent. Most of it analytical, almost all of it analytical. If we do things like zinc and copper, in a fairly large river, you're probably talking variability of a couple percent. And that's just sampling one point in the river. Now there's considerably more variability across a river. You get into issues of compositing. Different systems are going to behave differently as a function of time. But if you were able to collect a true replicate, instantaneous collection of three samples, the analytical error is going to be in the neighborhood of 10 percent, for the very low levels that we're talking about, and a couple percent for zinc and copper.

Silver in the Waters of Connecticut: Analyzing for a Trace Metal with Ultra-Clean Techniques

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Clean techniques were used to measure silver concentrations and distribution between filter-retained and filtrate fractions in three Connecticut rivers. Clean procedures used in this study fulfill three conditions: 1) samples contact only Teflon or low density polyethylene surfaces that have been extensively acid-cleaned in a filtered air environment, 2) samples are collected and transported taking extraordinary care to avoid contamination from field personnel or their gear, 3) all other sample handling steps take place in a filtered air environment and using ultrapure reagents.

Acid cleaning consists of 48 hr soaking in 33% HCl at 60 °C, followed by soaking in hot, ultrapure 1% HNO_3 (Seastar brand) for 48 hr, and rinsing with > 18 Mohm water (tested for trace metals). Acid soaking took place in a HEPA filter-supplied, all polypropylene, Class-100 clean fume hood in a positive-pressure, Class-100 clean room. Baths were tested weekly for contamination. Sample bottles were stored and transported to the field filled with .03 M ultrapure HNO_3 as a final wash/storage solution, and contained in double plastic bags. Water was filtered during collection by passage through acid-cleaned 0.4 μm Millipore Durapore filters. We have found these to give results similar to Nuclepore membranes. Filter membranes were contained in acid-cleaned 47 mm diameter Teflon filter holders that were loaded within a laminar-flow clean bench and stored in double plastic bags. Separate filter assemblies were prepared in advance for each sample, since changing filters cleanly in the field is impossible. Using this protocol our filter blanks were consistently below our detection limit (see below).

In the field, extraordinary precautions were taken to prevent contamination of water column trace metal samples. Samples were collected from downwind and down-current by personnel wearing shoulder-length clean room polyethylene gloves, which were changed frequently during collection of each sample to avoid contamination, and Tyvek coveralls.

Water was collected by peristaltic pumping through acid-cleaned Teflon tubing into acid-cleaned low density polyethylene bottles. Trace metal water samples were returned to the laboratory in the original double bags, stored on ice. Samples were acidified in a clean bench within a few hours of collection using 2 ml of ultrapure HNO_3 per liter of sample. Filters were unloaded from their sample holders in a clean bench and transferred to acid-cleaned Teflon beakers for digestion.

Water samples were preconcentrated by evaporation with nitric acid in Teflon beakers within a filtered-air clean fume hood (Class-100) constructed entirely of polypropylene. Evaporation is a suitable method for preconcentrating samples as long as Na^+ does not reach excessive levels that reduce trace metal recoveries. Filters were heated with 20% ultrapure HNO_3 in Teflon beakers for 1 hr before evaporation. Metals were measured by background-corrected graphite furnace atomic absorption spectroscopy. Significant matrix interferences were judged to be absent because selected samples gave similar results whether measured by method of additions or by external standard series. Blanks and spikes were carried through all stages of sample collection, pretreatment, and analysis to evaluate recovery, accuracy, and potential contamination. Field blanks consisted of pre-analyzed distilled water, which was "collected" in the field using the standard protocol. Recovery blanks consisted of standard reference river water SLRS-2 (National Research Council of Canada) collected in the normal way after adjusting pH to approximately 6.0. During GFAAS analyses, samples were measured in triplicate (or quintuplicate for very low concentrations), and repeated if relative standard deviation exceeded 15%. Mid-range control standards were analyzed every six samples, and the instrument recalibrated if they were not measured within +10% of the nominal value. A blank and an aliquot of SLRS-2 were analyzed with every batch of 10 samples. Blanks always fell within the instrumental standard deviation, and we routinely measured SLRS-2 within its 95% confidence limits (Pb = 129 ± 11 ng/l, Cd = 28 ± 4 ng/l). Temperature, conductivity, pH, alkalinity, turbidity, total suspended solids (TSS), and total organic carbon (TOC) were measured at the same time by standard methods.

Detection limits were calculated as the product of the slope of the calibration curve and three times the standard deviation of the blank. They varied depending on the original volume taken for evaporation, and the stability of the graphite furnace when analyzed. Using 100 ml original sample volumes, detection limits near 1 ng/l were possible for the three metals.

The Quinnipiac River, Connecticut, has a highly urbanized and industrialized watershed, and previously supported an extensive silver plating and fabricating industry. Silver levels there are below <u>routine</u> detection limits, but still show systematic variations and the influence of anthropogenic contamination when measured using clean methods. Silver in the Quinnipiac can be divided into three zones according to concentration and presumed source: a) headwater streams, where total silver is <5 ng/l (parts-per-trillion), b) the mid-river reach, where levels are 50 to 100 ng/l, and c) the lower river, where levels rise to 500 ng/l. We hypothesize that the three concentration ranges result from: a) natural background (i.e. weathering, groundwater), b) sewage effluent and non-point source pollution (e.g. urban runoff), and c) resuspension or diffusive release from sediments contaminated with silver from historical industrial activity in this water shed. This latter possibility is supported by the observation that total Ag levels increase linearly with TSS for samples collected repeatedly at one location over varying discharge and TSS.

The Naugatuck River was historically Connecticut's most badly polluted. Today, Ag levels are near background (< 5 ng/l) in its headwaters and increase to between 50 and 100 ng/l in urbanized, industrialized portions. We have also completed collection of a set of samples from the length of the Connecticut River from its headwaters to its mouth, and these are currently being analyzed for comparison with the Quinnipiac and Naugatuck.

Silver has been proposed as a non-degradable tracer for sewage contamination, since it has a low natural background concentration and is used almost ubiquitously by industrialized societies. High resolution sampling was conducted along the Quinnipiac River above and below the outfall of the Meriden, CT, sewage treatment plant. These measurements revealed a rapid drop-off in both total and filtrate silver over a distance of about 0.5 km. Using conductivity as a conservative tracer of the effluent, silver concentrations were shown to decrease purely through dilution over this distance, representing a travel time of $\leq$ 1 hr. Additional experiments using fluorescent tracers are underway to track silver over longer time periods, when non-conservative behavior may become apparent.

There is a tendency for silver partitioning between particles and solution to correlate with the total amount of particulate matter, but the effect is not statistically significant over the small TSS range in the Quinnipiac River alone. Combining Pb data from the Quinnipiac River with that in other northeastern water bodies reveals a highly significant decrease in K_d as TSS increases. Additional measurements in the Quinnipiac, Naugatuck, and Connecticut will be used to test whether the same is true for Ag.

Questions & Answers: Silver in the Waters of Connecticut: Analyzing for a Trace Metal with Ultra-Clean Techniques

Q. JIM LEAGAN (Eastman Kodak): Your series of silver showing high levels of total silver at high levels of flow, I would suggest that you investigate whether there are CSO's, combined sewer overflows, in some of those cities. If you're getting high levels of suspended solids, which may be scouring of sewer pipes that may have solid particulate silver in the bottom of those sewer pipes, [that] is then being suspended and removed to the river during high rain events.

A. That's a very good point. In fact, we haven't even taken the step of doing a direct analysis of the effluent under either of those conditions. But, point very well taken.

Q. JIM KRAMER (McMaster Univ.): On your relatively high dissolved levels compared to what we've seen, first question, was this 0.45 µm filtered material, or have you done others? The whole colloidal game is what I'm after. What is your explanation?

A. These are on 0.4 µm Nucleopore filters. And we have not done any ultrafiltration on these particular samples. We've done that on lead, but that's actually a different set. We haven't yet done that on these. That's going to be one component of the ongoing research. The other thing is to try to take a stretch of the river and prepare a mass balance, including direct measurements of the sewage inputs, contributions from CSO's, atmospheric, weathering off the watershed, and all those different sources.

Q. MICHAEL BOTHNER (USGS, Woods Hole, Mass.): I just wanted to ask a question of those of you who sample rivers routinely downstream of an outfall. I was always struck by a color picture of a tributary to the Amazon coming in with a different color than the Amazon and showing no mixing across the river for miles. And then I always wondered what happens when you have a little outfall pipe from a municipal treatment center that dumps at the edge of the river. And then we go downstream and try to figure out what's an average concentration, downstream some mile or so. I just wondered if that's a concern that you've solved.

A. It's something that I've been very worried about. And, actually, I had a funny experience that way, working on one of those Texas estuaries that I talked about on Monday. We were collecting samples and it seemed that there was almost a completely random pattern of salinity in this particular estuary. We would be going up and down, and sometimes the salinity would increase up, and decrease down. Just by chance, a few days later, I happened to see either a LANDSAT or some type of aerial photograph of that system. There were two streams coming in at the head of it, and they were just remaining completely unmixed throughout a reach which was very, very wide. Admittedly, a broad estuary isn't the same thing as a river; turbulent conditions are different, and such. But it's something I worry about a lot.

And it's something, if I can editorialize a little bit, [that] we as environmental chemists have to be worried about. Unfortunately, the analyses we do are so difficult that we are largely limited to go out and take a sample, or take a couple replicates of three. But whenever we're able to look at the variability of systems, either spatially or temporally, by using things like remote sensing, we see that there's a lot more variability than we usually recognize. We like to draw nice smooth contours. Instead we usually have lots of festoons and little, completely random variations over relatively short distance scales. Something I'm concerned about.

The more practical answer to the specific question you're asking, [is that] we tried to get far enough downstream so we felt that the system was pretty well mixed. It turns out that the Quincy I'm talking about is actually called a river, but for most of us I think we'd call it a stream over a lot of its length. So it is quite turbulent, and I think relatively well mixed. But we tried to stay far enough downstream from the sewage effluent such that we could still see the signature, but not so close that we would be just grabbing sometimes pure sewage, and sometimes pure river water.

Q. JIM KRAMER (McMaster Univ.): I'd like to make a comment on the last point. I agree [on] that [statement about] mixing. You can see, sometimes, Lake Huron water mixing into the middle of Lake Erie, halfway into the lake, going right along the sides, with the old salt mining operations, and laminar flow. But I think one of the things we can do, if we're looking at these areas where we have municipal discharges in particular, is to do some TDS profiles across the river, because invariably chloride and so on will be elevated. You can probably get a good idea of how that mixing is, and gear our sampling to that.

A. That's a good point. You can use some of the more conventional parameters that are easily measured in real time, like total dissolved solids, or turbidity or conductivity, or any of those. That can be a very useful guide.

Q. DAVID BLISS (Astro Color Lab): Being the only fellow here from a photo lab, I want to get some of the heat off of me if I can. Has anyone ever taken any steps to document what the average person in these big cities contributes in, let's say, different phases of body waste — hair analysis, fingernail analysis, in the per capita amount contributing to the sewer, in silver?

A. Well, I don't know if I'm the best person to answer that. Maybe one of the speakers from the first day, when they were talking about the distribution and uses of silver. I certainly don't have an answer to that question at all.

A. JEROME NRIAGU (Univ. of Michigan): I can make a comment on this. Actually, to my knowledge, you cannot get silver if I take a sample of hair from here and go to the laboratory and try to analyze. But if I try to find mercury poisoning, then I think that hair is a good indicator to find out about toxicity of mercury to that person. But I think no work has been done on silver in hair or nails, so far as I know.

Q. ROBERT CAPPEL (Eastman Kodak): I can just tell you from my experiences with a number of wastewater treatment plants around the country, generally they see from domestic flow about three to five µg/l of silver. That's what I've seen as experience.

Measurement of "Active" Silver in Environmental Samples by Anodic Stripping Voltammetry: Towards Development of a Robust Analytical Method

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Introduction

Speciation of silver in surface waters is important because of the effect silver ion may have on aquatic animals. It has been shown that silver is most toxic when it exists as the hydrated ion ("active" silver). It is our goal to develop a robust, reliable, and cost-effective electroanalytical method to measure "active" silver in surface waters. We have chosen Osteryoung Square Wave Stripping Voltammetry (OSWSV) as a method because of its simplicity, low cost, and successful application to other trace metal determinations (1,2). OSWSV also allows minimum sample handling before the analysis when compared to other methods.

Silver in the environment can exist in a variety of forms, i.e., silver sulfide, silver bicarbonate, silver chloride, metallic silver, or silver adsorbed onto sediment. Toxicological studies have shown that the toxicity of silver compounds is highest when silver exists as a hydrated ion. Silver thiosulfate and silver sulfide are 17,500 and 15,000 times, respectively, less toxic than silver ion as measured on aquatic animals.

Normally, the procedures used for the determination of silver in environmental samples (e.g., atomic absorption spectroscopy, neutron activation analysis, inductively coupled plasma-mass spectroscopy) measure the total amount of silver. Stripping voltammetry is perhaps the best technique currently available for direct measurement of metals of prime environmental concern, i.e., lead, cadmium, zinc, and copper in seawater (1). The ability of stripping voltammetry to distinguish between different physico-chemical forms of metals in solution is one of the most important features of electroanalysis.

Background

OSWSV is an electroanalytical technique which combines high sensitivity (detection limit ca. 5×10^{-11}M), multielement measurement capability, and speciation of metal ions with speed. Stripping techniques involve two steps. First, "free" metal ions and metal ions from labile metal complexes are deposited onto an inert electrode surface at a constant potential. During the deposition step, the analyte of interest is brought to the surface of the electrode by diffusion and/or convection. This preconcentration step is followed by a stripping step which causes dissolution of the deposited metal.

In OSWSV, a symmetrical potential waveform superimposed on a ramp changing at a fixed frequency is applied to the electrode during the stripping step. The peak current (or the peak area) that is measured is directly proportional to the amount of metal deposited on the electrode. The preconcentration step can be viewed as an effective electrochemical extraction in which the analyte is concentrated on the electrode surface to a considerably higher concentration than it exists in solution. This technique has been successfully used and widely applied for trace metal measurements in a variety of aquatic samples.

Experimental

A Bioanalytical Systems (BAS) Model 100B electrochemical analyzer with a BAS rotator and a carbon paste rotating disk electrode Model MF2065 was utilized for all measurements. Results were printed on an Epson Model FX-85 printer or stored on a PC for further analysis. Carbon paste was purchased from BAS (CF-1010). Carbon paste electrodes were prepared and polished following the instructions provided by BAS. The counter electrode was a platinum wire. The reference electrode was a saturated calomel electrode (SCE).
Silver standard solutions were prepared daily by appropriate dilutions of a Spex Industries (1000 µg/mL) silver nitrate standard with Milli-Q and a 9:1 mixture of synthetic water (3) to 0.1 M potassium hydrogen phthalate (primary standard ACS, 99.5%-100.5% GFS Chemicals) buffer (pH 4.5) to result in concentrations between 5 to 0.2 ng/mL of silver and protected from room light. An NIST (#1643c) trace element fresh water standard with a silver concentration of 2.21 +/- 0.2 ng/mL was also used for calibration and testing.
The deposition of silver took place at -0.400 V vs. SCE at a rotation rate of 3000 rpm. The stripping peak was measured at a frequency of 50 Hz, an amplitude of 50 mV, and a step height of 2 mV. The

deposition time varied between 5 to 10 minutes. After each stripping step the electrode potential was kept at +0.800 V vs. SCE to assure total dissolution of all silver deposited.

Results

Silver gives rise to one major stripping peak. The potential of this peak depends on the concentration and the electrolyte composition of the test solution. A second, significantly smaller stripping peak may be observed at a lower potential.

One of the major challenges in developing an analytical method for the determination of labile silver in effluents and surface waters has been to improve the reproducibility of the measurements.

A carbon paste electrode was chosen over glassy carbon and platinum electrodes because of lower background currents and better precision. A strong dependency on the electrolyte used and a possible ionic strength effect was identified. For example, in Figure 1 voltammograms for a 1 ng/mL silver standard are shown as a function of water hardness. As the hardness of the water increases, the stripping peak shifts to less positive potentials (e.g. the stripping peak in soft water is at 0.252 V vs. SCE whereas in hard water the same peak may be observed at 0.228 V vs. SCE. In hard water the stripping peak is sharper than that observed in soft or moderately hard waters.

A full factorial experiment was designed with four factors to determine sources of variability originating from concentration, day, renewal of the electrode, sample preparation, and electrode. The design consisted of 48 points. The measured peak area was the response used in a multiple linear regression model. The results of this analysis show that there was significant day-to-day variability in the measured peak area and the renewal of the electrode also had a significant effect on the results. Electrodes, preparation of solution and replicate number did not make a statistically significant difference.

A series of calibration experiments was performed over seven days to estimate the precision of the test. Four silver levels between 0.2 ng/mL and 2.0 ng/mL were used to generate a total of 28 data points. Of this data, 18 randomly selected data points were used to create a calibration model. A plot of this data is shown in Figure 2. The following equation describes the relationship between the measured peak current and the silver concentration in the samples:

$$y=0.048+0.446x$$

where y is the estimated silver concentration in ng/mL, and x is the peak current in µA. The correlation coefficient for the fitted straight line was 0.991. The curvature term for peak current in the model was not significant. The remaining 10 data points were used to test the model to estimate the precision of this method. A plot of the known vs. predicted values is shown in Figure 3. The precision estimated from this set of data was 7.2% R.S.D. at one standard deviation using a 95% confidence interval of the individuals (4).

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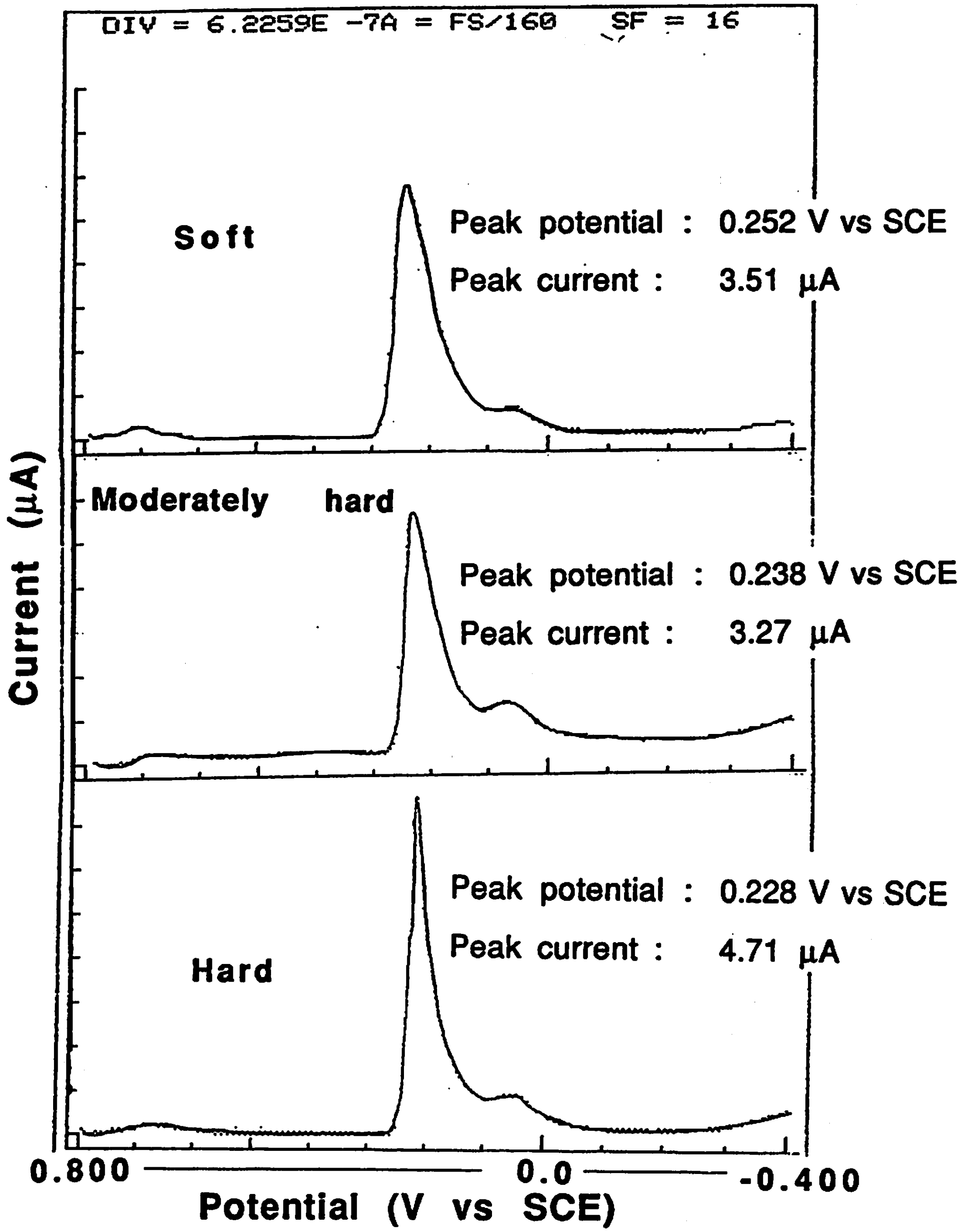
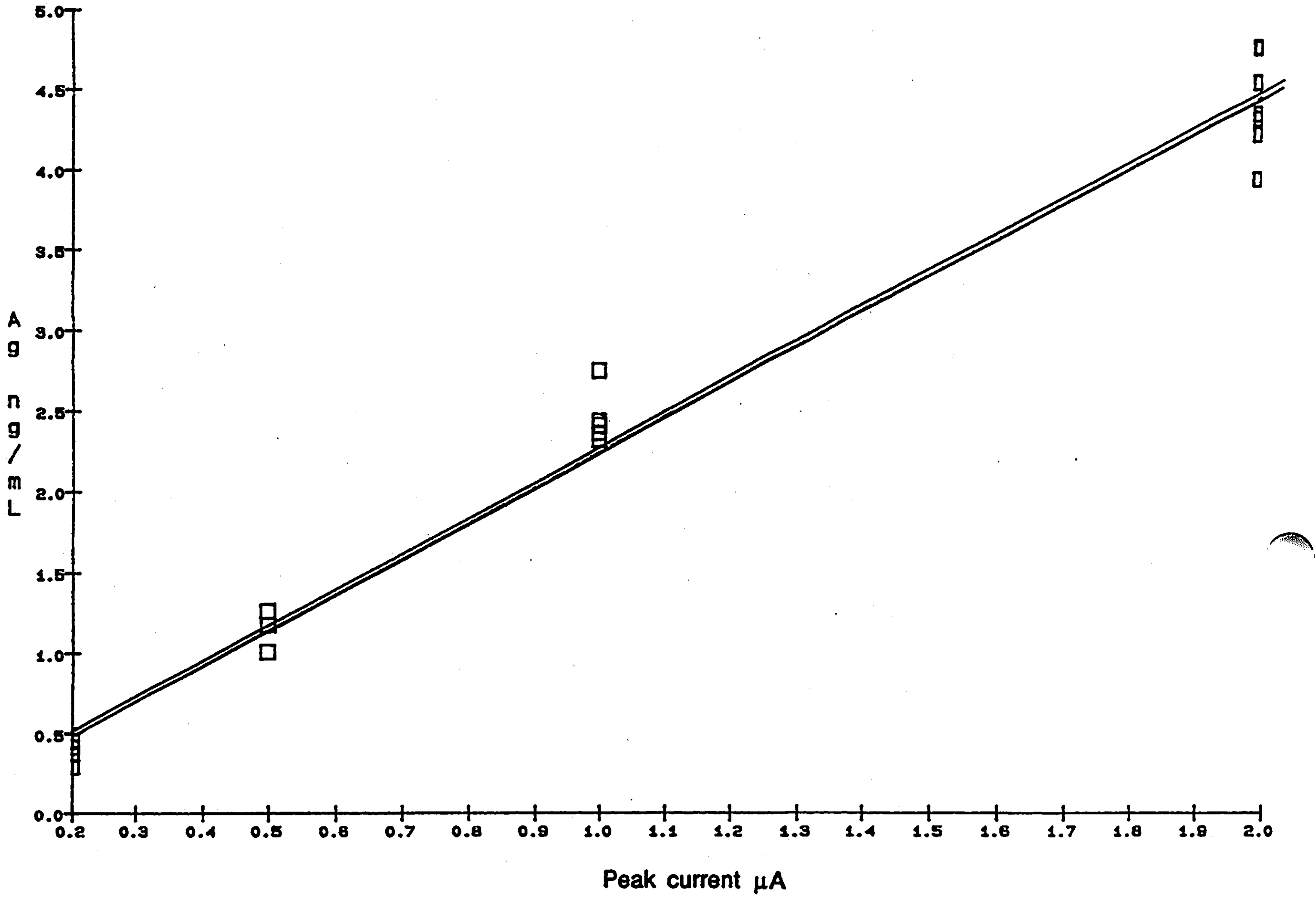


Figure 1. Comparison of stripping voltammograms for a 1 ng/mL silver nitrate standard at a carbon paste electrode as a function of water hardness.

Figure 2. Calibration model to show the relationship between the measured peak current and the silver concentration.



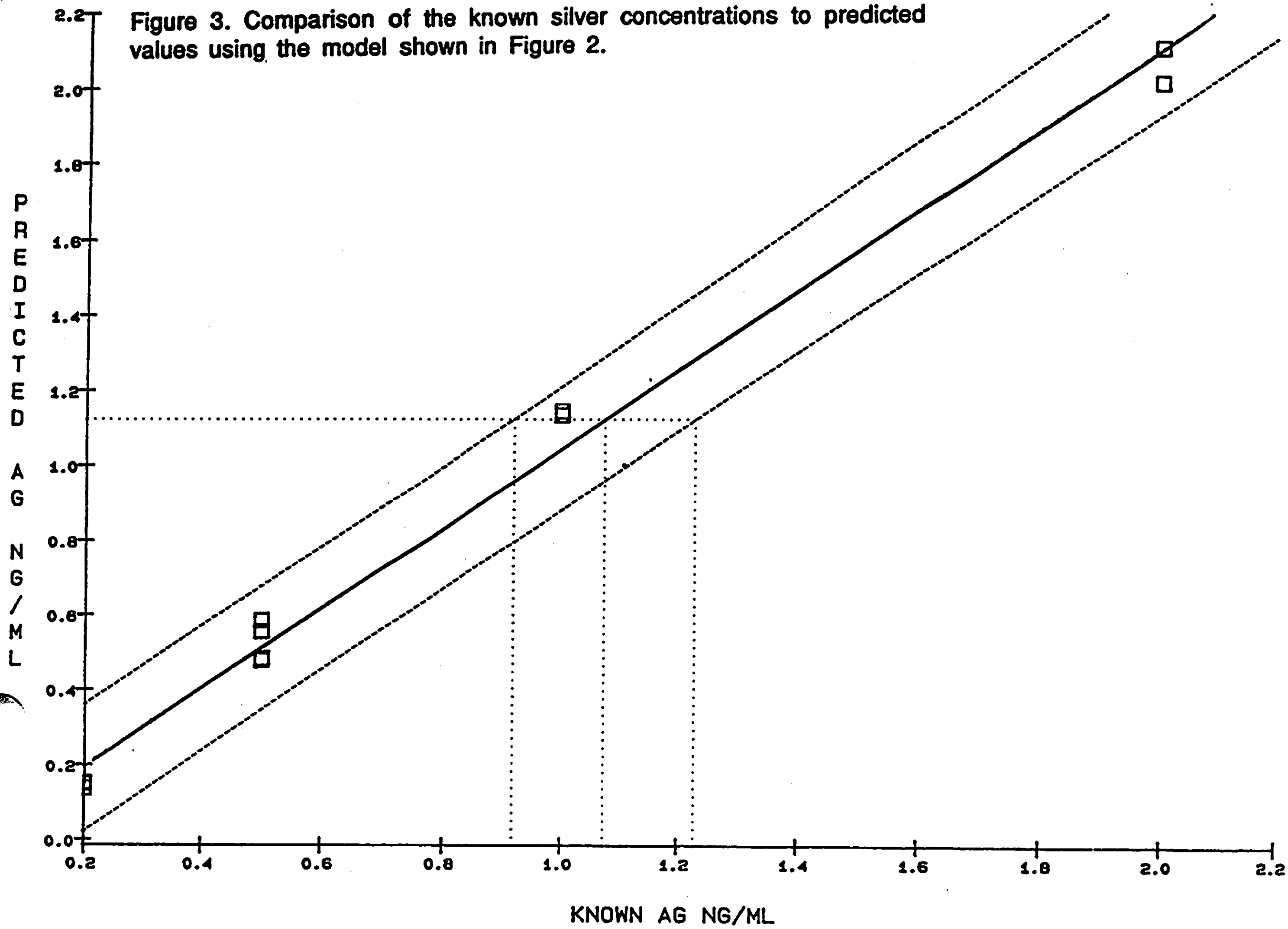


Figure 3. Comparison of the known silver concentrations to predicted values using the model shown in Figure 2.

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1 sigma error of prediction = 0.077571 RSD = 7.228082  %
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Questions & Answers: Measurement of "Active" Silver in Environmental Samples by Anodic Stripping Voltammetry: Towards Development of a Robust Analytical Method

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Q. . . . Not recorded (tape change).

A. No. It's not possible to do cathodic stripping. What the anodic and cathodic stand for is: anodic means you deposit the metal on the electrode surface, and you strip it. Cathodically, I don't know how you would do that. Usually cathodic stripping will involve some kind of a complex formation, such as with mercury, and you can't do that in this case.

Q. What I was referring to is, there's a whole host of work that's being done in the oceanographic community right now, particularly to look at speciation where you complex the inorganic ligands with a chelating agent. I think you mentioned some of this already. And what you do then is just adsorb this metal chelate onto the surface of, they use mostly hanging mercury drop electrodes, in cathodic stripping. So you avoid the problems of having an actual amalgam form. But, rather, you strip onto the surface of the electrode the metal ligand complex. And then you strip back off and you get a similar sort of peak. There's been a number of metals that have been done this way. I've never seen one done for silver, and I'm curious.

A. I don't think you can do that with silver. You just can't do it for silver. Because of mercury. Mercury dissolution potential and silver dissolution potential are too close. The signal from the mercury would be too big to be able to see the silver signal.

Q. What is the frequency of the pulse in the plating routine, and what is the duration of the ramp?

A. We have been using 50 Hz as the frequency, and the duration of the ramp is over in a couple of seconds.

Q. All right. Now, is this just a rectified signal, or are you using a programmable pulse plating machine?

A. We have the equipment that has the waveform that's included in the program.

Q. I'm going back to when I was doing gold plating. And we had a programmable plate that would give you so much on and so much off time that you could select and program in. I was wondering if that's what you're using.

A. Well, I'm using state-of-the-art electrochemical equipment which allows you all kinds of different choices. In terms of frequency, you can go from 15 Hz to 2000 Hz, and you can also select the amplitude of your square wave. You can select your resolution. You can change the time; you can go from milliseconds to seconds. Measurements are really fast.

Q. What I was wondering was, would you get better accuracy if you had a longer or shorter off time relative to the on time?

A. It depends on the concentration of your solution. When you have low concentrations, you may want to use a longer time. But what happens if the concentration of your silver solutions increase, then you get complications if you are depositing on longer times, because the growth of silver on the electrode is a three dimensional process, and it's a very complex process. So you don't gain anything; actually the reproducibility suffers if you use longer times at higher concentrations.

Q. GABOURY BENOIT (Yale Univ.): I know that you're trying to keep the method as simple as possible, so that's why you want to have kind of a generic calibration curve that's good from day to day. This is more of a suggestion or comment than a question. I know that people who do ASV for other metals typically use a method of additions because of that very common problem of variability, even on a time scale of hours, let alone days. So it's another possibility, although, of course, it does lengthen the analysis time. The other thing is that it's a little bit hard to be sure of what your limit of detection is here. You're talking about a fraction of a part per billion, it looks like. In order to improve the sensitivity, what others who do ASV, as well as extending the period of stripping, they also go to rotating electrodes, where you're no longer diffusion limited for the stripping step.

A. I guess I forgot to mention that I did use a rotating electrode. The electrode is rotated at 2000 rpm, so there's both diffusion and convection to the electrode surface. And to answer the first part of your question, we cannot use standard addition to these samples because of the complexing nature of surface water samples. It's like you can titrate these samples. There are times that there are unknown complexing agents that bind the silver, so that we don't see a signal for the standard additions that we make.

Panel Discussion

Setting Effluent Standards for Metals: Informational Requirements for Regulatory Agencies

Panel Chair:
J.R. Sullivan, Wisconsin Department of Natural Resources, Madison, Wisconsin

Panel Members:
D.E. Armstrong, University of Wisconsin-Madison
R.J. Erickson, U.S. Environmental Protection Agency, Duluth, Minnesota
S.N. Luoma U.S. Geological Survey, Menlo Park, California
A.B. Mukherjee, University of Helsinki, Helsinki, Finland
J.G. Sanders, Academy of Natural Sciences, Benedict, Maryland
C.M. Wood, McMaster University, Ontario, Canada

Panel Discussion: Setting Effluent Standards for Metals: Informational Requirements for Regulatory Agencies

Panel Chair: **Jack R. Sullivan**
Panel Members: **David E. Armstrong**
Russell J. Erickson
Sam N. Luoma
Arun B. Mukherjee
Jim G. Sanders
Duane Schuettpelz
Chris Wood

ANDERS ANDREN (Univ. of Wis.) [opening comments]: We have now come to the end of the formal presentations, that part of the program, and we'd like right now to move quickly into the panel discussion that we have asked a number of people to participate in. The topic of our panel discussion is, "Setting Effluent Standards for Metals: Informational Requirements for Regulatory Agencies." I think that this is a question that is of interest to all of us. It is very germane to scientists. I believe strongly that we should try to support our colleagues who are faced with these sorts of problems and do research that supports the decisions that are made, both for those that are regulated and for those that set regulations. I think there are a number of issues that we have covered in this conference that should perhaps help us arrive at some of these decisions. The chair of the panel, like last year if you remember, is John Sullivan. John has since changed jobs, but we thought he did such a great job that we asked him to come back as chair again. Just a little bit of background for those of you who don't know John. John is a water chemist by training, and was quite instrumental in participating in the Great Lakes Initiative. I forget what section you were particularly involved in, but you can tell people whether it was the mammals and birds or the humans. But anyway, Jack is now Chief of Analytical Services for the Wisconsin Department of Natural Resources, but is still quite close to effluent standard problems. He also brought along Duane Schuettpelz, who is the current chief of Surface Water Standards and Monitoring. We have invited Duane to participate as well. The panel members are: Dave Armstrong, University of Wisconsin-Madison, a water chemist by training — you have seen some of his work reported on by Martin Shafer; Russell Erickson, who all of you know by now, presented work on toxicity; Sam Luoma, who all of us heard talk today, from the U.S. Geological Survey; Arun Mukherjee, from the University of Helsinki, who all of us know as well; Jim Sanders, from the Academy of Natural Sciences, Benedict, Md.; and we've also asked Chris Wood from McMaster University to participate. So, if the panelists would come up here, what we have basically done is ask each panelist to just spend a few minutes to get a discussion going to address the title of our panel discussion, "Informational Requirements for Regulatory Agencies."

SULLIVAN: Thank you, Anders. We did have a good time last year talking about regulatory requirements, and maybe it's appropriate that we close talking about regulatory requirements at a conference like this. We do have a great panel, so I won't answer many questions, I'll just try to moderate. I do have a few opening remarks that I would like to make. Oftentimes it's research, like has been talked about at this conference, that leads to some form of potential need for regulation, and then, because someone at an agency somewhere gets interested in regulating something, it often then drives the research, so that it's done correctly. We're somewhere in the middle of all of this.

I just want to throw out some ideas that are interesting to myself, and maybe some of you, as a regulator, because that is part of my job even though, as Anders said, I have switched duties. I'm still with a regulatory agency. I'm still a data user, and we use the information that you generate, both the chemical-specific information and the biological information, and try to make some sense of all of it, and then apply it in the real world environment. Just a couple of things — we're going to talk about metals standards, and maybe some regulations. I'm going to use Wisconsin as an example. I'm going to talk about the occurrence of metals, and, mostly, I'm going to keep my comments to point source discharges in the state. I'll talk about their occurrence, talk about something called "water effects," where we deal with what might be the real toxicity of a metal in the environment — how do you know whether it's dissolved, particulate, that kind of thing. And then something about standards, to talk about how you set standards for metals. I want to talk about something called anti-degradation as it relates to background concentrations, because it brings up some very interesting needs with respect to metals.

What I have here for us to look at is in the state of Wisconsin, where we have data, and this data spans over 137 different industries, 184 different municipalities in the state of Wisconsin. I've listed on the left-hand side a series of metals, and at the bottom I've compared it with a couple of organic compounds, PCBs, DDT and dioxin, just for comparative purposes. What I have listed is the percent occurrence, how often do we see it, and, of course, that can be very dependent upon the detection level that you use, and the complexity of the effluent, and whatnot. But how often do we see it, given current technology that comes out of our commercial laboratories and required methods, and what percent of time do we, as an agency, regulate that substance. Let's take a look at that. For industry, cadmium, chromium, total chromium in this case, lead, nickel, silver, zinc and mercury are the metals that I have data for, and you can see in industries anywhere from mercury 15 percent of the time to zinc, which seems to be the most commonly occurring, at about 66 percent of the time. And then we regulate them anywhere from 10 to 30 percent.

Now, you can be regulated in our state for toxicity to fish and aquatic life in the surface water. You may be regulated for effects on wildlife, which is the part I was interested in in the Great Lakes Initiative. Wildlife drives the mercury regulation in the state of Wisconsin. Or you could have a limit, if you are a facility, for toxicity to human health on that basis. Usually fish and aquatic life, either acute and/or chronic toxicity, will drive what we're calling in this chart "regulation." If you look at municipalities (and I don't have lead data, the computer didn't want to spit it out), the occurrence running anywhere from 19 to 66 percent of the time, with zinc being up at the top, and we don't regulate it quite as often, and there's a variety of reasons for that.

But you can see that, if we contrast it with some of the organics that people may be familiar with, PCBs, DDT and dioxin, against the same information, percent occurrence, we don't often see much PCB or DDT or dioxin in effluents anymore, and in municipalities we see very little to none. And it is a large database, over a lot of years. However, normally when we do see one of these, we usually regulate. You can see dioxin: we found it three times, we've regulated it three times. But by and large, most of the people in the state of Wisconsin, when they have a permit, a discharge permit, they have limits for metals, that's the most likely thing. And when you have a limit in a permit, it's going to cost you money, because you have to comply with that permit limit. And of course that's why we have a great interest in metals.

Now, I've listed just a number of ways that one can go about meeting the limits — there may be more — I've just thrown some out for discussion. Once you use pollution prevention, you can move away from, let's say, a copper-based dye and do some kind of substitution. You can spend lots of money in terms of treatment technology, some form of tertiary treatment. Dilution is allowed in the state of Wisconsin. Basically, here we're talking about high rate diffusion, hydraulic engineering, where you can get better dilution factors to meet your limits. That's real commonly used in our state — high rate dilution. Or, alternately, you can look at it from a *toxicological* standpoint, and come up with some kind of site-specific criteria. I've listed that under water effects because that seems to be gaining a lot of momentum in the United States where, basically, people say, "Well you've got this criteria that you're basing our limit on, but you know you did that in the laboratory, and that's really not what happens out in the environment." So we want to measure this same type of thing, but we want to do it out in the natural environment, and then we want to apply some kind of a ratio, because we know that metals speciate, we know that they may be attached to particulates and may not be available to express their toxicity. So we want to apply some form of water effect ratio. And we do have a number of these under consideration in our state right now — where people are out there doing the work, doing the toxicology work — trying to figure out how the metals speciate, and how the toxicity may be attenuated in natural waters.

I think the last thing I'd like to point out, and this may be a new concept to some of us here, but talking about standards, I said I'd talk about anti-degradation. The word is self-explanatory; basically, do not degrade the water. In our state, we have a water quality standard called anti-degradation. And what we've done, and this does come down in the United States from the federal level, but it's applied very differently across the country. In Wisconsin, what we have done is, we have divided our waters into what I'll call different levels. We call them "outstanding waters;" "exceptional waters;" "fish and aquatic life waters" — Lake Mendota, out the window, would be an example of a "fish and aquatic life water;" other types of waters that may be of more limited value; and then "Great Lakes waters." So we've divided our waters, and by dividing these, it places a value judgement on them, and what we say is, you have to meet different requirements, depending upon the type of water that you want to discharge to.

I'm just going to pick one example. If we take "outstanding" (that's our highest level of protection in the state of Wisconsin) and what we have politically said — and it really is politics — . . . [inaudible on tape], if you want to discharge to an "outstanding" body of water in our state — and we have a big one coming up now, we have a proposed mine, metallic mine in northern Wisconsin — silver, copper, zinc, gold — it's got the whole nine yards, it happens to be where you have the potential to discharge. They're going to mine it there, they're going to process it there. The only discharge that's available are some of our most beautiful white-water trout streams in northern Wisconsin. So what that facility is faced with is: you must meet background concentrations, where we say that for "outstanding waters," you must not exceed the background in the environment. One of the things that our agency, and Duane, who's here today, has to struggle with is: What is the natural background for, let's say, silver, or mercury or some other substance in the natural water? What is that variation? How long do you consider that variation over time? And at what level, then, do you set the requirement so that facility knows what is expected of it, so that it can discharge to those waters? So that's another area that we're very interested in, and of course metals, being naturally occurring, come right to the forefront when we talk about meeting background. Maybe people have some comments for us today, and maybe some answers and questions related to that. So I'll stop at that, and we can open it up to any kinds of questions or comments that you might like to bring to the table.

TOM BOBER (Eastman Kodak): I think one of the big topics that's come up at this conference is the effect of chloride, and whether chloride is indeed a protective agent, or is a toxicity-increasing agent, and I think there are several panelists here that might address that. You've had different views expressed in your papers, and we saw a little bit of potential controversy, and I think we'd like to stimulate that if possible.

SULLIVAN: I wasn't paying attention. I apologize, it looked like he was looking towards the end.

ERICKSON: I guess it was our test which engendered most of the controversy, so I might as well start. I should preface it with saying that this was just one test that was meant to be a preliminary exploration of what factors we needed to follow up on, and I don't expect this one test to be anything more than perhaps a caution to not come to hasty conclusions about this. I'm personally of the opinion that metal complexes — and I'm not talking just about silver, but about other metals I've dealt with — metal complexes can participate in toxicity in a variety of manners, so that when you look at toxicity tests, it might either be toxic or have the appearance of toxicity. I should emphasize the appearance, because there's been a good recognition in the last 10 years that the chemistry of what happens at the gill surface is quite a bit different from what is happening in the bulk test water. So it can appear to be toxic simply because the complex can be transported to the surface or even through the surface, then re-speciate into a toxic form. But there are such things as mixed ligand complexes; silver chloride, even though it's a neutral species, still has a strong affinity towards chloride itself, to a ligand, and there are the possibilities of forming mixed chloride complexes that can participate in toxicity. Beyond that, going back to Galvez' and Wood's paper, I think their data set is actually stronger than ours, showing something in the opposite direction. Ours is just the one data point. In looking at Richard Playle's work you talked about last night, I was of the opinion that it left unresolved, to some degree, whether again there was this — the chloride didn't seem to have the gross effect you expected it to, if it was unavailable. But again, there's the two possibilities of re-speciation at the gill surface, or participation of a mixed ligand complex. And as Chris brought up on the first day, these results are not necessarily contradictory. You have different organisms, different end points, different test conditions; this is where it gets important to do detailed physiologically based work to resolve the mechanisms that are really regulating toxicity.

We don't necessarily need to have detailed mechanistic descriptions built into regulations, but we need to have the underlying understanding of how things work so that we can interpret properly the empirical data. The bottom line is, I think it's unresolved, and at least on the top of my list is going back and trying to repeat what I saw, what we saw at UW-S, testing multiple levels and to actually, first, see if that was an aberration.

WOOD: I think, basically, I just really support what Russ has said. Our feeling, overall, is that chloride should be protective, but we're not very confident in the range in which it's going to be protective. If you look in detail at Russ' tests, they're done at quite a low range of chloride. For the work that Playle presented, or that sort of range of chloride, then it's quite possible, in fact, that you could offload silver from the chloride on to the fish gill and, in fact, you would not have any protection. What I feel, however, is that there is a need to really look at this question of how water chemistry affects silver nitrate toxicity if, in fact, there are going to be regulations based on some sort of an equation.

We feel, right now, that the hardness equation has some problems with it. If one looks at how that hardness equation is derived, then some of the best data that was available at the time didn't seem to be used, which I think is rather strange. What we think, in fact, is that part of the hardness effect that was put into that equation really was a chloride effect, but we don't know how much of it. So I think there really is a need to consider hardness, chloride, and probably DOC, as the three really important things which are going to affect silver toxicity. So, I guess I'd support Russ' view that, basically, we have to look at these whole questions in more detail again.

SULLLIVAN: Before we move to another question, Anders reminded me that some of the panel members here, and maybe most of them or all of them, may have some comments that they'd like to make. So before I move to any additional questions, I want to give each of them an opportunity to speak their piece of mind, whatever that may be. We'll start with Dave.

ARMSTRONG: Well, I'll just make a few comments, to keep things brief here. From my perspective, I think what we're looking for is information related to what the levels of silver are in effluents, and also what the forms are, and how rapidly silver is dissipated, what happens to it as the effluent is discharged. I think from the discussions we've had here, some very interesting things are developing in this regard, as to what factors about the composition of the receiving water might be important. These have already been mentioned to some extent. Of course one that seems to be quite important is the suspended particulate matter, because of the partitioning of silver to particles. One that's less well understood, I think, is DOC. We see evidence that DOC affects silver levels, suggesting that there's association with DOC; but we know less, I think, about the *relationships* of that association to the effects on bioavailability and biological effects. So that seems to be a more, perhaps, open area. The fact that what we call "dissolved" silver is largely colloidal is also, I think, an important factor in understanding what the true biological effects of silver are in the environment.

I think for me, one of the interesting things that's been raised in this conference is the chloride. Perhaps Sam might, when it's his turn, comment more on this. But from what I've heard, it's been raised that there's a real difference between estuarine and freshwater systems in terms of the bioavailability of silver, and that this, perhaps, is related to chloride. So maybe, when it gets down to the other end, Sam can comment further on that. But that's an interesting idea, at least from my perspective, that's been raised here, that would be nice to get some further discussion on, I think.

MUKHERJEE: Actually, when I started this work, or when the folks at ANJE told me to do this work in Helsinki, after a couple of weeks, the National Board of Waters and the Environment asked me, "Why are you working with silver? Is it toxic?" They are just laughing at me. And I said, "Okay, let's see what I can do." Actually, I don't know how much you know about the United Nations' EC Task Force, and their policy about heavy metals in the environment. It is simply that they have taken 10 metals in the program (biology), and among these 10 metals are mercury, lead, cadmium, zinc, chromium and a few others. And actually, for most of the scientists, we know the toxicity index of these metals but, unfortunately, we don't know anything about the toxicity index of silver. If I tell silver is a toxic metal, people laugh at me, "How can you say it? It is such an expensive metal! How can we put this metal into the environment?" So I think that this is a high time for us to find out where we will put this metal. If I go to the board, I can show that toxicity of the metals, particularly heavy metals, how it is decreasing — mercury, lead, cadmium, zinc, chromium and so on. But where will we put silver? Should I put silver at the end or in the front?

Here is one paper, unfortunately it is in the Finnish language, it is simply what the European Union, they have made a blacklist of heavy metals, or chemicals, and then they have made some lists where there are no rules and regulations. And there, I can find out, they have put silver; it has no importance, and they have put it just at the end. For example, uranium, vanadium, cobalt, thallium, tellurium, silver, boron and many others. But in many countries, silver is recovered from the film industry, or jewelry, or electronic scrap, and even the government authorities, they do not know the standard. What should be the standard of silver in the effluent? Only in the community, I mean the special district, this board, they decide whether it will be 0.1 mg silver per liter of effluent, or 1 mg per liter of effluent. And it also varies from one county to another county. And it depends on how big is this industry. Is it small or big? So according to that, these inspectors, they put these standards. So I think that in this conference, we should really place silver where it should be. We should find out what is the toxic index of this metal. And after that we should find out the standard. What should be the standard, or allowable level of silver in the effluent? This I'd like to postulate, then to, perhaps, draw attention to these things to all of you.

SANDERS: If I can, before I get on my soapbox, I want to make a point, and a thanks to Anders and the rest of the organizing committee. I think this is a very important kind of conference for us to hold, because too often the academic scientists go to national meetings and talk to themselves, and the regulatory agencies and some of their for-profit consultants go somewhere and talk to themselves. We don't intermingle enough. This is a perfect example of why I think it's important for us to intermingle. Because we have an issue here which was brought up early on about the fact that we do have to have regulations, and we need to have some kind of good way to form those regulations. We're stuck in a situation where we have to deal with regulations based on, or largely on, bioassays or techniques that look at high levels of a metal in systems that are loaded with artifacts, and we know that's true, and then try to, somehow, bring that to bear in an actual system.

I think that was brought out very well when Russ, for example, showed his differences in LC_{50}'s of Daphnia and some of the other critters between his laboratory water and a real water. Sometimes there were almost two orders of magnitude differences. From the preliminary data that he showed, you couldn't simply explain those large differences between laboratory water and natural water. I don't think that I have to say again, that it is extremely important, as we develop good physiological mechanisms for determining toxicity, that we also make certain that we understand completely and fully the geochemistry of that solution. As Chris and Russ alluded to, it's one thing to know how geochemically silver is moving through an aquatic system. It's another thing entirely to know how that speciation of silver can change when you get to the surface of a cell or a gill, and we have to understand both of those. The only way that we'll ever be able to take these out into the real world and work up any kind of water effects ratios, for example, is to make sure that we understand completely what's happening within our test tube, or within our test systems.

SCHUETTPELZ: I guess I don't have too much more to say than what Jack said. I'm Duane Schuettpelz from the DNR, one of Jack's colleagues. I guess the couple of items I'd like to mention is that, even though the Great Lakes Initiative in its initial draft publication didn't have silver on the list of chemicals for which a criterion was derived, it indeed is on the list of important chemicals and, presumably at some point in the process, a criterion will be derived for silver as part of the Great Lakes Initiative effort. Also, in conjunction with the Great Lakes Initiative, EPA has just recently put out for public notice a series of publications, including one that was done at the Duluth lab by Chuck Stephan, that are related to dissolved metal and freshwater toxicity tests and the whole issue of water effects ratios, etc. So that this is something, if somebody's interested and they have not heard about this, this is out for comment right now. We're in the process of looking at it in our agency to see what sort of comment we might have on this document.

As it was probably alluded to last year, Wisconsin has been, perhaps, one of the agnostics on the whole issue of water effects ratios, and whether or not that is something we should support, endorse or be opposed to. One of our concerns with respect to water effects ratios is, what does it mean for the total loading of metals into the environment? Is it going to result, not necessarily in an increase, but at least in a continuing discharge of metals? How does that affect sediment toxicity? One of our emerging programs in our agency, and in the Great Lakes as a whole, is the effects of contaminated sediments on our water resources. We have lots of locations around the state which have contaminated sediments. They are continuing to load up the aquatic systems out into the Great Lakes particularly. Most of them are related to PCBs and substances like that, but there are some metals locations where sediments are contaminated. And that's one of our concerns, about potentially loosening up, or relaxing the requirements on discharges.

Lastly, I guess I'd just like to point out another emerging problem that we're going to be faced with, and that is the issue of non-point sources, particularly stormwater. How do we deal with stormwater, and the effects of metals in stormwater, and the impacts on surface waters? We are in the process of generating a lot of data on stormwater toxicity, and it's sort of coming out of the laboratory day to day. We do know there are metals like zinc and cadmium in stormwater that are potentially, and probably, toxic. A variety of other things also. So this is something that's going to need further investigation, and how do we incorporate stormwater management into either our regulatory programs, or at the local level, into management activities that municipalities can implement to control the discharge of stormwater, and the pollutants in it.

WOOD: I think any good conference sort of highlights some important issues. And to my mind, really, there's three issues that came out of this conference that are really important. One of them Russ and I have been talking about, that's the particular role of water chemistry in affecting silver toxicity. How important is silver chloride? Is chloride protective, or is the silver chloride complex additionally toxic? And that's probably going to be a very different question in freshwater than in seawater, I suspect. That's one issue. The second issue is that we've learned now that what we used to think was dissolved may not be dissolved — so it passes through an 0.4 µm filter but not through an 0.1 µm filter — that is some sort of colloid. There seems to be a lot of really good research going on in this right now, and I think it's going to be very important for us to understand if that colloidal fraction can act as an important silver donor to animals or not. Is that bioactive or is it not bioactive?

Finally, there's a third area that I think was highlighted, and where there doesn't seem to be too much research going on, and I think it is an important area. That is, what are the long-term population impacts of silver accumulation in organisms? We've heard about some excellent research in San Francisco Bay, some excellent research in England on marine bivalves. These animals incorporate a lot of silver in their tissues over long periods of time, but we really don't know what the population impacts are. We also know that freshwater fish, when exposed to chronic low levels of silver, will induce metallothionein, and will incorporate and immobilize silver internally. We don't know what costs are there. And I think if, in fact, there's going to be long-term discharges of silver into the environment, it's important to understand population level effects, and subtle metabolic costs. Those experiments are difficult to do — they're time-consuming, they cost a lot of money — but, I think it's probably important that we understand long-term effects as well as short-term effects.

ERICKSON: Since the topic of the panel is what the research needs are for regulatory applications, I think we first have to think about what water standards are intended to accomplish. And despite — the enabling legislation often refers to things like "integrity of biological communities," which is relatively undefined, and we often refer to trying to define exposure conditions which are below that which exert undesirable toxic effects. Those are often based on laboratory data, or typically based on laboratory data. And that raises two main questions. First of all, when going from the lab to the field, what are the exposure conditions which change the toxic response? This is Sam's geochemical effects that he mentioned before. The other thing is, are the endpoints that we measure in laboratory tests really relevant to — really the important ones for — protecting natural populations? Chris just alluded, in part, to that. Now, any kind of standard we come up with is going to have some uncertainties with respect to those, and there are two major approaches for addressing those uncertainties now. One, Jack Sullivan talked about, is water effect ratios. Another, is trying to build more predictive capability into the criterion.

Though my research has most typically dealt with water chemistry effects on toxicity, I'd sort of like to mainly highlight some missing areas that are — and while I think there's research needs regarding that, and we've talked about it — I'd like to sort of highlight some other areas that I think are even in more dire need. And first, again, Chris just mentioned long-term chronic effects, especially ones that might not be the typical ones, but that might really relate to population impacts in the field. And as part of that, the whole issue of accumulation through the food chain. Again, water-based exposures in the laboratory might miss a significant part of the exposure organisms in the field. Related to that is the issue of sediment toxicity as an important area. What we've heard about the fate of silver in the environment, and what happens to it, emphasizes the potential importance of sediment toxicity. And it becomes increasingly important as we talk about mitigating factors that might — again, repeating something that was already said — that water effect ratios are mitigating factors which might lead to greater discharges of metals, we would start talking about greater sediment contamination of metals.

Finally, I think there needs to be more attention to the kind of work Sam does, in terms of really looking at, looking more at the field, to look at . . . [tape changed at this point] . . . there's ground-truthing, so to speak, what we've learned in the laboratory. That brings me back to the laboratory, and I, again, echo what Chris said, that there's various factors that need to be better understood. We just don't have the predictive capability to talk about them.

LUOMA: I can't add much more to all that. Maybe one thing about the chloride controversy. I think it's really interesting — I haven't said anything revolutionary here in terms of marine chemistry — I think what we've all been talking about in terms of marine chemistry and the importance of the chloro complexes is established knowledge and has been for a long time. So it's interesting to be with these two groups of people. I think there's nobody whose work more clearly demonstrates the chloro complex, or the possibility that the chloro complex is available, than what Jim Sanders showed us again from marine chemistry. So this is a unique situation where an available complex seems to be somewhat abundant, is what it looks like. That's the kind of the marine end of the controversy, and it just means learning more about that complex.

I guess one other thing, other than to say I really liked Chris' three points, or three areas of research, especially the toxicity one, but the other dilemma, with regard to regulation, is what do the regulators and regulatees do in this circumstance where we have a lot of uncertainties still? And this is really the case in a lot of environmental regulations — you throw up your hands and say, "Too much uncertainty, let's just give up." Or there's another way to approach this, although it doesn't fit very well into the legal system, and that is to think: Are regulations, as we establish them, really experiments? They might be expensive experiments, but they are experiments. And when we do an experiment in the laboratory, we monitor the results. Well, we've been doing experiments with regulations since the late 1960s, and we haven't done very much watching nature and watching how nature has changed as we've changed the stuff that comes out of these pipes. We've done a very poor job of that, I know, in San Francisco Bay, and I would guess in a lot of other places.

And so, one of the things that we might think about is to take a certain small chunk of what we're using to support these things and kind of relax a little bit about time, and put a little effort into watching how systems change as we change what comes out of these pipes. If we do that in a creative way, we'll do more than just collect data. We can also learn about science, and I don't think there's anybody who's illustrated that better than Bill Langston's talk, where they have worked for decades looking — one aspect of what they've done is looking at a similar problem through a lot of different areas — and at the end of that time period, or at this point in time, they've really learned a lot, both scientifically, and about the distribution and influence of a lot of these contaminants. So I think that there's a certain element of patience that has to be involved in recognizing regulations as an experiment. It has to be involved in what we do.

SULLIVAN: All good comments from the panel. We're hearing marine chemistry vs. freshwater. I'm hearing population effects, maybe landscape-scale type decisions, managing more at an ecosystem level and all the questions that are inherent in that. Maybe we have the basis for the Third International Conference on Silver and its mysteries. But with that — and those are all really good comments, and I agree with those — maybe we can open it up to the audience here now and see some of the questions that they might have related to these comments.

DONALD AXELRAD (Florida Dept. of Environmental Protection): Jack Sullivan, you mentioned as regards mercury, wildlife protection drives the standard. Do we have any feel, or would anyone hazard a guess, as to what the case will be for silver? Will it be toxicity in the water column, sediment toxicity, wildlife, human health concerns, or other?

SULLIVAN: Right now, I know in Wisconsin our regulations — and Duane, you can back me up here — it's acute and chronic toxicity to fish and aquatic life that will currently drive it. There is, as other people have said, not a wealth of toxicological information. And so I don't have any insight into the future of that.

ERICKSON: I don't think you're asking the right people.

AXELRAD: Are there the right people to ask?

ERICKSON: We've dealt a little bit with wildlife hazard, in terms of fish and fish-eating birds and mammals. I would tend to have the reaction that it would be driven by aquatic life in the case of silver. I mean that would be my guess.

AXELRAD: Water column or sediment?

ERICKSON: Based on some of the data that we saw from the sediment contamination, especially some of the higher porewater concentration, I would tend to be looking more at that. Getting back to the wildlife, you have route of exposure, and silver isn't particularly bioaccumulative as far as being a significant route of accumulation. And you're talking about water consumption of wildlife. Unless you have a wildlife species that is remarkably sensitive to silver compared to any aquatic species, it would seem that the aquatic species would drive it. And regarding sediment, the data I've seen, in terms of sediment contamination of porewater, I would hazard that that should have a closer look. I would guess that in a lot of situations it would be more important than the water column toxicity. But I should qualify that with, that it is a guess.

AXELRAD: We've heard that a number of chemical species reduce silver toxicity. We've heard chloride, obviously, and thiosulfate and sulfide and pH and Eh are important. We even heard copper has an effect. For regulators: I don't think we're going to write a grand equation considering all these things. Is there one that we believe is far more important than others, or do we have to do more research to answer that question?

WOOD: I think you answered the question with the last half of your comment. I think we have to do more research. I don't think there's a simple answer right now.

ERICKSON: I would agree that, based on what we've seen, there's enough of effects — of a variety of them — that you just can't take one variable. I mean the data we had suggested that organic matter might be a predominant one, but not so much that you can ignore the other ones. It really gets down to the uncertainty. Even with the point I made earlier in this conference — with the hardness equation and the 1980 EPA criteria, I agree with Chris that there are other data that show, when you have different co-variations of different water chemistry, that you get a different result in terms of using hardness as a master variable. The crux of that is that it isn't just a hardness effect. It might be just minorly a hardness effect, per se. Now you're not going to get a good answer with either one equation or the other, because it depends upon how the chemistry co-varies at your site. Either will produce a certain amount of uncertainty for you. The bottom line is how much uncertainty you want to live with, and how you manage that uncertainty; if you use a criteria as a standard, as a starting point, against which to do more site testing or not, as to how well-predictive it has to be. But if you really want something that's predictive within — you know, even in the narrow range of saying predictive of a particular toxicity endpoint, which ignores some of other subtleties, but predictive in that sense — within a factor of two or three, no there isn't just one factor that you can do that with.

AXELRAD: I'm happy to be patient about research, but having typed criteria in Florida, we affect industries. And industries, of course, have reasons not to be patient. Given the complexity of this issue, and the need for further research, do you, Russ, recommend an empirical approach, a water effects approach, or, as Sam said, looking at the biology and seeing at what concentrations we see community effects?

ERICKSON: Well, from the standpoint of applying toxicity data to making a prediction, I would certainly think that the use of site testing of water effect ratios is about the only approach, only immediate answer to addressing the uncertainties, if you need a quick answer. I don't have another answer. Looking at the natural communities, and other people can better comment on that, is fraught with difficulties itself, in terms of sensitivity and such.

SCHUETTPELZ: Just another comment on the point. Sometimes I think we worry a little bit too much about splitting hairs — exactly what the number, the effluent limit number should be. You know, should it be 0.08 or should it be 0.0075, or whatever the number might come out to be. I think the whole issue is one of how flexible can we be and still be within the range of how we regulate facilities. And I think that goes the other way, too. The regulated community has to recognize that some of these things are not sort of cut in stone always, and that we need to have a little bit of flexibility in how we implement some of these regulations. Jack's example of how many facilities we include effluent limits for each of the parameters — well, he's got 15 percent or 10 percent or 30 percent, whatever the number might be. You have to recognize that the way we put numbers in permits is that if anybody is within 20 percent of the final calculated value, that number becomes a limit in the permit. So the discharger could be discharging at 30 percent of what the actual limit is, but that still is a limit in the permit. They may be nowhere near the actual permitted level.

So again, is that important to the industry to have that sort of a cushion? Should we back off on how it is, and when we put a limit in a permit? What is the frequency of violation? You get into all sorts of enforcement issues at that point in time. Is it okay if there's an occasional excursion? What are the enforcement and compliance implications of that sort of thing? So there's a whole variety of sorts of things that come into play, in regulating materials that come out of the ends of effluent pipes. I know the issue that you're facing. We face that all the time also here.

LUOMA: Since I brought up the monitoring question, I should respond partly to that. I think I've been in lots of these monitoring discussions and the comment always comes up, well, should we monitor the community, and, as Russ said — and he's absolutely right — that's a difficult thing to do and to interpret. But just as was stated here, in terms of monitoring, if we try to go for the absolute answer, of whether or not there's effect, we're going to fail. I mean we don't have to have the absolute answer. What we need is some simple measure of whether what you're doing is improving things or not. And just things like tissue burdens can, if monitored through time, tell you if whether or not what you're cleaning up is indeed showing a clean-up in the environment. It doesn't show you whether there's a change in effects, but it's the first step towards that. And a few simple — I mean monitoring has to be something simple that you can do over and over and over, and in itself is interpretable — even a few simple things like that can feedback in a positive way to the people that are being regulated, and they can see what they're doing, or what has been done is having some positive influence. I think we've seen that happen with the people I work with in Palo Alto. So, I think the hardest things don't have to be done. I mean those are research questions. But we can work maybe with some of these simpler tools, and also from a non-regulatory point of view, it seems like flexibility is something that has to be built into this system. Because if you're going to have monitoring, then you've also got to have feedback to say this is or is not working; do more or do less.

SULLIVAN: Other questions?

MARY COMPTON (Industrial Economics): This is more of a comment than a question, I guess. My company's been working with the Office of Policy, Planning and Evaluation for over a year on a sustainable industry project, the photographic industry — a lot of you are intimately familiar with it. I spoke to a number of the people on the panel a year or so ago, and expected them to just be able to tell me, well, is silver from the photo industry toxic or not? We're becoming increasingly aware that the scientific issues behind the problems are very complicated, and, as a consequence, we're working on, hopefully, policy options that are going to result in increased recovery of silver so that the question of the impact on the environment isn't going to come back to haunt us. Issues such as silver on the Toxicity Characteristic list, mass-based limits, things like that.

But I think that the final resolution of a lot of the problems is going to come back to the gold book standards, and the water quality limits, the issue of the hardness-based standards, and things like that. And that is, as Sam said, going to require a certain amount of patience. It's going to be a long-term process. But I did want to reassure you all that the agency is listening. I spoke to Bob April from the EPA's Office of Water before I came here this week and he's very anxious to get the results of the conference. So I would encourage you to continue to try to communicate with them, to hold sessions like this, where you invite people in the regulatory and the regulated community, so that the dialogue continues and you don't end up with segments of knowledge that people aren't aware of. Thank you.

SULLIVAN: I think that's a good comment. And that the other thing that we need to remember is, as we move these issues forward — and silver is the one we're talking about here — we need to move forward in partnership. You know when we get into tight economic times, research dollars are less; everyone has to do more with less. And it seems as we move forward, and join, and come together in partnership, that we find solutions that are workable for everyone. And so forums like this indeed are important. Any more questions or comments out there?

EUGENE KRASNOV (Kaliningrad State University, Russia): First of all, I would like to support the suggestion of Arun, from Finland, about toxicity index calculation. Because for silver — our conference was connected first of all with silver, as a metal in the global environment — we haven't heard this today. Second, for different regions in the world, you have different situations about metals in the environment. For example, for Great Lakes or some other places in the United States, you haven't major problems about PCB or DDT, but in Russia and the Baltic Sea, around to Poland and to other countries in Eastern Europe, we have great problems, compounded with metals, not only, for example, silver or mercury. This is a combined effect. And combined effects, for standards, are also very important. Third, about the necessity to have more profound, more representative data, through time and space. Because natural effects, for living organisms, have long-term distance to adaptations, to co-adaptations, but now we have talked only after some short experiments about toxicity for animal or for human health, connected to metal contents in the environment.

Maybe after this Second International Conference, connected to these sources, fate and transport of metals in the environment, it is necessary to have some approach to the foundation of an international program for future investigation, before the third conference. For example, in our country, in 1975, in Odessa was organized the first international symposium entitled, "Interaction Between Water and Toxicants to Living Organisms," (or living matter) after Vernodsky. Immediately after this conference, by letter, or by some informal contact between people, was founded an international program for investigation. We first found this program to be necessary to have a list of priorities for future investigation, an interdisciplinary approach; this program is absolutely necessary to have after this meeting here in Madison, Wisconsin.

And finally, we would like to have at Kaliningrad State University a regional center for the analysis of databases and regional or national standards, for metal contents in the environment. But for this it is necessary to prolong our discussion, not only from a scientific point of view, but necessary to have some multi-site agreement between, for example, agencies, state regulators, scientific approach, and company and industrial people also. Without this multi-site agreement, it is impossible to have more, high representative of standards. This is all. Excuse me, because my language was not so good, but I think this is also important.

SULLIVAN: Thank you. My watch says we're about running out of time. I want to thank the panel members and the people that participated in the discussion, and I think at this point we'll turn it back over to Anders.

ANDREN: Thank you very much, Jack, and thank you very much panel participants. I have prepared a few summary comments about some of my impressions of presentations and, if I may, I thought I'd just take a couple of minutes to give you some of my impressions on what we have heard, some of the progress that we've made, and some of the progress that needs to be made. But first of all, I'd like to again emphasize that I think the concept for this sort of a conference is really good.

We separated the talks last year, and have continued to do it this year, into metal speciation, environmental cycling, toxicity of metals, food chain transfer, and analytical chemistry. Certainly for the sake of convenience, each of us have our niche in the research community. But I think it's important that we keep in mind that we ought to join all of this together somehow, and that's where a lot of the regulators are faced with integrating all of that material. The ecosystem approach, or the holistic type approach to managing ecosystems is emerging more and more, and these interdisciplinary types of meetings and discussions are becoming increasingly important. The compartmentalized way of dealing with increasingly complex issues are often good if you want to push the frontiers. But if we want to look at broader questions, this is a good way of doing things.

When it comes to metal speciation, my sense is that all of us think that it is still really important to address both the physical speciation aspect of silver and metals, as well as the chemical speciation — the two are related. We still need to know an awful lot, and especially develop predictive capabilities for transport, for bioavailability, and for toxicity. We still need to push the frontiers, and we still have a long way to go. What struck me from this conference is that when it comes to particulate matter, we haven't spent the amount of time looking at speciation. We have mainly addressed the dissolved part.

In terms of particulate matter, there are some techniques now which are becoming available, admittedly for cleaner surfaces, but such analytical methodology as atomic force spectroscopy, internal reflectance spectroscopy — Fourier series IR, can tell us a lot about the solid/water interface, and I think exciting opportunities are opening up in those areas to teach us more about the nature of the interface and the speciation of particulate matter.

Another aspect is the intriguing part about the colloids. Now for those of us in the aquatic chemistry area, we've been talking for a long time about the colloids and, in a sense from a transport theory, they are transported perhaps more as a dissolved component. But they have a finite lifetime — they aggregate and form large particles, and we need to know much more about the physics of transport of colloids in nature, as well as chemical speciation considerations. But there is a barrier here, I believe, and everybody who talks about colloids is sensitive to the possible analytical artifacts that you have to deal with. I think we need to work very hard to overcome these difficulties. When it comes to the dissolved part, I think we've all been convinced that the role of reduced sulfur compounds and the role of DOC in modifying transport, bioavailability and toxicity, should be explored extensively.

Finally, when we get down to the sediment, and related to suspended sediments, the sediment quality debate, we just need better techniques to look at speciation in the solid phase. There's a lot to be done there.

When it came to environmental cycling, I think that this conference has consolidated some of the knowledge that is out there with respect to sources. But there again, compared to some other metals like copper or lead, we've got a fair way to go to really understand natural vs. anthropogenic cycling. But we are making a stab at it and, hopefully, will continue to do so.

When it comes to partitioning, I think we are making real progress in this area. The laboratory data on partitioning right now is beginning to converge vis-a-vis measurements made out in the field. I see promise with respect to partitioning information and of being able to model transport. What is still missing, however, is a detailed knowledge of complexing sites on the solid.

When we get to the area of toxicity and the food chain, I'm treading on much thinner ice for me, in terms of my background. Just a few comments, and I think they were articulated very well in the panel discussion. We still have a fair way to go when it comes to reconciling laboratory data with environmental observations. And it probably emphasizes more than ever the concept of doing bioassays, toxicity testing, on several different levels. We have to do them in a geochemically consistent sense, from the point of view of the speciation of the metal in question, but also from, perhaps, the lifetime of the organisms, because we have to look at, perhaps, both population levels as well as successive generations. And we've got to reconcile those data, and I still think that we need to do that. At the same time, the kind of work that's done by Wood, the kind of mechanistic understanding, has to go in a parallel stage. In order to get at the long-term chronic effects, I think we have to use the environment much more intelligently to tell us what's happening.

I also agreed with the comment about the food chain. I think this is an area that is underfunded with respect to research. There are so many different routes of uptake. And we know a few things: that it is very difficult to understand the dynamics of uptake from water to phytoplankton, because phytoplankton are so dynamic in the way they grow. We perhaps can do conceptually a better job from phytoplankton to zooplankton, than zooplankton to invertebrate, but we need to quantify those steps much better than that. We need to quantify how the transport occurs from sediments to organisms.

Finally, on the analytical end, what seems to be the case here is that we improve our limit of detection by an order of magnitude per decade or so. But we're still looking mostly at total concentration. Methods for solids analysis are lagging; I still think we've got to put a fair amount of effort in there. But we have to realize that there's not going to be any one technique that we will rely on. We probably will rely on spectroscopic-type techniques for a long time to come for the total, and address the complexation in a variety of ways, the most promising there being electrochemical techniques, which are improving. As new electrodes are becoming available, I think there are exciting opportunities on the horizon, so that in the not-too-distant future, we can do a better job. Within the not-too-distant future, I also hope that we might be able to bring up the knowledge of the silver complexation, associations, partitioning, to the level of, perhaps, copper. And I don't think it will be too long before we can bring up our level of understanding of silver — analytical techniques vis-a-vis speciation, association, partitioning — to that of copper.

I think for last year and this year we have invited certainly some of the most prominent researchers in the area of silver — fate, transport, toxicity — and I hope we will be able to continue this, and will scour the landscape even further to help bring fresh perspectives to what we are doing. I'd like to thank each and every one of you — the organizing committee, the active participation of everybody, the speakers — and I hope you've enjoyed yourself in our beautiful city. Thank you very much for your participation.

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Poster Session

Transport, Fate and Effects of Silver in the Environment

The University of Wisconsin-Madison

2nd International Conference

Calcium Versus Chloride — Which is the Important Protective Factor Against Silver Toxicity?

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The purpose of water quality criteria is to give an accurate assessment of the ecological effects of a pollutant, based on current scientific knowledge. This allows regulatory agencies to correctly assign a maximum acceptable level for the particular toxicant. Greatly influenced by data later published by Lemke (1981), current water quality criteria regulating maximum total recoverable Ag levels, incorporate a major modifying role of water hardness (mg/L as $CaCO_3$) [(US EPA, 1980)]:

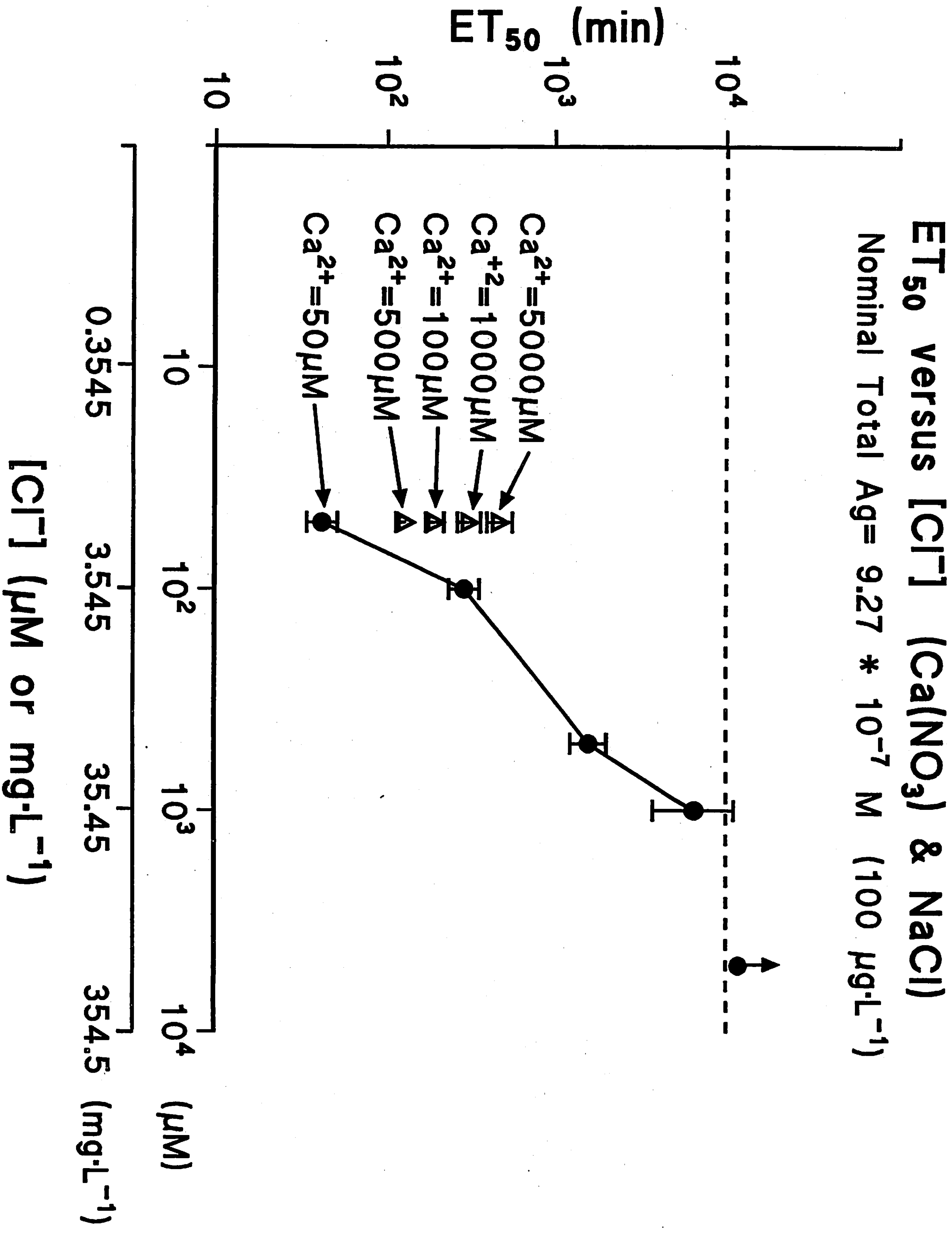
$$\text{Max. Total Recov. Ag } (\mu g/L) = e^{(1.72[\ln \text{hardness}] - 6.52)}$$

However, various studies directly question the validity of this hardness correction. Davies *et al* (1978) observed only a 2-fold decrease in 96 h LC_{50} for $AgNO_3$ in rainbow trout when water hardness was decreased from 350 mg/L to 26 mg/L. According to the "hardness correction", such a variation in water hardness should have generated a >80-fold difference. Similarly, water hardness failed to produce significant effects on acute Ag toxicity in other fish species (Goettl and Davies, 1978), and had no effect on chronic $AgNO_3$ toxicity in *Daphnia* (Nebeker et al, 1983). In addition, reanalysis of Lemke's tabulated data indicates no effect of water $[Ca^{2+}]$ but a marked effect of water chloride $[Cl^-]$ on 96 h EC_{50} values. Consequently, it is possible that the hardness relationship has been misinterpreted through co-variation of Cl^- with "hardness", and that the real protective agent is Cl^- rather than Ca^{2+}.

The objective of the present study was to determine the relative influences of water $[Ca^{2+}]$ and $[Cl^-]$ in ameliorating acute toxicity of $AgNO_3$ to freshwater fish. Juvenile rainbow trout (*Oncorhynchus mykiss*, 2.9 - 10.7 g) were acclimated to synthetic soft water ($[Na^+]= 0.05$, $[Cl^-]= 0.05$, $[K^+]=0.05$, $[Ca^+]=0.10$ mequiv/L, pH= 8.0, 15 ± 1°C) for at least two weeks prior to the onset of bioassays. Classical LT_{50} tests (static with daily renewal) were performed in aerated water in 75 L polyethylene tanks. Each tank (except controls) had a total [Ag] (as $AgNO_3$) of 100 μg/L and an independently varied $[Ca^{2+}]$ (as $CaNO_3$) or $[Cl^-]$ (as NaCl) using semi-logarithmic progressions between 0.05 and 5.00 mmol/L.

When $[Ca^{2+}]$ was increased 100-fold (Cl^- maintained at 0.05 mmol/L) survival time only increased about 10-fold (Fig. 1). However, when water $[Cl^-]$ was increased 100-fold (Ca^{2+} maintained at 0.05 mmol/L), acute toxicity of 100 μg/L of $AgNO_3$ was prevented over the 7 day period. Only a 2-fold increase in water $[Cl^-]$ was required to produce the same protective effect as a 100-fold increase in water $[Ca^{2+}]$.

Figure 1. Trout acclimated to softwater (with equimolar amounts of Ca^{2+} and Cl^-) were exposed to 100 µg/L as $AgNO_3$. Increasing water [Ca^{2+}] 100-fold as $Ca(NO_3)$ increased survival. Note the much greater protective effect of elevating water [Cl^-] by equivalent amounts.



Another set of toxicity tests was performed to ensure that the protective effect of Cl^- was not attributable to its counterion (Na^+ in NaCl), or that the decreased protective effect of Ca^{2+} was not a result of the anion used (NO_3^{2-}). Selected tests with KCl and $CaSO_4$ using the same semi-logarithmic range of $[Ca^{2+}]$ and $[Cl^-]$ produced results similar to those seen in the previous series of toxicity tests. When water $[Ca^{2+}]$ was varied from 0.05 to 5.0 mmol/L, ET_{50} increased by approximately 10-fold (Fig. 2), whereas similar variations in water $[Cl^-]$ resulted in >100-fold change in ET_{50}. Therefore, irrespective of the counterions used, water $[Cl^-]$ was shown to have a greater protective effect than water $[Ca^{2+}]$ on Ag^+ toxicity.

Speciation modelling with $MINEQL^+$ (Schecher, 1991) was used to study the effects of Ca^{2+} and Cl^- on the concentration of free Ag^+, $Ag(Cl)_n$ and cerargyrite in water. Although variations in water $[Ca^{2+}]$ had only negligible effects, changes in water $[Cl^-]$ dramatically influenced Ag speciation (Fig. 3). At 0.05 mmol/L Cl^-, approximately 90% of the total [Ag] (100 µg/L) was in the form of free Ag^+, while the remaining 10% was AgCl. When $[Cl^-]$ was increased to 5.0 mmol/L, Ag was predominantly found to precipitate as cerargyrite (~72%), while only 1% remained as free Ag^+ and 17% as $Ag(Cl)_n$ species. The majority of the Ag speciation effects were observed to occur at $[Cl^-]$ below 1.0 mmol/L.

Since Cl^- has such a strong ability to complex Ag^+ as $Ag(Cl)_n$ and to precipitate it as cerargyrite, small changes in water $[Cl^-]$ can be expected to have a dramatic influence on Ag toxicity. This same speciation model can also explain the inability of water $[Ca^{2+}]$ to greatly ameliorate Ag toxicity, based on the continued presence of a high percentage of free Ag^+. These results suggest that the "hardness correction" should be reconsidered and the incorporation of water $[Cl^-]$ into the criterion is recommended.

Supported by a grant from the National Association of Photographic Manufacturers/Silver Coalition)

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Figure 2. The results of an experiment, parallel to that of Fig. 1, in which water [Cl⁻] was manipulated using KCl and water [Ca^{2+}] as $CaSO_4$. These results demonstrate that the much greater protective effect of [Cl⁻] over [Ca^{2+}] is specific to these ions, and not a function of the relative anions or cations.

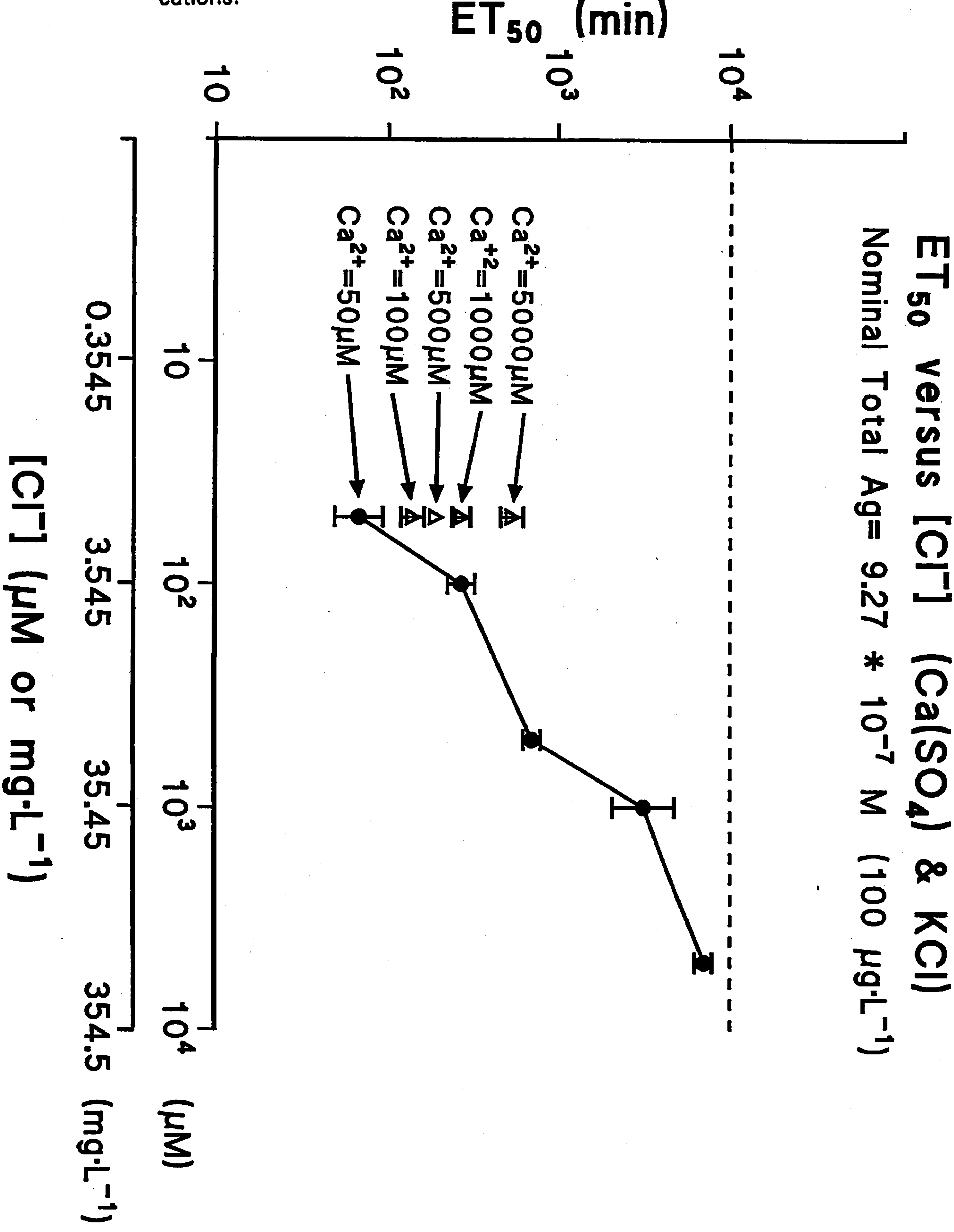
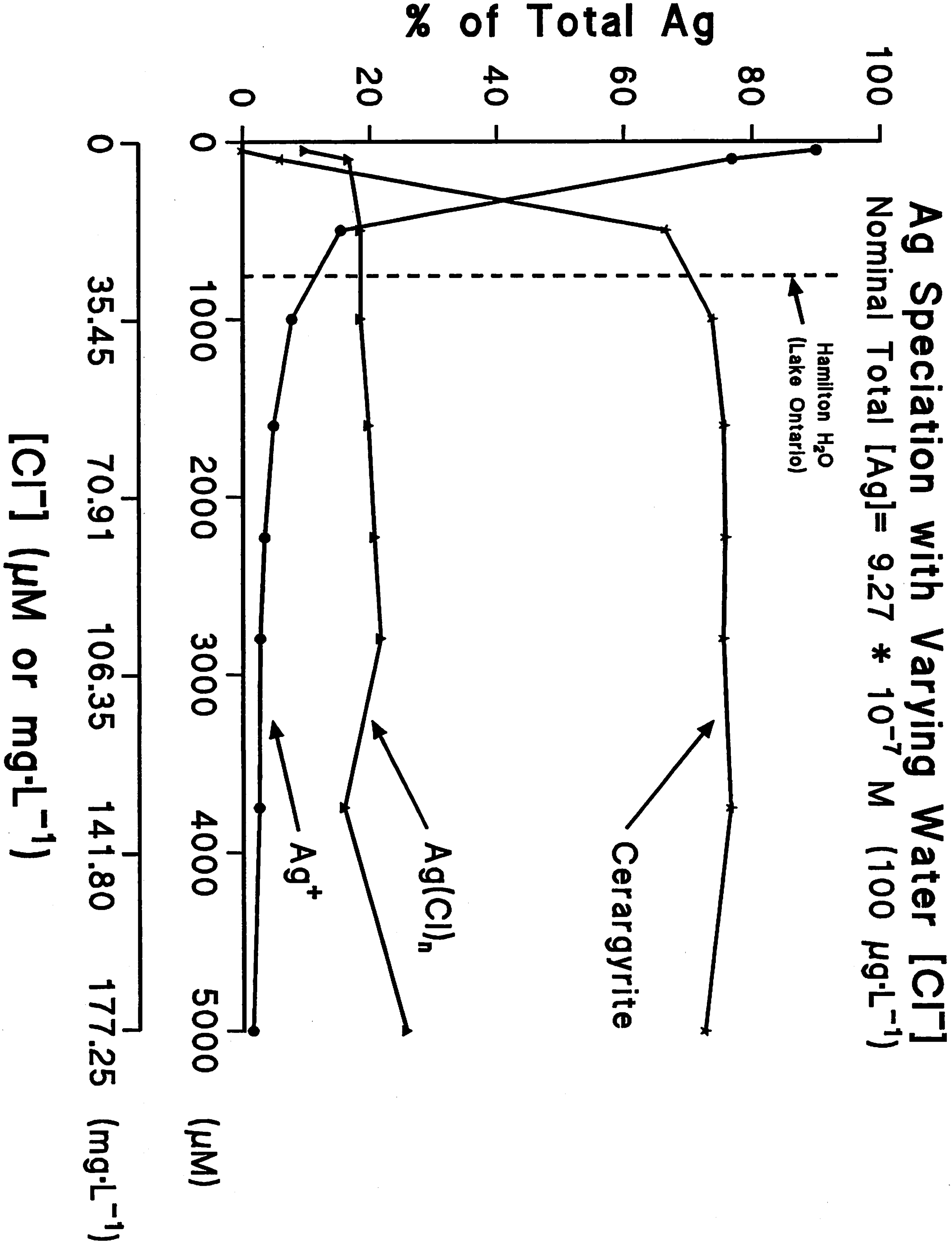


Figure 3. Ag speciation calculations using MINEQL$^+$ illustrate the ability of [Cl$^-$] to remove ionic Ag$^+$ from solution. Changes in water [Ca^{2+}] have a negligible effect on speciation.



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