

## The Silver Cycle and Fluxes in the Ocean

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The biogeochemical cycle of silver has rarely been reviewed, even though the silver ion ( $\text{Ag}^+$ ) is extremely toxic to some organisms. Its concentration is still rising sharply because of increased anthropogenic activity, specifically the discharge from the film industry (mainly, silver thiosulfate:  $\text{Ag}(\text{S}_2\text{O}_3)^{3-2}$ ). Recently, a number of researchers have quantified the major fluxes and reservoirs of silver in the open ocean, bays, and estuaries. A review of the available information for Ag cycling in the open ocean shows that the riverine input (from human activity and weathering processes:  $7 \times 10^6$  kg/yr and  $5 \times 10^6$  kg/yr, respectively) is the dominant source of Ag to estuarine and coastal regions. Most of the silver (90% of riverine input silver) is removed in coastal sediments by the physical-chemical character of silver due to its high partitioning with particulate matter. On the other hand, in the open ocean the atmospheric input (wet and dry deposition:  $1.48 \times 10^6$  kg/yr and  $1.94 \times 10^5$  kg/yr, respectively) becomes more important as a source of silver than riverine input. The residence time of silver calculated from available data is 1250 yrs in the deep ocean below 500 m, but only 3 yrs in the surface ocean.

### INTRODUCTION

Recently, significant knowledge has been reported about the biogeochemical cycle of several trace elements. However, relatively little is known about the biogeochemistry of silver (Ag), even though silver is one of the most toxic elements for some plants and invertebrate. Silver ions competitively inhibit the synthesis of copper plastocyanins in green plants, eucaryotic algae, and cyanobacteria (Bryan, 1971). Its concentration is still rising sharply because of increased anthropogenic activity, specifically the discharge from the film industry (mainly  $\text{Ag}(\text{S}_2\text{O}_3)^{3-2}$ ). At this points, an adequate evaluation of the impact of silver on aquatic systems, from any point or nonpoint source (such as cloud seeding), requires a knowledge of background levels of silver in aquatic environments and of the quantity of anthropogenic silver added. A number of recent researchers have quantified the major fluxes and reservoirs of Ag in the open ocean, bays, and estuaries (Martin *et al.*, 1983; Sanudo-Wilhelmy and Flegal, 1992; Smith and Flegal, 1993; Flegal *et al.*, 1995; Saiz-Salinas *et al.*, 1996). These studies, however, have not systematically investigated the cycling and transport of anthropogenic Ag and the flux of each source and sink in the global cycle. In this paper, I focus on an assessment of the

primary fluxes of Ag to and from the ocean in an effort to obtain a well-constrained budget of global Ag cycle from the available information. Moreover, I examine the speciation, toxicity, spatial-temporal distribution, and physico-chemical mechanisms of Ag to understand the general character of Ag in the environment. Finally, in spite of the limited information of silver, this study briefly reviews the biogeochemical cycle of silver in estuaries and the open ocean in order to evaluate the anthropogenic effect on the global cycle of silver.

### Speciation

It is necessary to know the equilibrium distribution of silver among various aqueous complexes and solid phases, as well as the sorption potential of the various solute species for inorganic and organic substrates. In order to predict effects on ecosystems, the accumulation of silver by various biota and the consequent toxicity effects need to be known for the pertinent solute species at the activity level which will occur.

First, inorganic silver species were examined in the aquatic environment (Jenne *et al.*, 1978; Miller and Bruland, 1995). The activity of the soluble silver complexes varies with salinity from fresh to marine water. As the salinity decreases from 33.5 to

approximately 0.13‰, the activity of uncomplexed silver ( $\text{Ag}^+$ ) increases sharply while the activities of chloride complexes, except  $\text{AgCl}$ , decrease. Therefore, for fresh water  $\text{Ag}^+$  (71%) and  $\text{AgCl}$  (28%) are the dominant inorganic species and for marine waters  $\text{AgCl}_2^-$  (82%) >  $\text{AgCl}_3^-$  (17%) >  $\text{AgCl}_4^{3-}$  (1%) >  $\text{AgCl}$  are distributed as such (see for detail example Jenne *et al.* 1978). However, in anoxic environments with high concentrations of hydrogen sulfide, in particular,  $\text{AgHS}$  is the most dominant species of silver, with  $\text{Ag}_2\text{S}$  (s) also forming.

Secondly, silver species were not indicated in any significant quantity of organic speciation in seawater by Miller and Bruland (1995). It is not surprising that strong complexation was not evident in seawater. Like lead and mercury, the silver ion binds preferentially with soft anions and ligand donor atoms such as chloride and sulfur. Thus, stability constants for silver complexes with ligands like EDTA, which have oxygen and nitrogen donor atoms, are relatively small. Such ligands are unable to effectively compete with chloride for silver ion in seawater. Unlike copper, where organic complexation can dramatically reduce adverse biological effects from contamination, we apparently do not have this particular safety net for silver. On the other hand, Miller and Bruland (1995) also suggested that in freshwater with not only less chloride but also fewer hard cations such as calcium and magnesium to bind the oxygen-donor ligands, organic complexation may be able to play a greater role.

As mentioned above, the character of silver speciation has implications for silver cycling and availability in aquatic environments. In addition, the ligands most likely to overcome the strong affinity silver has for chloride are thiols and sulfide itself, but these species are unstable in oxygenated waters. Therefore, ligands strong enough to out-compete chloride could be more important for silver speciation in suboxic and anoxic waters than in oxic waters. As previously discussed, we should reconsider dominant silver species in any specific environment, such as anoxic areas, estuaries, and hydrothermal vents.

### Toxicity

Silver is one of the most toxic elements for some organisms and invertebrates because silver ions competitively inhibit the synthesis of copper plastocyanins in green plants, eucaryotic algae, and

cyanobacteria (Bryan 1971). Sanders and Abbe (1989) also indicated that flagellated species were considerably more sensitive to silver than diatoms. Differential sensitivity to a pollutant means that under conditions of chronic loading of the pollutant, sensitive species of phytoplankton may be removed from the community while more resistant species continue to grow unimpaired. Thus, within the phytoplankton community, where rapid growth and species succession are the norm, the result of low levels of silver may be a shift in the dominant algal species toward silver-resistant forms, but not an overall decrease in primary productivity. Such a shift, seemingly of little import and difficult to detect after the fact, can be of great significance to the ecosystem if the species that have disappeared were important food items. In general, pollution-induced shifts in species dominance tend to favor forms that are undesirable as food to herbivores. As many predators are quite selective in their prey, the disappearance of preferred food items can lead to shifts in the trophic structure of the community, impacting the success and survival of members of higher trophic levels (Sanders and Abbe, 1989). Therefore, an apparently small impact at the lowest trophic level can lead to large, unpredicted changes to higher trophic levels and to the structure of an aquatic ecosystem.

In addition, metabolic pathways of silver accumulation were examined by Abbe and Sanders (1990) and Connell *et al.* (1991). They showed that oysters and grass shrimp accumulated  $\text{Ag}$  dissolved in water, but did not accumulate it from sediments or from algal food. Even though silver is readily taken up by phytoplankton and once incorporated remains tightly bound to cell membranes,  $\text{Ag}$  in or on the phytoplankton cell is passed through the consumer, such as oyster or shrimp, and is excreted in the feces. Therefore,  $\text{Ag}$  is available for uptake by organisms in the dissolved form (mainly  $\text{Ag}^+$ ) which is the most toxic form.

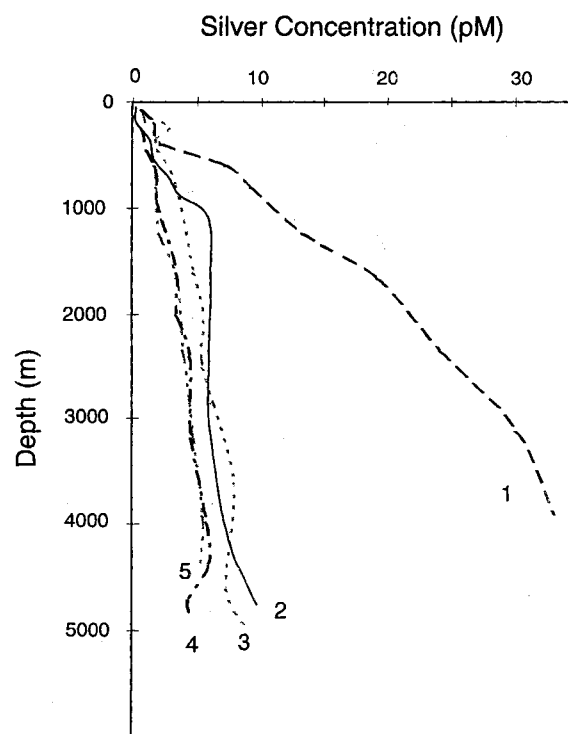
### General distribution and concentration of major environments

The cycle of silver is not well known. Even though, there have only been a few published measurements of silver in the environment (Martin *et al.*, 1983; Arimoto *et al.*, 1990; Sanudo-Willhelmy, 1992; Smith *et al.*, 1993; Flegal *et al.*, 1995) as shown at Table 1, these studies supply

**Table 1.** Dissolved silver concentration ( <0.45  $\mu\text{m}$  ) in major environments

Location	Concentration (pM)	Reference
Atlantic Ocean:		
Surface	$\leq 0.7$	Flegal <i>et al.</i> (1995)
Deep	3.8-5.9	
North Pacific Ocean:		
Surface	1.0	Martin <i>et al.</i> (1983)
Deep	22.9	
San Francisco Bay:		
Contaminated water	250	Smith <i>et al.</i> (1993)
Uncontaminated	3-6	
Southern California Bight:		
Coastal	3-11	Sanudo-Willhelmy (1992)
Bays	66-307	
New Zealand atmosphere:		
Aerosol	$2.4 \times 10^{-4}$	Arimoto <i>et al.</i> (1990)

very important information in terms of both natural biogeochemical processes and anthropogenic perturbations. Martin *et al.* (1983) and Flegal *et al.* (1995) indicated that the distributions of silver in the open ocean, particularly the Eastern Atlantic and North Pacific, showed a nutrient-type distribution similar to that of silicate. Ag was depleted in surface-waters, and a systematic enrichment of deep-waters was found along advective flow lines from the North Atlantic to North Pacific. In contrast to deep-waters, the gradient of relatively elevated silver concentration in surface waters of the North Atlantic Ocean than the South, may be due to either the aeolian transport of natural silver along with other trace metal such as aluminium associated with Saharan dust, or anthropogenic input from Europe (Fig. 1). Additionally, Smith and Flegal (1993) studied spatial gradients of silver concentrations and anthropogenic effects in the surface waters of San Francisco Bay, where silver is mainly affected by anthropogenic source. Moreover, they indicated that benthic fluxes of silver may be comparable to the anthropogenic inputs during periods of intense diagenic remobilization and, thus, they suggested the cycling of silver between contaminated sediments and overlying waters might continue in spite of further reductions of silver in wastewater discharges to the estuary. Silver concentrations measured along the Southern California Bight by Sanudo-Willhelmy and Flegal (1992) showed both nearshore and offshore gradients associated with anthropogenic inputs and natural scavenging processes in coastal



**Fig. 1.** The vertical distributions of silver concentration in Pacific and Atlantic Ocean (taken from Martin *et al.* (1983) and Flegal *et al.* (1995)). \*Numbers indicate the sampling location as 1: North Pacific (36°N), 2: South Atlantic (30°S), 3: South Atlantic (15°S), 4: North Atlantic (24°N), and 5: North Atlantic (34°N).

waters. The result of this study showed that 90% of silver from riverine and coastal sources might be removed during the transportation from nearshore to open ocean by physico-chemical process of silver. In contrast to the study of Smith and Flegal (1993), declines in silver recently appear related to decreased mass emission rates by wastewater treatment facilities, now more effective in reclamation efforts for areas such as California coastal waters (Stephenson and Leonard, 1994).

In this manner, factors such as anthropogenic input, water circulation pattern, and etc., influence silver's oceanic distribution and biogeochemical cycle.

### *Special process and character*

In order to better understand the biogeochemical cycle of silver, some specific processes and characteristics of silver were examined. First, no bioaccumulation of silver through food chain: Ag is available for uptake by organisms in dissolved form, but that Ag associated with food appears to be unavailable for incorporation by these organisms

due to the ability of Ag to adsorb rapidly to cell surfaces and remain tightly bound despite changes in pH or enzymatic activity, unlike other metals such as Cu and Zn (Abbe *et al.*, 1990; Connell *et al.*, 1991). Secondly, microbes can control silver mineralization at hydrothermal sites-The bacterial filaments near hydrothermal vents are selectively replaced by proussite ( $\text{Ag}_3\text{AsS}_3$ ), pearceite ( $\text{Ag}_{14.7-x}\text{Cu}_{1.3+x}\text{As}_2\text{S}_{11}$ ), chalcopyrite ( $\text{Cu FeS}_2$ ) and rarely by galena (PbS). Zierenberg *et al.* (1990) suggested that bacterially mediated processes selectively precipitate silver, arsenic, and copper and that biological processes may contribute to precious-metal enrichment in some sea-floor hydrothermal base-metal sulfide deposits. Partitioning and transport of Ag is important in estuaries (such as Jin-Hae Bay in Korea and Chesapeake Bay) where silver sorbs readily at low salinity to both phytoplankton and suspended sediments. As salinity increases, the degree of sorption decreases. Nearly 80% of silver sorbed to suspended sediments at low salinity will desorb at higher salinity, but desorption does not occur when silver is associated with phytoplankton. Thus, silver incorporation onto/into cellular material will increase the retention of silver within the estuary, reducing its rate of transport (Sanders *et al.*, 1987). As illustrated in Fig. 2, the tendency of silver to desorb from nonliving particulates reduces their importance as transport mechanism in the lower estuary although silver has a similar affinity at all salinities for both particle types (nonliving and

phytoplankton). Therefore, biological uptake and adsorption can be an important modifier in the cycle of silver through estuaries (Sanders *et al.*, 1987).

These specific processes and characteristics of silver, as discussed above, should be considered in terms of the specific regional cycle of silver because they mainly control transport and removal processes of silver.

### BIOGEOCHEMICAL FLUXES, SINKS, AND PATHWAY

Here, the major fluxes and reservoirs of the global silver cycle are quantified using available information. An estimation of the global Ag flux is illustrated in Fig. 3. Anthropogenic and geological silver input rate of mobilization are computed from annual river discharges to the oceans (Phillips, 1995), and the volume of the oceans is taken from R. L. Nace (1964). The regeneration fluxes of Ag from deep layer to surface layer and from sediments to deep layer were negligible because these values were relatively small (0.005 and 0.27 kg/yr, respectively). Currently, the ocean receives about 60% of its Ag through wet and dry atmospheric deposition. Although anthropogenic effect through atmospheric deposition have not yet been quantified, a significant fraction of the Ag in precipitation may be affected greatly by anthropogenic sources such as cloud seeding or aeolian transport. The evasion flux of Ag from the ocean, although it has not been

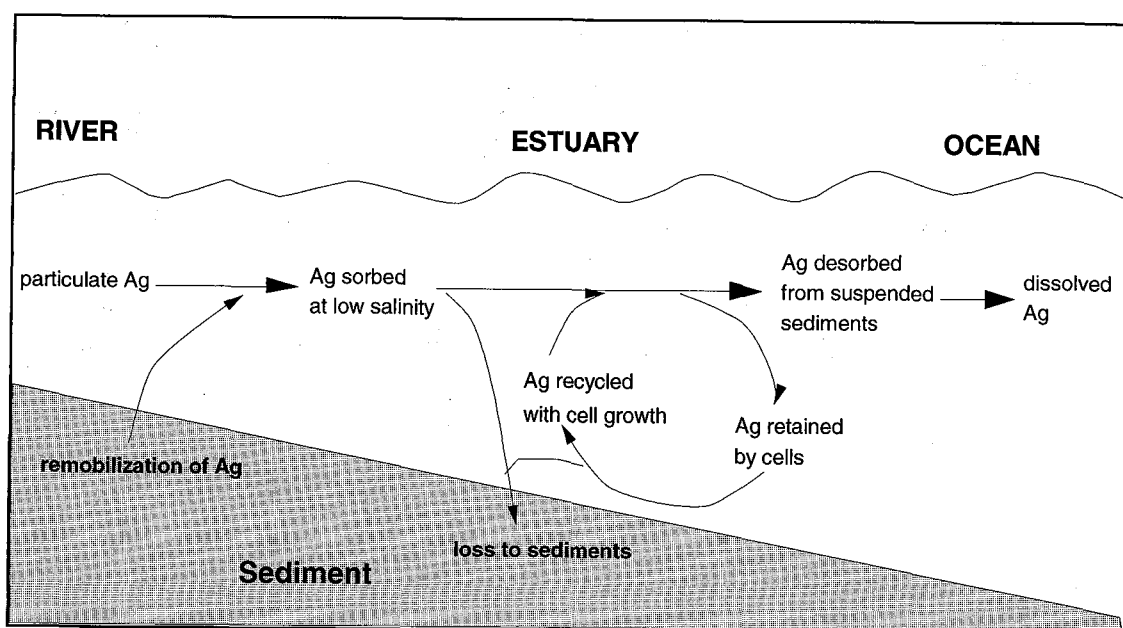


Fig. 2. Silver transport and cycle in estuaries (taken from Sanders and Abbe (1987)).

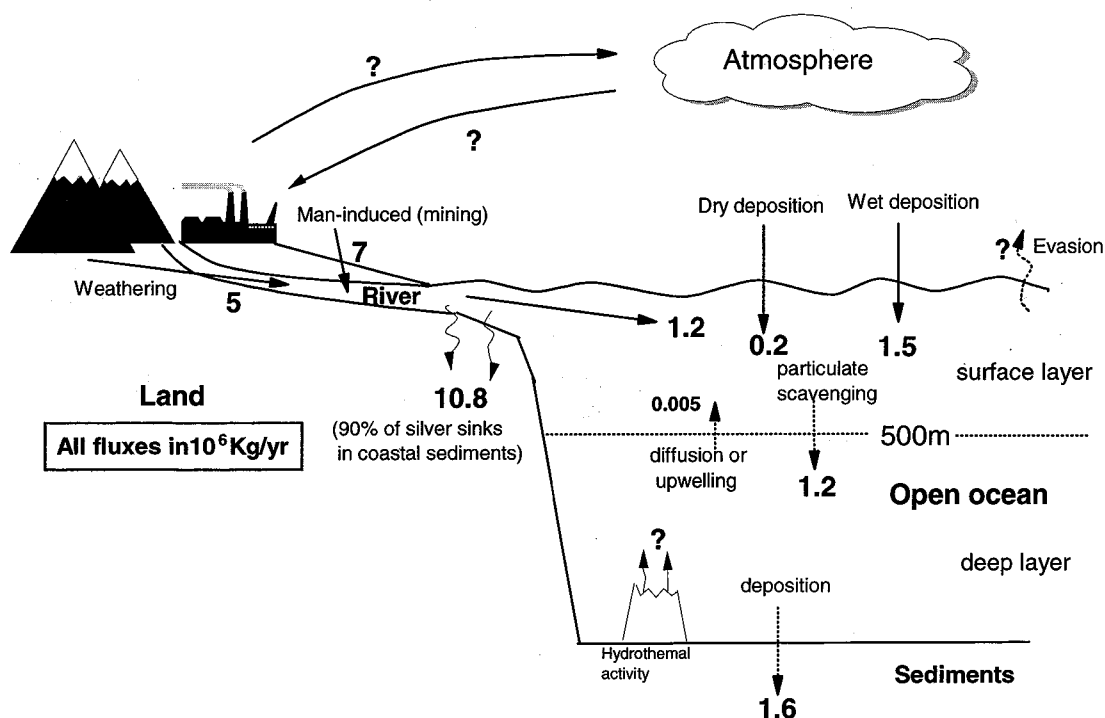


Fig. 3. The biogeochemical fluxes of Ag in the open ocean (total volume of the ocean= $1.37 \times 10^{21}$  L).

determined, may be approximately equal to atmospheric input, if atmospheric deposition fluxes are accurate, calculated by mass balance in this review. Particulate scavenging and removal to the deep ocean (below 500 m) is comparable to the estimated riverine Ag flux (Fig. 3). If evasion is less than atmospheric deposition, the removal of silver from surface oceans is probably underestimated. Most of anthropogenic silver is deposited in the estuary and coastal sediments. The residence time of silver in the ocean was calculated from these flux data to be 3 years for the surface layer and 1250 years for the deep layer in the ocean.

## CONCLUSIONS

The biogeochemical flux of silver, as shown in Fig. 3, suggests there is no steady state because of several possible reasons. These reasons are 1) not enough information for silver, 2) no studies of the effect of evasion, hydrothermal activity in silver cycle (source and sink), and 3) silver data taken from diverse papers (no consistency). However, this study supplies the valuable information that is the major source of Ag in the estuary and coastal ocean is riverine input (human activity and weathering process), but in the open ocean, atmospheric input

becomes the most important source of Ag through the biogeochemical cycle. Answers to the missing silver budget, the difference between input and output of silver in the ocean, are left for future studies. Also, in order to better understand the global silver cycle, we should preferentially study the evasion of Ag from the ocean, the atmospheric input and deposition of Ag on land, and the effect of hydrothermal activity. In addition, declines in silver appear related to decreased mass emission rates by waste water treatment facilities and more effective reclamation efforts (Stephenson and Leonard, 1994). In future studies, we should also consider these facts in terms of the flux of silver in the global cycle.

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