



Characterization and Fate of Produced Water in Shallow Waters

Final Technical Summary

Final Study Report



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Prepared under MMS Cooperative
Agreement Nos. 14-35-0001-30471 & 14-35-0001-30761
by
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Suggested Citation

The suggested citation for this report is:

Flegal, A.R. Characterization and Fate of Produced Water in Shallow Water. MMS OCS Study 99-0020. Coastal Research Center, Marine Science Institute, University of California, Santa Barbara, California. MMS Cooperative Agreement Numbers 14-35-0001-30471 and 14-35-0001-30761. 58 pages.

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FINAL TECHNICAL SUMMARY

STUDY TITLES:

Study I. Characterization and Fate of Produced Water Discharged in Shallow Waters

Study II. Characterization of Metal Constituent Patterns at a Produced Water Site

REPORT TITLE: Characterization and Fate of Produced Water Discharged in Shallow Waters

CONTRACT NUMBERS: Study I: 14-35-0001-30471; **Study II:** 14-35-0001-30761

SPONSORING OCS REGION: Pacific

APPLICABLE PLANNING AREA(S): Southern and Central California

FISCAL YEAR(S) OF PROJECT FUNDING:

Study I: 1989-90; 1990-91; 1991-92; 1992-93; 1993-94

Study II: 1994-95

COMPLETION DATE OF REPORT: February 1997

COSTS: FY 89-90 - \$75,000; FY 90-91 - \$75,000; FY 91-92 - \$75,000; FY 92-93 - \$37,500; FY 93-94 - \$37,500; FY 94-95 - \$30,000

CUMULATIVE PROJECT COSTS: STUDY I: \$300,000; **STUDY II:** \$30,000

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KEY WORDS: Santa Barbara Channel; produced water; hydrocarbons; sediment; trace elements

BACKGROUND: The trace element analyses conducted at UCSC for the MMS/SCEI program were unusually successful in several respects. These included (1) the publication of a great deal of original data along with interpretations of natural biogeochemical processes and anthropogenic perturbations that accounted for its temporal and spatial variations; (2) the

development of interdisciplinary collaborations with faculty and students at UCSB; and (3) the involvement of numerous undergraduate, graduate, and postdoctoral students at UCSC in

the program. Consequently, we are quite pleased with the opportunity that this unique program has provided us.

The MMS/SCEI research resulted in numerous scientific publications in primary peer-reviewed journals (see below). Many of these publications included the first accurate measurements of trace element concentrations in the Southern California Bight. These quantified both baseline levels and degrees of anthropogenic perturbations in those coastal waters, which were often much lower than commonly believed. As a result, there is now a benchmark for future studies of potential effects of inorganic contaminants in coastal waters of the Southern California Bight.

The proposed interactions between faculty and students at different campuses that were a basic premise of the MMS/SCEI program actually occurred. As indicated in the list of publications by our group, there one article and one chapter in a scientific text included a UCSC graduate student, a UCSC faculty, and several UCSB faculty. Based on those collaborations, the student (Khalil Abu-Saba), subsequently received an award as the outstanding student in the University of California Toxic Substances Research and Teaching Program.

Three other UCSC student that participated in the MMS/SCEI program received a major award in recognition of the quality of their research in that program. Sergio Sañudo-Wilhelmy was one of two students in the nation selected for a Doctoral Research Fellowship from the Organization of American States. Don Smith was selected for the Institute of Marine Resources Dissertation-Year Fellowship Award, and he subsequently received the Young Investigator Award for his presentation at the Trace Elements and Mineral Metabolism Conference. Ignacio Rivera-Duarte was selected as a University of California Presidential Scholar. Not surprisingly, the first two have already acquired tenure track positions at research universities (Sañudo-Wilhelmy at SUNY, Stony Brook and Smith at UCSC), and the third (Rivera-Duarte) is on the short list for several academic positions. Their graduate theses titles, as well as those of Ben Owen and Pewter Ritson, who have also obtained research positions based on the success of the research in the MMS/SCEI program, are listed below.

It should also be noted that several undergraduate students at UCSC participated in the MMS/SCEI program. For example, Rachel Ramirez continued the studies initiated by Peer Ritson, who traced the dispersion of produced water off Carpinteria by its isotopic composition. After she presented the results of those analyses at a meeting of the Geological Society of America last spring, she received a letter from the Editor of Environmental Geology requesting that she publish the study in that journal. Consequently, Rachel will have published the results of her research in the program before she receives her undergraduate degree.

STUDY PRODUCTS: Publications (listed chronologically; * indicates most important publications: reprints included as the Final Study Report):

Publications

- Flegal, A.R. and S.A. Sañudo-Wilhelmy. 1993. Comparable levels of trace metal contamination in two semi-enclosed embayments: San Diego Bay and South San Francisco Bay. *Environmental Science and Technology* **27**:1934-1936.
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FINAL STUDY REPORT

Silver contamination in aquatic environments, Flegal, A.R., I. Rivera-Duarte, and S.A. Sañudo-Wilhelmy. 1996.. *Reviews in Environmental Chemistry and Toxicology* 148: 139-162.

Silver Contamination in Aquatic Environments

A.R. Flegal*, I. Rivera-Duarte*, and S.A. Sañudo-Wilhelmy†

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I. Introduction

Within this decade, measurements have revealed low (picomolar, pM), but still relatively elevated, concentrations of dissolved ($<0.45 \mu\text{M}$) silver in some aquatic environments. This is due to the extremely low ($\leq 1 \text{ pM} \approx 0.1$ parts per trillion) concentrations of silver in remote oceanic surface waters and a small freshwater lake compared to the relatively high concentrations ($\geq 300 \text{ pM}$) of silver in some embayments, estuaries, and fresh waters. The relatively high silver concentrations commonly correspond with elevated concentrations of silver in sediments and aquatic organisms in those water bodies. These, in turn, often have received relatively large anthropogenic inputs of industrial silver.

The two-orders-of-magnitude range in silver concentrations in aquatic habitats has raised concerns that some aquatic organisms are being exposed to toxic concentrations of silver (Flegal and Sañudo-Wilhelmy 1993; Luoma et al. 1995). While those concerns are partially substantiated by a few preliminary studies that indicate silver is extremely toxic to some invertebrates (Berthet et al. 1992; Bryan 1984; Bryan and Langston 1992; Johansson et al. 1986; Luoma and Phillips 1988; Martin et al. 1984), the validity of many silver toxicity studies is suspect (Luoma et al. 1995). This is be-

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Reviews of Environmental Contamination and Toxicology, Vol. 148.

cause most bioassays have not measured dissolved silver concentrations with trace-metal-clean techniques, not measured or calculated the species of dissolved silver, and not used appropriate concentrations of silver.

Consequently, this review is limited to a brief summary of the levels of silver contamination in aquatic environments. It is further abbreviated to a review of a few recent measurements of dissolved silver concentrations that have utilized trace-metal-clean techniques since these are required for accurate measurements of picomolar (pM) concentrations of elements (e.g., silver) in ambient waters (Benoit 1994; Berman and Yeats 1985; Bru-land 1983; Flegal and Coale 1989; Patterson and Settle 1976; Windom et al. 1991). For silver, the peer reviewed literature is limited to the initial measurements of silver in oceanic waters of the Pacific, which were reported by Martin et al. (1983) and Murozumi (1981) in the previous decade, and a few measurements of silver in other aquatic environments, which have been reported within the present decade.

II. Background

The surprising dearth of historic information on silver contamination in the aquatic environment is presumably due to previous perceptions that it is negligible. Since it is a rare and precious metal, there have been no intentional discharges of large amounts of silver waste to aquatic environments, in contrast to some other contaminants. For example, large amounts of lead have been released into the environment for millennia as a waste product in the extraction of silver from galena by cupellation (Patterson 1971, 1978), while most industrial uses of silver (e.g., in jewelry and silverware, photography, coinage, electroplating, brazing, mirrors, dentistry, and batteries) have included extensive efforts to recover it from the effluent (Silver Institute 1994). Consequently, the largest amounts of silver released into the environment, on a global scale, appear to be from its emission as a trace constituent ($< 3 \mu\text{g/g}$) in the combustion of fossil fuels (e.g., coal, oil, and peat) and as a trace constituent of other metals (e.g., copper and zinc) during their refinement (Smith and Carson 1977).

However, there has been a pronounced increase in information on both silver contamination and toxicity in the aquatic environment within the past few years. This has resulted from the use of trace-metal-clean techniques to measure silver in natural and contaminated waters and from expanded efforts to resolve the toxicity of silver to aquatic organisms. This proliferation in information has also been catalyzed by three international conferences on the transport, fate, and effects of silver in the environment. The conferences, organized by Andren (1993, 1994, 1995), have been supported by a consortium of academic institutions, regulatory agencies, and industries. While data from those proceedings have not been cited in this report because they have not gone through a peer review process, the proceedings do contain some of the most recent and comprehensive information on silver contamination and toxicity in aquatic environments.

In addition to the numerous reports of silver toxicity to bacteria in medical and microbiology journals, there is a relatively recent review of silver toxicity to larger organisms (Luoma et al. 1995). This excellent review includes 53 references that focus on factors influencing the fate, bioavailability, and toxicity of silver in marine and estuarine environments. These references include several reports on bioassays of estuarine and marine species and life stages that are highly susceptible to silver toxicity (Calabrese et al. 1973, 1977; Dinnel et al. 1982; Eyster and Morse 1984; Lussier and Cardin 1985; Nelson et al. 1983; Sanders et al. 1990; Soyer 1963; Wilson and Freeberg 1980; Zoto and Robinson 1985), which report toxicities at silver concentrations ranging from <10 to 130 nM (<1 – 14 $\mu\text{g/L}$). Those reported toxic concentrations are then put in the following perspective by Luoma et al. (1995).

“These are low concentrations for the toxicity of any trace element. Nevertheless, widespread concentrations of Ag in the $\mu\text{g L}^{-1}$ range are rarely reported even in polluted natural water. The highest concentrations of dissolved Ag reported (using reliable chemical techniques) in open waters of San Francisco Bay are 0.025 $\mu\text{g L}^{-1}$ (Smith and Flegal 1993). Thus, a disparity exists between experimental toxicity and natural dissolved concentrations of Ag. This is balanced by the likelihood that toxicity tests, because of their simplistic designs, are less sensitive than natural systems. For example, the tests do not employ the most sensitive species from nature (and sensitive life processes are not fully known). Experimental toxicity tests rarely account for multiple pathways of exposure, nor can most designs consider the complex, often secondary interactions that influence toxicity in ecosystems (Luoma, in press). The toxicological uncertainties imposed by chemical disparities and biological insensitivities suggest that no conclusion can yet be drawn about Ag toxicity in polluted waters.”

In summary, orders-of-magnitude variations in total dissolved silver concentrations have heightened concerns about its potential toxicity to aquatic organisms. Those concerns have been exacerbated by the absence of recognized natural levels of silver in different aquatic environments. Therefore, this review includes both a summary of the range of silver concentrations reported for different water bodies and estimates of their natural dissolved silver concentrations. Together, these provide a perspective on the levels of silver contamination found in different aquatic environments.

III. Natural Levels of Silver in Oceanic Waters

The natural concentrations of silver in oceanic waters are illustrated in Fig. 1, which is based on vertical profiles of silver concentration gradients in remote regions of the Northeast Pacific (Martin et al. 1983) and the Northeast Atlantic (Flegal et al. 1995). Comparisons of the Pacific profiles of total dissolved (<0.45 - μm -diameter) silver and the Atlantic profiles of total (total dissolved and particulate) silver are based on measurements indicating that essentially all ($>80\%$) silver in oceanic waters is <0.45 μm (Martin et al. 1983). The systematic variations in those profiles are characteristic of the geochemical cycling of nutrient-type elements from the North Atlantic

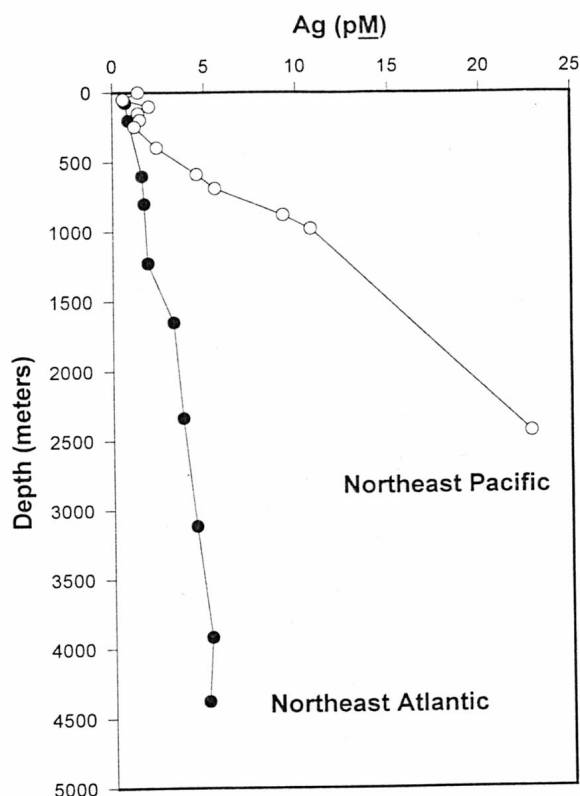


Fig. 1. Vertical profile concentrations of total (dissolved and particulate) silver (Ag) (pM) in the Northeast Atlantic (Flegal et al. 1995) and total dissolved (<0.45- μ m-diam.) silver in the Northeast Pacific (Martin et al. 1983). The profiles are comparable based on measurements (Martin et al. 1983) indicating that dissolved silver is the predominant ($\geq 80\%$) phase in oceanic waters.

to the North Pacific, which is described in detail elsewhere (Broecker and Peng 1982).

The nutrient-type cycling of silver in oceanic waters is evidenced by its positive covariance with silicate. This is illustrated by the following, highly significant ($p < 0.001$), simple linear regressions of silver [Ag] and silicate [H_4SiO_4] concentrations in the Atlantic (Flegal et al. 1995) and in the Pacific (Martin et al. 1983).

Equation 1: Ag in the Atlantic Ocean:

$$Ag \text{ (pM)} = 0.685 + 0.107 \times H_4SiO_4 \text{ (}\mu\text{M)} \quad (R = .916)$$

Equation 2: Ag in the Pacific Ocean:

$$Ag \text{ (pM)} = -0.691 + 0.111 \times H_4SiO_4 \text{ (}\mu\text{M)} \quad (R = .897)$$

Several factors contribute to differences in the intercepts of the two regressions. Some of the principal factors are these: the number of analyses

in both data sets is small; there is analytical imprecision in measurements of silver concentrations as they approach zero (< 1 pM) in oceanic surface waters; and there are physical, biological, chemical, and geological differences within and between oceanic water masses that may alter the ratio of silver and silicate. Therefore, additional measurements are required to distinguish between analytical and natural variations in $[\text{Ag}]:[\text{H}_4\text{SiO}_4]$ ratios in oceanic waters.

The utility of the natural covariance of silver and silicate in oceanic waters as a measure of contamination is two-fold. First, the systematic increase of silver and silicate concentrations in the oceans indicates that the distribution of silver in the open ocean is governed by natural biogeochemical processes that have not been markedly perturbed by anthropogenic processes. Second, anthropogenic perturbations of the silver cycle in coastal (neritic) waters may be quantified by deviations from those oceanic $[\text{Ag}]:[\text{H}_4\text{SiO}_4]$ correlations. Consequently, the natural concentrations of silver in oceanic surface waters are considered to range from ≤ 0.7 pM in the Atlantic to ≤ 2 pM in the Pacific, and natural concentrations of silver in subsurface waters are considered to be ≤ 10 pM in the Atlantic and ≤ 23 pM in the Pacific.

Based on the preceding characterizations, silver concentrations in remote surface waters of the North Atlantic may be relatively contaminated. Surface water concentrations in the two vertical profiles in the North Atlantic ranged from 0.25 to 0.70 pM, while surface water concentrations in the two vertical profiles in the South Atlantic were ≤ 0.24 pM (Flegal et al. 1995). The apparent hemispheric disparity in surface water concentrations suggests that ambient silver concentrations in some North Atlantic surface waters may be elevated two- or threefold above their natural concentrations by the atmospheric deposition of industrial silver aerosols advected by prevailing westerly and easterly winds. This hypothetical level of silver contamination is based on parallels with the documented level of lead contamination in the North Atlantic (Veron et al. 1994).

The apparent enrichment of silver in the North Atlantic surficial waters may also be attributed to aeolian inputs of natural silver in Saharan dust advected to the North Atlantic (Flegal et al. 1995). This hypothetical natural enrichment is consistent with complementary measurements of aluminum in those waters (Measures 1995). Since silver concentrations in oceanic surface waters of the North Atlantic are still less than natural silver concentrations in oceanic surface waters of the North Pacific, it may be conservatively concluded that natural concentrations of silver in oceanic surface waters are ≤ 2 pM.

IV. Silver Contamination in Neritic Waters

There are substantially elevated (≈ 10 -fold) concentrations of silver (up to 40 pM) in some coastal or neritic surface waters, relative to adjacent oceanic surface waters, from point-source discharges of industrial silver to

coastal waters (Bloom and Crecelius 1984, 1987; Sañudo-Wilhelmy and Flegal 1992). This perturbation is evidenced by excesses of silver relative to silicate within the Southern California Bight, using the preceding regression for their covariance (Eq. 2) in the adjacent North Pacific. The excesses occur near ocean outfalls off Tijuana, Mexico, and San Diego, California, U.S.A., which discharge relatively large amounts of silver to the Southern California Bight (≈ 25 tonnes/yr).

The initial measurements of elevated silver concentrations in some neritic waters are consistent with other reports of silver contamination in the coastal environment. These include reports of elevated concentrations of silver in marine sediments (e.g., Bloom and Crecelius 1987; Bothner et al. 1994; Bryan 1984, 1985; Bryan et al. 1985; Hornberger et al., in manuscript; Luoma and Bryan 1978, 1981; Luoma et al. 1990, 1995; O'Connor 1992; Rutherford and Church 1975) and marine invertebrates (e.g., Alexander and Young 1976; Berthet et al. 1992; Bryan and Hummerstone 1977; Bryan and Langston 1992; Calabrese et al. 1984; Cherry et al. 1983; Flegal 1980; Goldberg et al. 1983; Luoma and Bryan 1982; Luoma et al. 1995; Martin et al. 1984, 1988; O'Connor 1992; Thomson et al. 1984) collected near point-source discharges. In total, those parallel measurements of elevated silver concentrations near wastewater outfalls attest to the industrial origins of silver excesses in neritic waters.

V. Silver Contamination in Estuarine Waters

A preliminary diagnostic measure of silver contamination in estuarine waters may be derived from a plot of dissolved silver concentrations relative to salinity (Fig. 2). Excesses in silver relative to salinity within an estuarine gradient, which are characteristic of a nonconservative input of silver within the estuary, have been observed in California (Smith and Flegal 1993), Texas (Benoit et al. 1994), and New York (Sañudo-Wilhelmy, manuscript in preparation) estuaries. While those excesses may result from inputs (atmospheric, point-source, and non-point-source) of anthropogenic silver (Davis et al. 1992), they may also be due to the natural desorption of silver from estuarine sediments (Davis 1977). The latter process is indicated by the covariance of truly dissolved (< 10 kDa) silver and aluminum in the San Francisco Bay estuary (Sañudo-Wilhelmy et al. 1997), which is attributed to the diagenetic remobilization of silver from contaminated sediments.

The relationship between elevated concentrations of silver in surface waters and benthic sediments was first documented with analyses of the distribution of silver in two semienclosed embayments (Flegal and Sañudo-Wilhelmy 1993). Comparable levels of contamination were observed in surface waters of San Diego Bay and South San Francisco Bay, where the dissolved silver concentrations ranged up to $300 \mu\text{M}$. The elevated concentrations corresponded with elevated silver concentrations in benthic sediments in both embayments (Luoma and Phillips 1988). The sediments also

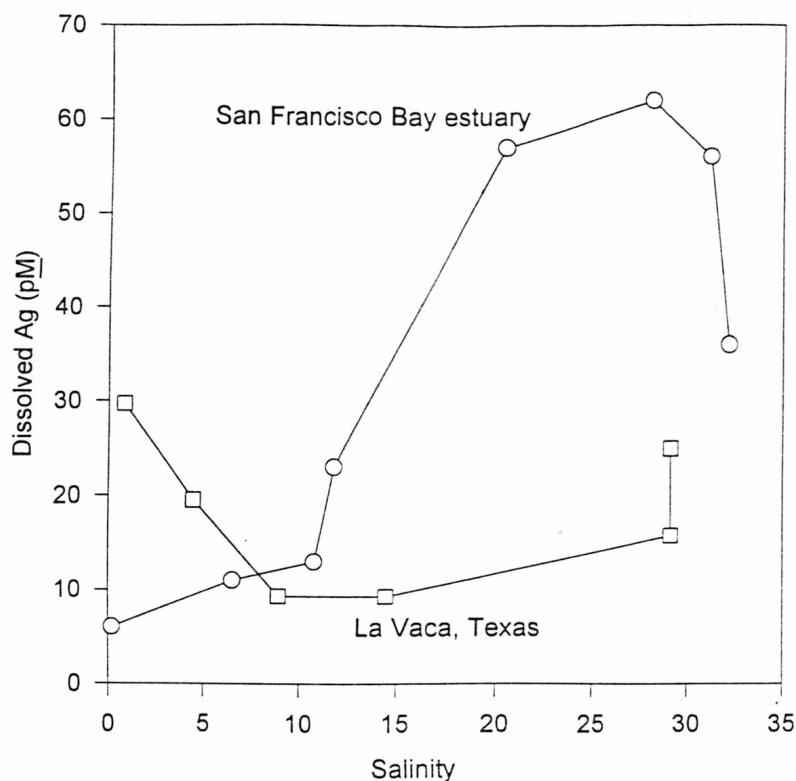


Fig. 2. Nonconservative distributions in total dissolved ($<0.45\text{-}\mu\text{m}$ -diam.) silver with salinity in two estuaries: San Francisco Bay, California (from Smith and Flegal 1993) and La Vaca, Texas (from Benoit et al. 1994). Silver concentrations above the mixing line defined by the freshwater and saltwater end members evidence an internal source of silver (e.g., San Francisco Bay), while concentrations below that line evidence an internal sink of silver (e.g., La Vaca) within an estuary.

appeared to be the primary source of silver contamination within San Diego Bay, because all point-source discharges to that bay were terminated three decades ago. This suggested that benthic fluxes of silver from previously contaminated sediments could be a persistent source of contamination in aquatic environments with limited hydraulic flushing (Flegal and Sañudo-Wilhelmy 1993).

The potential importance of inputs of silver from contaminated sediments to overlying waters within embayments was illustrated by mass-balance calculations of silver fluxes in the San Francisco Bay estuary (Smith and Flegal 1993). These data indicated that the benthic flux of silver from diagenetic remobilization from contaminated sediments in South San Francisco Bay was $\approx 1.7 \mu\text{g}/\text{m}^2 \text{ d}$ (235 kg/yr) and that the benthic flux of dissolved silver throughout the entire estuary was $\approx 1.2 \mu\text{g}/\text{m}^2 \text{ d}$ (540 kg/

yr). On a systemwide scale, the estimated benthic flux was an order of magnitude greater than the fluvial flux of silver to the estuary (12 kg/yr).

Those initial estimates were substantiated by an independent estimate of benthic fluxes in the estuary (Rivera-Duarte and Flegal 1996). The upper limits of the integrated net benthic flux (from both physical diffusion and biological irrigation of the sediment pore waters) of silver to South Bay were estimated to be 3–31 kg/yr. That highly qualified estimate indicates the net diffusive flux of silver could be up to 2.5 times the entire riverine input of dissolved silver to San Francisco Bay. The estimated diffusive benthic fluxes of silver were greatest at sites affected by wastewater outfalls with relatively elevated concentrations of silver in the effluent, where sediment concentrations are 15-fold greater than background concentrations in the estuary (Luoma et al. 1985). This validated the proposal that contaminated sediments could be a relatively important source to overlying waters in semienclosed embayments with limited hydraulic flushing.

Comparable concentrations of dissolved silver have since been reported for waters in six Texas estuaries (Benoit et al. 1994). The average dissolved ($<0.4 \mu\text{m}$) silver concentration in the Texas estuaries was commonly less than the relatively high detection limit of 1.0 ng/kg (9 pM) during the fall. However, the average ($\bar{x} \pm \text{SD}$) concentrations were markedly higher in the Sabine ($65 \pm 10 \text{ pM}$), Galveston ($72 \pm 9 \text{ pM}$), San Antonio ($37 \pm 6 \text{ pM}$), and Corpus Christi ($39 \pm 8 \text{ pM}$) estuaries during the summer. These analyses substantiate the proposal that silver concentrations in some estuarine waters may be one or two orders of magnitude above natural oceanic concentrations.

Additionally, the seasonal increases of silver concentrations in the Texas estuaries (Benoit et al. 1994) were consistent with seasonal increases of silver concentrations in San Francisco Bay (Smith and Flegal 1993). The highest concentrations (240 pM) there also occurred in the summer months. This was consistent with the proposal that the greatest elevations of silver concentrations in estuarine waters occur during periods of relatively low freshwater discharge (hydraulic flushing) and relatively high benthic activity, which maximize benthic inputs from diagenetic remobilization (Flegal and Sañudo-Wilhelmy 1993).

In summary, silver concentrations of several estuaries appear to be elevated by inputs from several anthropogenic sources. These include freshwater discharges, surface runoff, point-source discharges, and benthic fluxes from contaminated sediments. (Atmospheric inputs of industrial silver from fossil fuel combustion, smelting, and cloud seeding, which are relatively large on a global scale, are not considered to contribute to localized increases in silver concentrations in relatively small water bodies.) Although there is no currently recognized natural concentration of silver in estuaries, these comparisons indicate that silver concentrations in some estuaries are two orders of magnitude above natural concentrations. These are tentatively estimated to be $\leq 5 \text{ pM}$.

However, natural concentrations of silver in estuaries are expected to vary markedly with other parameters that influence its speciation. This is illustrated in Fig. 3, which shows pronounced differences in the percentage of total dissolved ($<0.45 \mu\text{m}$) silver in colloidal fractions ($>10 \text{ kDa}$) in the Hudson River and San Francisco Bay estuaries. The differences are attributed to higher concentrations of colloidal material in the Hudson, which increase its complexing capacity for silver.

VI. Silver Contamination in Fresh Waters

Benoit (1994) conducted the first extensive study, using trace-metal-clean techniques, of dissolved silver in freshwater systems. His analyses of dissolved ($<0.45 \mu\text{m}$) silver in the Quinnipiac River (Connecticut, USA) ranged from $\leq 9 \text{ pM}$ to $2.8 \mu\text{M}$ ($2,800,000 \text{ pM}$). The total (unfiltered) silver concentrations in that river ranged from $\leq 9 \text{ pM}$ to $4.6 \mu\text{M}$ ($4,600,000 \text{ pM}$).

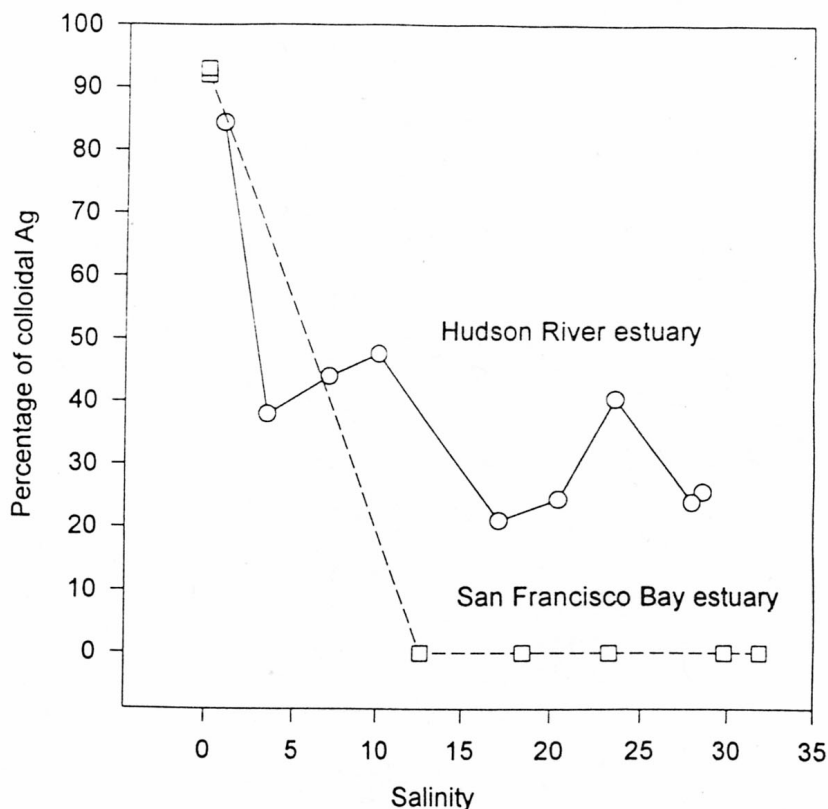


Fig. 3. Variations of total dissolved ($<0.45\text{-}\mu\text{m}$ -diam.) silver in colloidal phases ($>10 \text{ kDa}$) with salinity in the Hudson River (Sañudo-Wilhelmy, unpublished data) and San Francisco Bay estuaries (Sañudo-Wilhelmy et al. 1997). Both sets of data were acquired with the same sampling system and analytical techniques.

These extremely wide ranges in both dissolved and total silver concentrations were attributed to differences in silver concentrations between relatively pristine and highly contaminated fresh waters.

Representative total dissolved silver concentrations in those and other riverine systems are plotted in Fig. 4. The lower range in those concentrations suggests that natural concentrations of silver in freshwater systems are ≤ 10 pM. Based on that proposed baseline concentration, silver concentrations in some highly contaminated rivers appear to be orders of magnitude greater than natural concentrations.

The proposed natural concentration of silver in freshwater systems (≤ 10 pM) is supported by preliminary measurements of total dissolved silver concentrations in a small, freshwater impoundment, Davis Creek, in California (Sañudo-Wilhelmy and Flegal, unpublished data). The vertical profile of silver concentrations ($< 1-3$ pM) in that shallow reservoir brackets the concentrations of silver (≈ 1 pM) at corresponding depths in the Atlantic (Fig. 5). This suggests that natural silver concentrations in freshwater systems are comparable to those in oceanic surface waters, as is true for lead (Erel and Patterson 1994; Flegal and Coale 1989; Flegal et al. 1989).

As in estuaries, natural differences in dissolved silver concentrations between rivers may be partially due to differences in their complexation

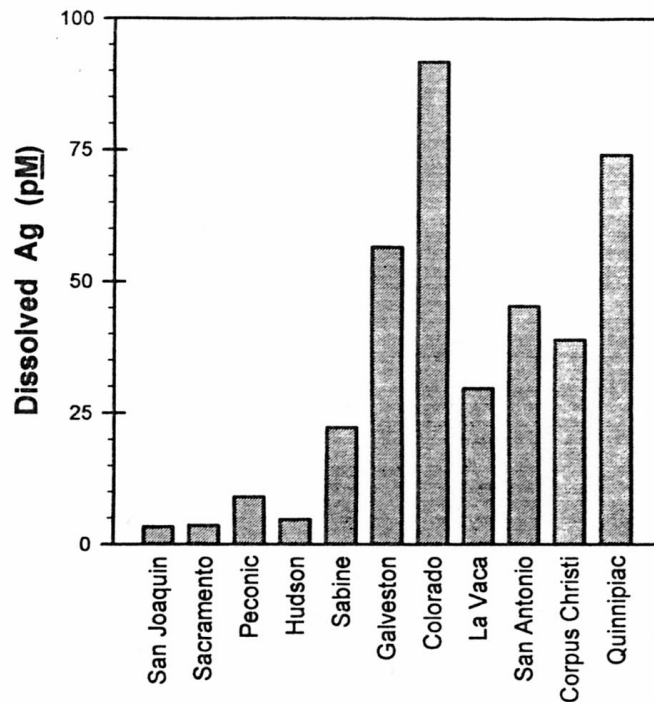


Fig. 4. Representative total dissolved (< 0.45 - μm -diam.) silver concentrations (pM) in 11 U.S. rivers (from Benoit 1994; 1995; Benoit et al. 1994; Sañudo-Wilhelmy et al., unpublished data; Smith and Flegal 1993).

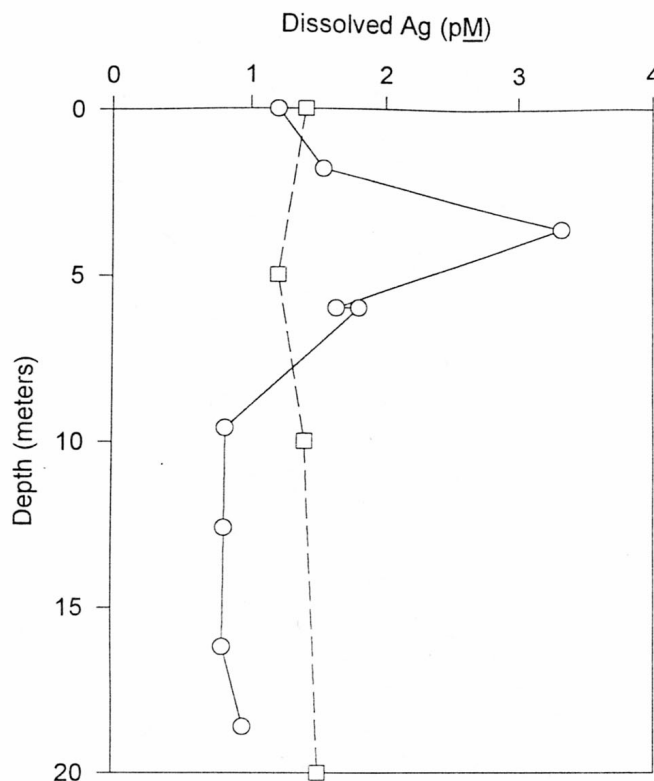


Fig. 5. Total dissolved ($<0.45\text{-}\mu\text{m}$ -diam.) silver concentrations (pM) in surface waters of the Northeast Atlantic (*squares*) and a small freshwater impoundment, Davis Creek (*circles*), in California. The ocean data are from Flegal et al. (1995); the freshwater data are from unpublished measurements using the same techniques (Sañudo-Wilhelmy and Flegal, unpublished data).

capacity (Benoit 1994; Cowan et al. 1985; Davis 1977; Engel et al. 1981; Luoma et al. 1995; Sañudo-Wilhelmy et al. 1997); this was indicated by the relatively high percentage ($>70\%$) of dissolved ($<0.45\ \mu\text{m}$) silver in colloidal phases (10 kDa to $0.2\ \mu\text{m}$) of rivers within the United States (Sañudo-Wilhelmy et al. 1996; Sañudo-Wilhelmy, unpublished data) and Japan (Tanizaki et al. 1992). That colloidal partitioning is shown in Fig. 6.

VII. Silver Contamination in Sediment Pore Waters

While there are very few reports of dissolved ($<0.45\ \mu\text{m}$) silver concentrations in sediment pore waters (Lyons and Fitzgerald 1983; Rivera-Duarte and Flegal 1996), these do provide unique insights on the biogeochemical cycling of silver in aquatic environments. The reports indicate (i) the importance of chloro-complexation on the solubilization of silver in natural sediment pore waters and (ii) the association of silver with anthropogenic

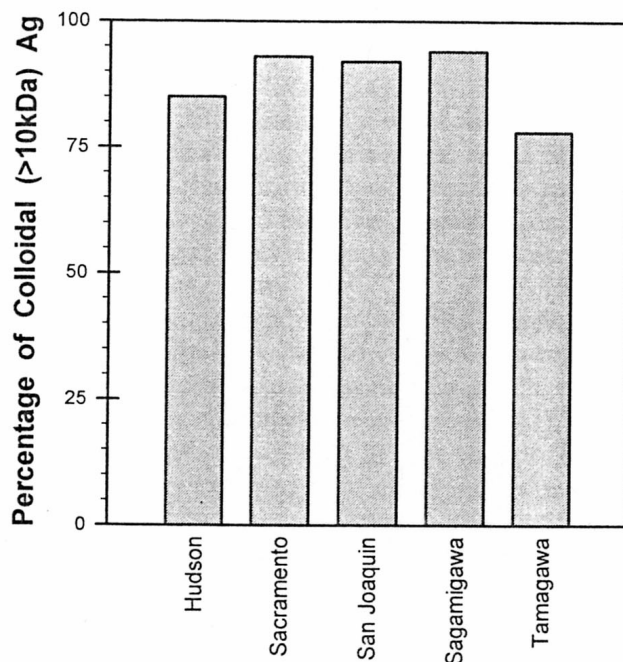


Fig. 6. Percentage of total dissolved ($<0.45\text{-}\mu\text{m}$ -diam.) silver in colloidal phases ($>10\text{ kDa}$) in the Hudson, Sacramento, and San Joaquin rivers in the United States (Sañudo-Wilhelmy, unpublished data) and in the Sagami-gawa and Tamagawa rivers in Japan (Tanizaki et al. 1992).

sources. This is depicted by the vertical concentration profiles of dissolved silver in Long Island Sound, San Francisco Bay, Tomales Bay, and Drakes Estero (Fig. 7).

Although relatively high concentrations (4500 pM) were found in pore waters near a large wastewater outfall (Mayfield Slough) in San Francisco Bay, the highest dissolved silver concentrations (up to 9000 pM) of silver were observed in pore waters from surficial sediment in relatively pristine sites (Mystic River Estuary in Long Island Sound and Tomales Bay). In contrast, pore water concentrations in Brandford tidal flat (Long Island Sound) were $<2000\text{ pM}$, and most of the sites sampled within San Francisco Bay and Drakes Estero had concentrations of $<300\text{ pM}$. The highest concentrations are tentatively attributed to chloro-complexation of silver in those pore waters and the reduction of iron and manganese oxides rather than to anthropogenic contamination (Lyons and Fitzgerald 1983; Rivera-Duarte and Flegal 1996). (This attribution is based on thermodynamic calculations on the speciation of silver in aquatic environments, which are briefly summarized in the following section.) Consequently, it is relatively difficult to estimate a natural concentration of silver in sediment pore waters or to quantify levels of silver contamination in those waters.

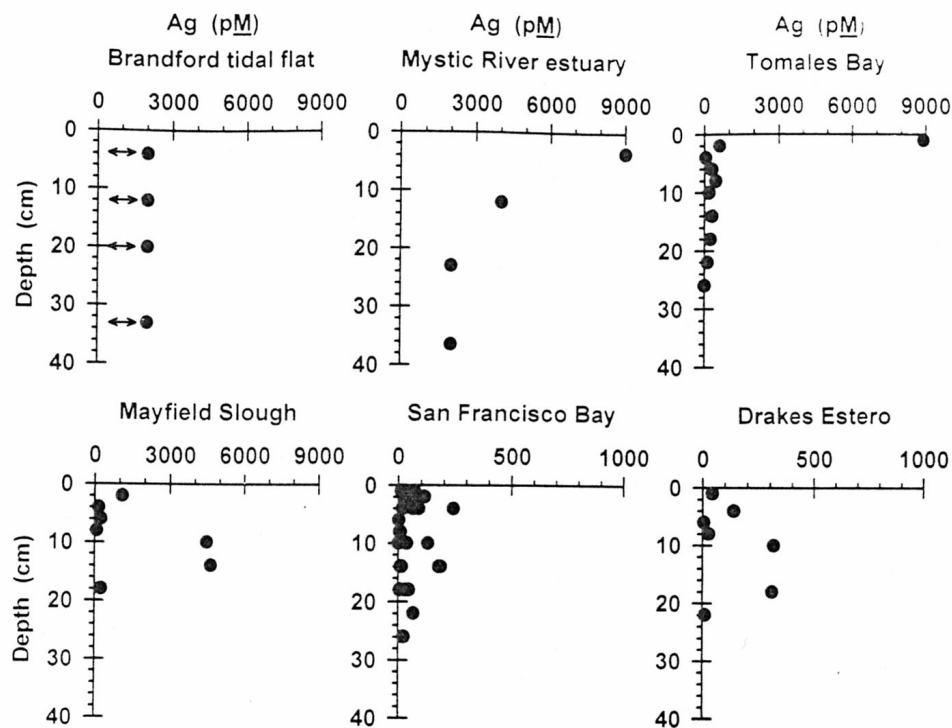


Fig. 7. Vertical profile concentrations (pM) of total dissolved (<0.45- μm -diam.) silver in sediment pore waters from the Brandford tidal flat and Mystic River estuary in Long Island Sound on the east coast of the United States (Lyons and Fitzgerald 1983) and from San Francisco Bay, Drakes Estero, and Tomales Bay on the west coast of the United States (Rivera-Duarte and Flegal 1996). Since silver concentrations in Mayfield Slough, which is a highly contaminated site in the southern end of San Francisco Bay, are markedly higher than those at other sites within the estuary, those concentrations are plotted separately.

VIII. Speciation of Dissolved Silver in Aquatic Environments

The chemical speciation of silver and the processes affecting its adsorption to particles strongly influence its bioavailability in natural waters. Thermodynamic calculations (see following) indicate that, in the absence of sulfides (H_2S and HS^-), silver is mainly present as the monovalent silver ion (Ag^+) in fresh water (Jenne et al. 1978; Whitlow and Rice 1985), but silver is predominantly a neutral silver bisulfide complex (AgHS^0) in fresh water with sulfide levels as low as 1×10^{-5} mg/L. In contrast, those thermodynamic calculations indicate that the neutral silver-chloro complex (AgCl^0) is the principal species in saline water (Cowan et al. 1985; Jenne et al. 1978). This theoretically reduces the relative adsorption of silver to particles in estuarine and marine environments (Davis 1977; Luoma et al. 1995), which is consistent with the report that silver desorption from inorganic particles increases with salinity in an estuarine system (Sanders and Abbe

1987; Sañudo-Wilhelmy et al. 1996). The chloro-complexation also influences the bioaccumulation of silver in those environments because of the relatively high bioavailability of AgCl° (Cowan et al. 1985; Engel et al. 1981; Luoma et al. 1995).

The preceding summary is based on a small number of detailed thermodynamic studies of the chemical speciation of silver in natural aquatic environments, which were pioneered by Jenne et al. (1978). They modeled (WATEQ2) the equilibrium distribution of silver among numerous inorganic solute complexes and solid phases and the changes expected during a transit through an estuarine system. Their model incorporated data from the San Francisco Bay estuary, from the fresh (salinity ≤ 0.13) to the marine (salinity = 33.5) water end-members (Figs. 8 and 9).

As a first approximation, they assumed that organic complexation of silver is not important in natural aquatic environments. Their assumption was tentatively corroborated for saline waters by Cowan et al. (1985), whose calculations with MINTEQ indicated that organically complexed silver represents $< 1\%$ of the total dissolved silver in marine waters, and by Miller and Bruland (1995), whose measurements indicated the absence of measurable organic complexation of silver in samples from both the Weddell Sea and South San Francisco Bay. However, subsequent studies on size-speciation of trace elements within San Francisco Bay indicate the association of silver in fresh water with colloidal material (10 kDa to $0.2 \mu\text{m}$), which could be either organic or clay-size minerals (Sañudo-Wilhelmy et al. 1997; Tanizaki et al. 1992), as illustrated in Fig. 6.

The effect of chloride complexation of silver in marine waters is depicted in Fig. 8a (Jenne et al. 1978). As the salinity increases from fresh water (0.13) to marine waters (33.5), the activity (A ; i.e., reactivity) of uncomplexed silver (A_{Ag^+}) decreases sharply (from 4×10^{-11} to 3×10^{-15}) while the activities of all the chloride complexes, except AgCl° , increase. For marine waters, $A_{\text{AgCl}_2^-} > A_{\text{AgCl}_3^{2-}} > A_{\text{AgCl}_4^{3-}} > A_{\text{AgCl}^\circ}$. The preponderance of silver chloride complexes was also indicated by independent calculations (MINEQL) for pore waters in suboxic coastal sediments (Lyons and Fitzgerald 1983).

The thermodynamic models indicate that bromide and iodide complexes account for only a minor portion of the dissolved silver at the concentrations of bromide, iodide, and chloride in marine and fresh waters (Fig. 8b). Even when bromide (and iodide) concentrations are considered 10-fold larger (Fig. 8c), the most abundant bromide complex (AgBr_2^-) in the marine end member is only 1.7% of the activity of the most abundant chloride complex (AgCl_2^-), and it is equivalent to the activity of the least abundant chloride complex (AgCl°). Iodide (Fig. 8c) and fluoride (8d) complexes are even less important in those environments.

The complexation with sulfide seems to be the most important in both fresh water and marine waters (Cowan et al. 1985; Jenne et al. 1978). Assuming concentrations of 1×10^{-5} mg/L for H_2S in the San Francisco

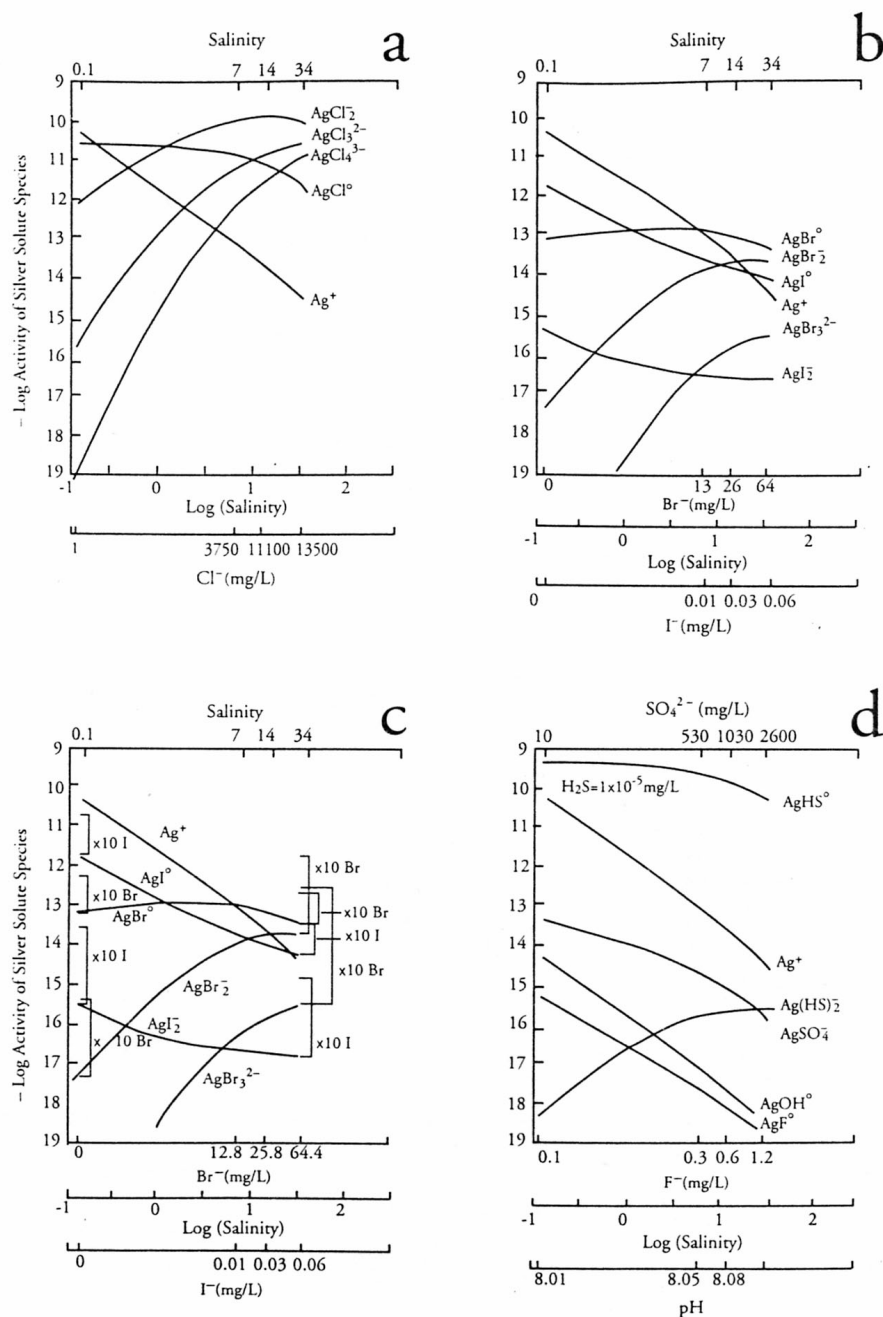


Fig. 8. The effect of halide complexes on the inorganic silver speciation in aquatic systems, with salinities ranging from fresh water (0.1) to sea water (34) (based on analyses of Jenne et al. 1978). See the text for discussion of variations in Cl^- (a), Br^- (b,c), I^- (b,c), and F^- (d).

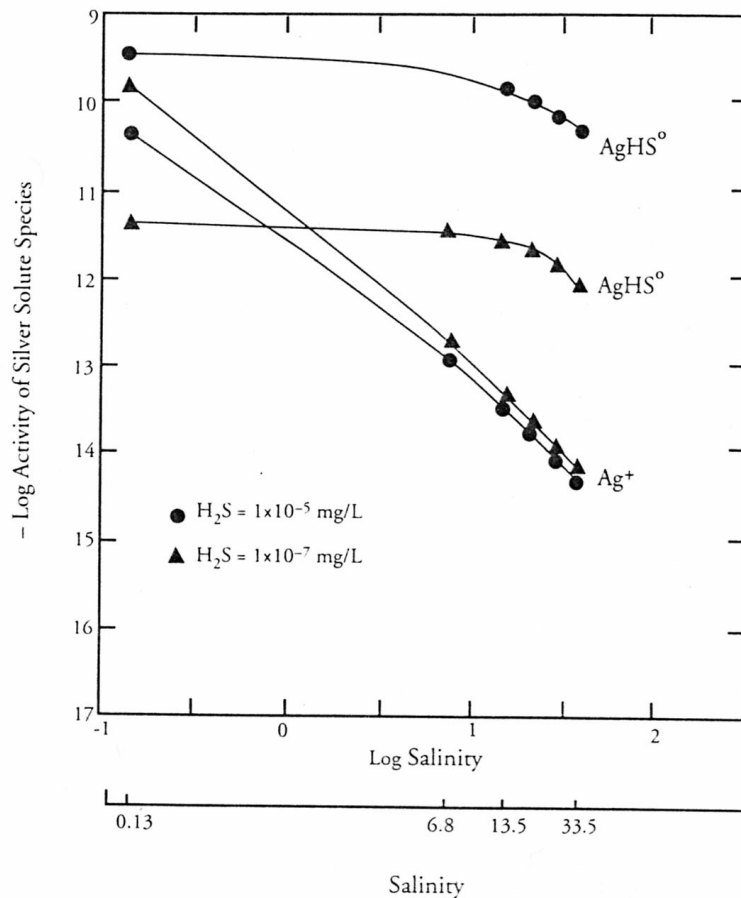


Fig. 9. The effect of sulfide complexes on inorganic silver speciation in aquatic systems, with salinities ranging from fresh water (0.1) to sea water (34) (based on analyses of Jenne et al. 1978).

Bay estuary, Jenne et al. (1978) calculated that the silver bisulfide ion pair (AgHS°) is the dominant species in the transition from the Sacramento River to the Pacific Ocean (Fig. 8d). Cowan et al. (1985) made the same conclusion for marine waters with S^{2-} concentrations above 1×10^{-5} mg/L. The silver bisulfide ion pair was also estimated to be the most important species in pore water from anoxic coastal sediment pore waters (Lyons and Fitzgerald 1983). A decrease in H_2S concentration from 1×10^{-5} to 1×10^{-7} mg/L produces a decrease of A_{AgHS° by 50-fold for marine and 100-fold for freshwater end members (Fig. 9). However, this decrease is not justified by recent measurements that indicate a concentration range of H_2S from $<3 \times 10^{-5}$ to 5×10^{-3} mg/L in waters of San Francisco Bay (Kuwabara and Luther 1993).

The speciation of dissolved silver in natural waters has been calculated with numerous thermodynamic models, as previously discussed. However, those models need to be substantiated with direct measurements. Additionally, more complex models including organic speciation have to be developed.

IX. Partition Coefficient of Silver in Natural Aquatic Environments

As previously indicated, there have been only a few measurements of total dissolved ($<0.45 \mu\text{m}$) silver concentrations in any natural waters. Since total dissolved concentrations are operationally defined by a filter size, they include silver in small particulates, colloids, complexes, ion pairs, and free species. Consequently, analyses of total dissolved silver concentration measurements are subject both to misinterpretation and overinterpretation.

With that qualification, the ratio of total dissolved silver to particulate silver in aqueous systems provides some useful diagnostic information (Benoit 1995; Smith and Flegal 1993). The distribution is termed the partition coefficient (K_d), which is defined by the following equation:

$$K_d = \frac{[\text{Ag}]_{\text{particulate}}}{[\text{Ag}]_{\text{dissolved}}}$$

As the ratio often varies by orders of magnitude, it is commonly reported as a logarithm ($\log K_d$). This is illustrated by the initial data for San Francisco Bay, where the partitioning of silver ($\log K_d$) ranged from 4.3 to 6.1 within the water column (Smith and Flegal 1993) and from 2.1 to 5.8 within sediment pore waters (Rivera-Duarte and Flegal 1996). The latter contrasted with the lower ratios of silver ($\log K_d$) in sediment pore waters of adjacent, relatively pristine, estuaries (Tomales Bay and Drakes Estero), which ranged from 1.2 to 4.2 (Rivera-Duarte and Flegal 1996). The differences are partially attributed to the larger grain size of the sediments and complexation of silver by chloride in these pristine embayments (Rivera-Duarte and Flegal 1996). This is consistent with previously discussed variations in pore water concentrations.

The variations in $\log K_d$ and the corresponding concentration gradients of silver in sediment pore waters indicate that contaminated sediments are a source of silver to overlying waters. The gradients attest to the remobilization of silver from particulate to dissolved phases during early sediment diagenesis. Dissolved silver within sediment pore waters may then be transported to the water column by both diffusive and advective processes. This movement would be accelerated by seasonal increases in benthic activity, which often correspond with summer periods of reduced hydraulic flushing in many aquatic environments.

The partitioning of silver is influenced by numerous natural and anthropogenic factors (Benoit 1995; Sañudo-Wilhelmy et al. 1997). By definition, the K_d of silver is inversely correlated to the total suspended sediment (TSS) load. It has also been proposed that relatively large amounts of colloids

substantially lower the K_d of silver in estuarine waters, due to the particle concentration effect (Benoit 1995). While preliminary measurements (Sañudo-Wilhelmy et al. 1997) indicate that most ($\approx 84\%$) of the total dissolved silver in fresh waters discharging into the estuary is in a colloidal phase (10 kDa to $0.2 \mu\text{m}$), there is essentially none ($< 1\%$) of the total dissolved silver in a colloidal phase within San Francisco Bay (see Fig. 6). Consequently, colloids may contribute to the particle concentration effect on the K_d of silver in some fresh waters or other estuarine systems, but they do not appear to contribute to that effect in San Francisco Bay or marine waters.

X. Scavenging and Remobilization

The partitioning of silver is primarily controlled by its speciation (Cowan et al. 1985; Jenne and Luoma 1977). Davis (1977) reported a striking effect of chloride on the adsorption of silver onto freshly made iron oxides (goethite). He observed that 80%–90% of the dissolved silver was adsorbed in 15 hr in the presence of traces of chloride (10^{-3} M), but $< 5\%$ was adsorbed in 15 hr when the salinity was increased to ≈ 5 ($9.4 \times 10^{-2} \text{ M Cl}^-$). These results are concordant with those of Sanders and Abbe (1987), who observed an increase in the desorption of silver from inorganic particles as salinity increased in an estuarine system, and with measurements of high pore water concentrations of dissolved ($< 0.45 \mu\text{m}$) silver in relatively pristine coastal sediments (Lyons and Fitzgerald 1983; Rivera-Duarte and Flegal 1996). In contrast, Luoma et al. (1995) reported that natural oxidized estuarine sediment adsorbed $> 99\%$ of the silver from solution in 24 hr at salinity of 20.

* Luoma et al. (1995) also found that the rate of adsorption was reduced when sediments were stripped of their natural reactive coatings (e.g., complex aggregates of iron oxides, manganese oxides, and organic material) and that 55%–85% of the adsorbed silver was extractable with a weak acid leach (0.5 N HCl), which solubilizes amorphous iron and manganese oxides. This is consistent with other reports of the affinity of silver to particulate manganese in fresh water (Anderson et al. 1973; Borovec 1993; Chao and Anderson 1974), and estuarine (Rivera-Duarte and Flegal 1996) sediments. Therefore, the scavenging and remobilization of silver from sediments appears to be strongly correlated with the formation and dissolution of ferromanganese (oxy)hydroxides in oxic and anoxic environments.

These and other factors influencing the bioavailability of silver in aquatic (marine and estuarine) environments are discussed by Luoma et al. (1995). As previously indicated, that review primarily addresses analyses of particulate silver concentrations in sediments and organisms, because there are relatively few measurements of silver in dissolved phases. Consequently, that review corroborates the hypothesis of this review, which is that future studies of silver bioavailability and toxicity need to incorporate trace-metal-clean techniques measuring dissolved silver concentrations and species.

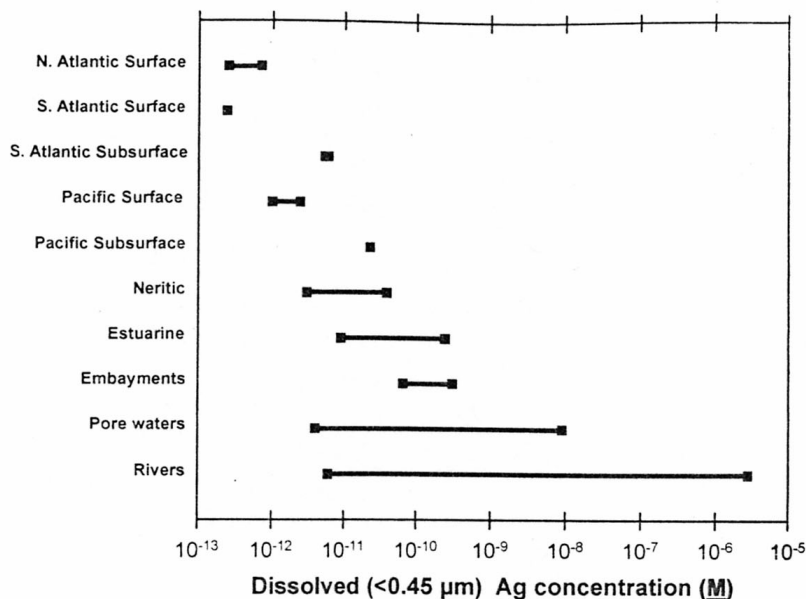


Fig. 10. Ranges of total dissolved (<0.45- μ m-diam.) silver concentrations (M) in aquatic environments (based on numerous references cited in the text).

Summary

Recent measurements have revealed a surprising range in dissolved silver concentrations in aquatic environments (Fig. 10). Concentrations in some neritic, estuarine, and fresh waters are one to seven orders of magnitude above natural levels in oceanic surface waters. These levels of contamination are relatively higher than those of any other element in aquatic environments.

While the bioavailability and toxicity of silver in those contaminated aquatic environments may be relatively high, they depend on its speciation. Speciation has, to date, only been calculated with simple thermodynamic models, and there have only been a few measurements of dissolved silver species in natural waters. Furthermore, most bioassays of silver toxicity with aquatic organisms have not utilized trace-metal-clean techniques to accurately measure the concentration of dissolved silver, much less its speciation. Therefore, the potentially adverse effects of anthropogenically elevated silver concentrations in some contaminated aquatic systems are still speculative.

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Manuscript received May 24, 1996; accepted June 1, 1996.

Trace element distributions in coastal waters along the US–Mexican boundary: relative contributions of natural processes vs. anthropogenic inputs

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(Received 30 May 1990; revision accepted 22 November 1990)

ABSTRACT

Sañudo Wilhelmy, S.A. and Flegal, A.R., 1991. Trace element distributions in coastal waters along the US–Mexican boundary: relative contributions of natural processes vs. anthropogenic inputs. *Mar. Chem.*, 33: 371–392.

Trace element concentrations (Pb, Cd, Mn, Fe, and Zn) were measured along four surface water transects across the continental shelf off Baja California, to evaluate the magnitude of heavy metal contamination in the coastal waters along the US–Mexican boundary. These initial measurements of trace elements in Mexican neritic waters revealed offshore concentration gradients, with the highest levels in coastal waters with high salinities and nutrient concentrations. There were also longshore gradients, with lower concentrations in the southern locations. Although the relative enrichment of metals detected at nearshore stations along the US–Mexican border appeared to correspond to wastewater discharges in that area, these trace metal enhancements were found to be primarily associated with physical oceanographic processes (upwelling and advection), rather than anthropogenic inputs. This was demonstrated both by metal–nutrient correlations and multivariate statistical analyses. Mass balance calculations also indicated that about 1% of Cd, 9% of Zn, and 29% of Pb were from urban discharges within the area.

INTRODUCTION

The coastal waters adjacent to the US–Mexican border, in the southern limit of the Southern California Bight, receive large inputs of contaminants from urban areas in the USA (Los Angeles and San Diego, California) and Mexico (Tijuana and Ensenada, Baja California). The average flow of municipal discharges to the Southern California Bight has increased, over the past decade, to approximately 10^9 l day⁻¹ (Schafer, 1984). The large amount of metals in these discharges has increased concern about coastal water quality along the US–Mexican border (Nishikawa-Kinomura et al., 1988; Sun, 1989).

The northern and central parts of the Southern California Bight are some of the best-studied coastal regions of the USA (Carlucci et al., 1986). Although there have been several reports on trace metal concentrations in coastal waters off California (Martin et al., 1976; Patterson et al., 1976; Bruland and Franks, 1978, 1979; Zirino et al., 1978; Schaule and Patterson, 1981; Lee, 1982, 1983; Flegal and Stukas, 1987; Johnson et al., 1988), there have been essentially no reports on trace metal concentrations in neritic waters off Baja California, Mexico. Consequently, metal concentrations are required to establish baseline levels and to identify areas affected by anthropogenic discharges.

As it is difficult to identify anthropogenic metal inputs on the basis of coastal water concentrations alone (Balls, 1988, 1989), alternative indirect approaches (e.g. mass balance calculations) are needed to quantify the extent of coastal contamination. These may reveal anthropogenic perturbations which alter the geochemical covariation of the elements. For example, Martin et al. (1976) showed that deviations in metal–nutrient relationships (e.g. Cd vs. PO_4) might be caused by anthropogenic inputs. Therefore, resolution of the effects of anthropogenic inputs in coastal waters requires both accurate and precise metal concentration measurements and rigorous statistical analyses.

This preliminary study was designed to evaluate the magnitude of the heavy metal (Pb, Cd, Fe, Zn, and Mn) inputs from urban discharges to coastal waters along the US–Mexican border. In this work, we used several indirect approaches, based on deviations in the geochemical covariation of trace elements, to identify whether anthropogenic sources influenced trace element concentrations in coastal waters off Baja California. These included comparisons of metal–nutrient relationships off coastal Baja California with those for open ocean areas, mass balance calculations, and multivariate statistical analyses (cluster, multidimensional scaling, and factor analysis).

Description of the study area

The Baja California coast is located in the southern limit of the Southern California Bight (Fig. 1). To the north lies the Los Angeles metropolitan area; to the east, the cities of San Diego, Tijuana, and Ensenada; to the south, the sparsely populated area of northern Baja California and to the west the California Current of the Pacific Ocean. This geographic region is located in an oceanographic regime which might affect trace metal distributions. The California Current System (CCS), which has a large shoreward component just south of the international border, brings cool, low-salinity water into the region (Reid, 1963; Bernstein et al., 1977). In this area, the flow of the current divides: part flows northward as the nearshore limb of the Southern California Eddy or the Inshore Countercurrent, and part continues to flow southward along the Baja California coast. The seasonal reversal of this equator-

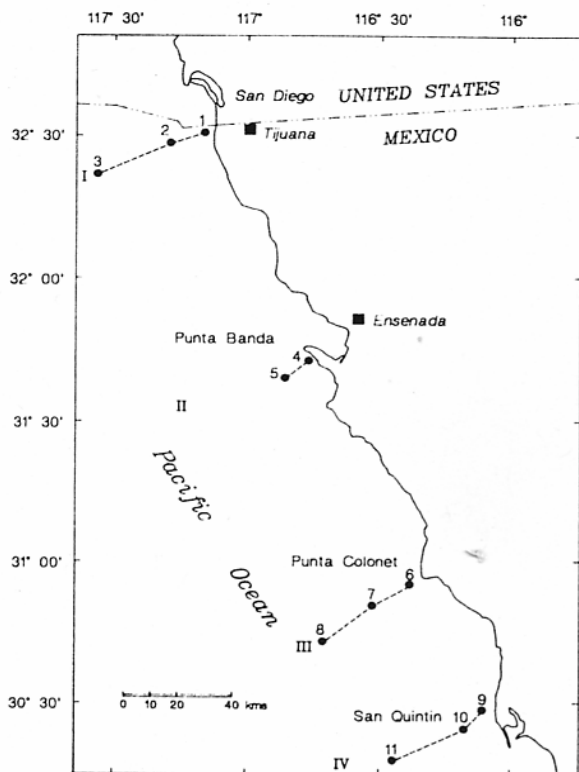


Fig. 1. Location of stations off the Baja California coast, ECOBAC I, 22–28 June 1988.

ward surface flow is very weak or nonexistent. South of the border, inshore surface flow is equatorward most of the year (Lynn and Simpson, 1987). The CCS transports waters rich in nutrients (e.g. phosphorus) from the north toward the Baja California coast (Haury and Shulenberger, 1982). This advective transport also introduces significant amounts of trace metals (e.g. cadmium) into the Southern California Bight (Martin et al., 1976).

Upwelling along the Baja California coast has been recognized as an important process that transports deep, nutrient-rich water to the surface (Gomez-Valdez, 1983). Although strong mesoscale upwelling events on the scale of hundreds of kilometers along the Mexican coast occur throughout the year, they are most intense during spring and summer (Bakum and Nelson, 1977; Torres-Moye and Acosta-Ruiz, 1986). Local coastal upwelling, which occurs within 20 km of shore, appears to influence water conditions strongly on the inner part of the continental shelf (Peterson et al., 1986). These nearshore upwelling events produce strong cross-shelf gradients in temperature, nu-

trients (Peterson et al., 1986), and metal distribution patterns (Bruland et al., 1978a; Bruland, 1980).

Anthropogenic trace metal inputs originate principally from wastewater discharges. Approximately 200×10^6 gallons per day of wastewater are discharged into the sea near the US–Mexican boundary, containing about 46 tonnes of suspended solids and associated trace metals (SCCWRP, 1987; Nishikawa-Kinomura et al., 1988). Bruland et al. (1974) calculated, based on sediment analyses off the southern California shelf, that the loading of metals from human activity equals or exceeds that from natural inputs. Although trace metal fluxes have decreased from their maxima around 1970, sewage is still the principal input affecting the sediment composition in the area (Finney and Hun, 1989a, b).

METHODS

Trace metal determinations

Unfiltered surface water (1 m depth) samples (2 l) were collected using trace-metal-clean techniques (Bruland et al., 1979; Flegal and Patterson, 1983) from a raft deployed from the research vessel 'Alejandro de Humboldt' during 23–28 June 1988 on the Estudios Costeros de Baja California I (ECO-BAC I) cruise. These samples were collected at 11 stations along four 45-km offshore transects across the continental shelf off the Baja California coast (Fig. 1). This sampling scheme was designed to obtain preliminary data on trace metal distributions in neritic and oceanic waters within the area.

The samples were stored in conventional polyethylene (CPE) bottles. These bottles were cleaned using methods described earlier (Patterson and Settle, 1976; Bruland et al., 1979), filled with ultra-clean 0.1% HNO_3 , and sealed in two CPE bags until use. The samples were acidified to $\text{pH} < 2$ with 4 ml of sub-boiling quartz-distilled ($2 \times$) 6 N HCl (Q-HCl). All shipboard-sample handling was carried out in a Class-100 laminar-flow clean-air bench. All bottle cleaning and analytical procedures were conducted in a Class-100 trace-metal-clean laboratory. Procedural details of sampling, sample handling, bottle cleaning, and storage have been described elsewhere (Patterson and Settle, 1976; Bruland et al., 1979; Flegal et al., 1985).

Metals (Pb, Cd, Mn, Fe, and Zn) were preconcentrated using a Chelex-100^R (Bio-Rad Laboratories, Richmond, CA) ion-exchange technique (Bruland, 1980). Trace element concentrations were determined with a Perkin-Elmer 5000 Atomic Absorption Spectrophotometer (Perkin-Elmer, Norwalk, CT) equipped with an HGA-500 Heated Graphite Atomizer and an AS-40 Autosampler. L'vov platforms were used in the furnace and the technique of standard additions was applied to correct for matrix interferences. Blanks ($x \pm 1$ s.d., $n = 5$) for the Chelex extraction were as follows: Pb, 4.0 ± 0.7 pmol

kg⁻¹; Mn, 2.0 ± 0.2 pmol kg⁻¹; Cd, 1.5 ± 0.4 pmol kg⁻¹; Zn, 0.038 ± 0.0069 nmol kg⁻¹; and Fe, 0.14 ± 0.081 nmol kg⁻¹. These values represented less than 10% of the lowest metal concentrations determined in this study.

Phosphate was determined by the methods of Murphy and Riley (1962), and the Strickland and Parsons (1968) method was used for silicate. Salinity was determined using an inductive salinometer.

Geochemical covariation of trace elements: multivariate statistical analysis

All the multivariate analyses were performed with SYSTAT (Wilkinson, 1987). The raw data were transformed (logarithmic transformation) and reduced using a similarity measure (correlation coefficients) before the statistical analyses. This transformation was consistent with log-normal distribution of trace metals in seawater (Bewers et al., 1976). A complete description of data reduction and transformation procedures has been given by Field et al. (1982).

Cluster analysis and Multidimensional Scaling ordination (MDS)

Hierarchical clustering was performed using dendrograms (average linkage method). A two-dimensional multi-dimensional scaling (MDS) ordination was also applied for further substantiation of the previous analysis. Both techniques operate by grouping initially unclassified objects on the basis of their similarities over a range of descriptors (Everitt, 1980).

Factor analysis

Factor analysis was performed from the correlation matrix of the log-transformed data. Quartimax rotation was used to optimize the results. The composition of each factor was obtained from the factor loading. A high factor loading means that a relatively large amount of the total information may be explained by that factor. The square of the factor loading ($\times 100$) provides the percentage of the total information explained by that factor. Factors are thought to reflect underlying processes that have created the correlations among variables (Tabachnick and Fidell, 1989).

RESULTS AND DISCUSSION

Trace metal concentrations

Most metal distributions along all four transects were characterized by both onshore and longshore concentration gradients (Table 1). The highest values occurred closest to shore (Stations 1, 4, 6 and 9), and were associated with high salinities (over 33.7‰) and high nutrient concentrations ($\text{PO}_4 > 0.359$ $\mu\text{mol l}^{-1}$; Table 2). This covariance with salinities and nutrients differen-

TABLE 1

Trace metal concentrations in Mexican coastal waters along the US-Mexican boundary (in nmol kg⁻¹, with exception of Pb in pmol kg⁻¹)

Location	Station no.	Distance offshore (km)	Cd	Pb	Mn	Zn	Fe
US-Mexican border	1	5	0.17	57	13	1.9	13
US-Mexican border	2	15	0.10	42	4.1	0.73	1.7
US-Mexican border	3	45	0.043	36	1.7	0.22	0.59
Punta Banda	4	2	0.15	28	16	1.1	7.1
Punta Banda	5	15	0.034	34	2.0	0.25	0.32
Punta Colonet	6	5	0.054	21	1.7	1.0	1.8
Punta Colonet	7	20	0.038	20	1.7	0.25	0.60
Punta Colonet	8	45	0.040	25	2.2	0.20	0.25
San Quintin	9	5	0.087	18	2.1	0.39	4.9
San Quintin	10	15	0.060	25	1.1	0.39	0.62
San Quintin	11	45	0.040	26	2.1	0.22	0.40

Samples were collected between 22 and 28 June 1988.

TABLE 2

Hydrographic and nutrient data from coastal waters along the US-Mexican boundary

Location	Station no.	Salinity (‰)	Temperature (°C)	PO ₄ (μmol kg ⁻¹)	Si (μmol kg ⁻¹)
US-Mexican boundary	1	33.715	17.48	0.53	2.9
US-Mexican boundary	2	33.693	18.38	0.32	1.1
US-Mexican boundary	3	33.683	18.92	0.41	0.60
Punta Banda	4	33.867	16.16	0.52	2.4
Punta Banda	5	33.730	17.19	0.31	0.40
Punta Colonet	6	33.862	16.26	0.36	0.79
Punta Colonet	7	33.641	18.62	0.34	0.89
Punta Colonet	8	33.717	18.18	0.30	0.50
San Quintin	9	33.790	14.98	0.52	1.4
San Quintin	10	33.692	15.84	0.41	1.6
San Quintin	11	33.663	17.59	0.32	0.60

Samples were collected between 22 and 28 June 1988.

tiates coastal waters containing relatively elevated metal levels from pelagic surface water sources in other regimes (Kremling, 1983; Balls, 1985).

Stations located in the north along the US-Mexican border and at Punta Banda had elevated trace metal concentrations compared with more southerly locations (Punta Colonet and San Quintin). Most elemental concentrations also decreased with increasing distance offshore by an order of magnitude (Stations 3, 5, 7, 8, 10, and 11; Table 1), to levels characteristic of the

TABLE 3

Average metal concentrations of Cd, Mn, Zn, Fe and Pb in surface waters of the Pacific Ocean (in nmol kg⁻¹, with exception of Pb in pmol kg⁻¹)

	California Current	Coastal upwelled water	This work
Cd	0.04 ^a	0.16 ^{a,b}	0.03–0.17
Mn	2–4 ^e	17 ^d	1.7–16
Fe	0.8–1.3 ^c	9 ^d	0.25–13
Zn	0.12 ^b	0.34 ^b	0.20–1.9
Pb	25 ^f	20 ^e –63 ^b	18–57

^aBruland et al. (1978a). ^bBruland (1980). ^cLanding and Bruland (1980). ^dMartin and Gordon (1988). ^eLanding and Bruland (1987). ^fSchaule and Patterson (1981). ^gMartin et al. (1985). ^hFlegal and Patterson (1983).

CCS (Table 3). Distributions of these trace metals are discussed individually below.

Cadmium

Cadmium concentrations increased toward the coast in all the transects, ranging from a minimum of 0.034 nmol kg⁻¹ offshore at Punta Banda (Station 5) to a maximum of 0.17 nmol kg⁻¹ at the US–Mexican border (Station 1). The latter figure agrees well with the value of 0.16 nmol kg⁻¹ reported by Martin et al. (1976) off San Diego, California. Similar coastal enrichments have been observed in other regions along the western USA, and are attributed principally to the upwelling of nutrient-rich waters (Bruland et al., 1978a; Bruland, 1980). Concentrations of cadmium at stations away from coastal influence and at several nearshore stations off central Baja California (5 km offshore; Stations 6 and 9) were within the range typical of nutrient-depleted surface waters of the California Current (0.04–0.05 nmol kg⁻¹; Bruland et al., 1978a; Bruland, 1980).

Manganese

Horizontal manganese concentration gradients, which were first observed by Bender et al. (1977) off California, were apparent off the coast of Baja California. Water enriched in manganese was confined to the continental shelf, with concentrations gradually decreasing offshore. Manganese concentrations increased by nearly an order of magnitude between offshore and nearshore stations (from 2 to 13 and 16 nmol kg⁻¹ at the border and Punta Banda; Stations 1 and 4, respectively). These values were similar to those reported by Landing and Bruland (1980, 1987) in the northeast Pacific, who also noted an order of magnitude increase between the central gyre and coastal waters of central California. Similar continental boundary gradients for Mn have been observed elsewhere in the North Pacific and in the Atlantic (Bruland and

Franks, 1983; Jones and Murray, 1985; Martin and Knauer, 1985; Martin et al., 1985).

Iron

Iron levels decreased with distance offshore, ranging from 0.3 nmol kg⁻¹ in offshore stations to 13 nmol kg⁻¹ in coastal waters along the US–Mexican border (Station 1). Horizontal gradients have also been detected off the California coast (Landing and Bruland, 1987; Martin and Gordon, 1988). The iron levels detected in the offshore stations were very close to the upper limit of the range of 0.15–0.40 nmol kg⁻¹ reported for open ocean surface waters of the northeast Pacific (Gordon et al., 1982; Landing and Bruland, 1987). The iron levels measured in coastal waters (1.8–13 nmol kg⁻¹; Stations 1, 4, 6, and 7) were within the 0.75–9 nmol kg⁻¹ range observed at nearshore stations along the California continental margin (Gordon et al., 1982; Landing and Bruland, 1987). This coastal enrichment has been primarily attributed to sediment diagenetic processes (Martin and Gordon, 1988).

Zinc

Zinc concentrations were an order of magnitude higher at the nearshore stations (Stations 1, 4, and 6), increasing from 0.20 nmol kg⁻¹ at the offshore stations to about 2 nmol kg⁻¹ at the US–Mexican boundary (Table 1). Enhanced zinc concentrations detected along the California coast have been attributed to wind-induced coastal upwelling (Bruland, 1980). However, sedimentary diagenesis has been suggested to cause coastal enrichment in the Mediterranean Sea (Sherrell and Boyle, 1988).

Lead

Lead concentrations ranged between 18 pmol kg⁻¹ (Station 9) and a maximum of 57 pmol kg⁻¹ at the international border (Station 1). The latter figure is in good agreement with the value of 63 pmol kg⁻¹ reported for offshore surface waters of Southern California (Flegal and Patterson, 1983). Lead concentrations at the remaining stations were within the range of 24–72 pmol kg⁻¹ reported for waters off the central California coast (Schauale and Patterson, 1981). The lowest lead concentrations were detected along the central part of Baja California (Table 1). ²¹⁰Pb levels are low along ocean margins, as a result of enhanced removal processes near the continental shelf. Enhanced removal results from increased biological productivity and elevated loads of organic and inorganic particles (Nozaki et al., 1976). The samples analyzed in this study were collected in summer, when coastal upwelling and primary productivity were intensified. Thus, the surface lead concentration minimum is tentatively attributed to enhanced sorption onto sinking particles (Flegal and Patterson, 1983).

Regional distributions

The trace metal distributions indicate that surface waters along the US–Mexican border were relatively enriched in trace metals. A comparison of surface concentrations in northern Baja California coastal waters (Stations 1 and 4) with those in the other locations revealed that concentrations of Cd, Mn, Zn, Fe, and Pb in this area were enriched by an order of magnitude (Table 1). Superficially, this could be attributed to anthropogenic metal discharges from the densely populated and industrialized cities (Los Angeles and San Diego, USA, and Tijuana and Ensenada, Mexico) in this coastal area. To test this hypothesis, the following indirect approaches were investigated to assess whether the trace metal enhancements detected along the US–Mexican border could be correlated with either anthropogenic or natural metal sources.

Metal–nutrient relationships

Some trace element concentrations (e.g. Cd and Zn) are positively correlated ($r > 0.95$) with those of the limiting nutrients (phosphate, nitrate, and silicate) in oceanic waters (Bruland, 1983). Because of the oceanographic consistency of such a covariation, deviations from this pattern might be indicative of anthropogenic metal enrichment near point sources (in areas where there is no reason for an observed deviation from the expected value) (Bruland et al., 1978a; Martin et al., 1980a, 1980b).

Most of our metal–nutrient data (Figs. 2a and 2b) correlated well with the cadmium–phosphate and zinc–silicate relationships established for the northeast Pacific (Martin et al., 1976; Bruland, 1980). This indicates that Cd and Zn concentrations off the Baja California coast are primarily controlled by the particle production and destruction of organic material characteristic of open ocean areas (Bruland, 1980). Small excesses of cadmium and zinc, relative to the metal–nutrient relationship, were present along the US–Mexican border and at Punta Banda. However, these excesses were relatively small (less than 10%) compared with the range of cadmium and zinc concentrations in surface waters. Outliers from the simple linear regression of the cadmium–phosphate plot have been observed by earlier workers (Fig. 2a) at coastal stations near major input sources (e.g. Point Loma discharge, San Diego, California) (Martin et al., 1976). These latter data were plotted in Fig. 2a for comparison, but were not included in the simple linear regression calculations.

Those regressions indicated (Fig. 2) that cadmium and zinc levels in surface waters along the Baja California coast should be of the order of 0.039–0.11 nmol kg⁻¹ and 0.060–0.32 nmol kg⁻¹, respectively. The observed concentrations were consistent with the predicted values at the offshore stations and for central Baja California (Table 1). However, only 50% of the metals

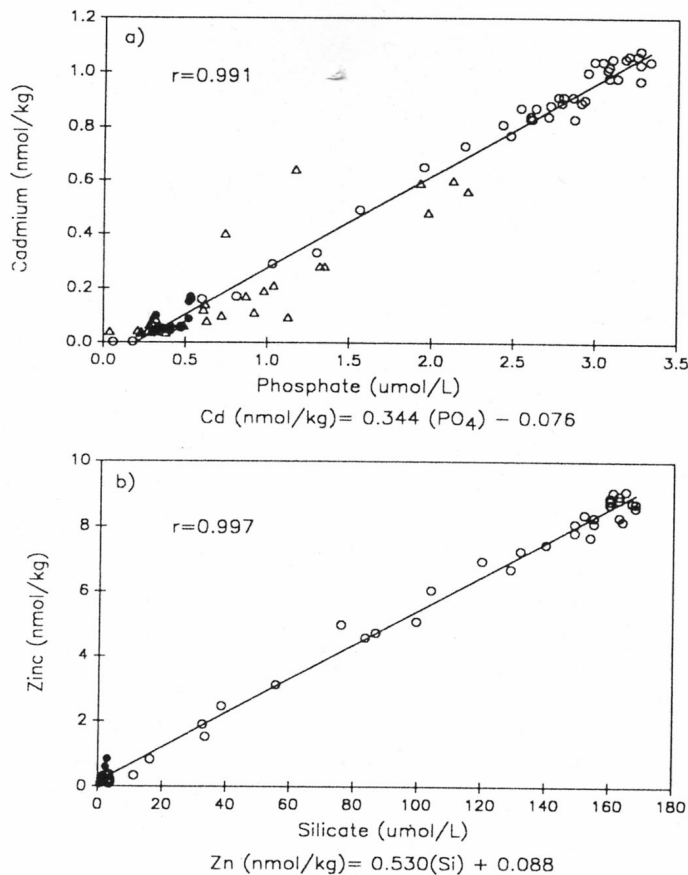


Fig. 2. Metal-nutrient relationships for waters of the northeast Pacific. Open circles, Bruland (1980); open triangles, Martin et al. (1976); filled circles, this work.

present at the nearshore stations along the US-Mexican border and at Punta Banda (Stations 1, 2 and 4) followed the predicted metal-nutrient relationship.

Analogous results were reported by Martin et al. (1976) at nearshore stations of the Southern California Bight, where the cadmium values were about twice those predicted by the cadmium-nutrient covariance determined for open ocean waters. Such metal excesses have been attributed to differential uptake of metals relative to nutrients and preferential regeneration of nutrients relative to metals in the upper thermocline, rather than anthropogenic inputs (Martin et al., 1976; Boyle et al., 1981).

Comparison of the levels of trace metals in coastal waters of Baja California with those in the northeast Pacific

The mean concentrations of total dissolved Cd, Mn, Pb, Zn, and Fe in surface waters of the Baja California shelf were similar to metal concentrations reported earlier for the North Pacific (Table 3).

The relatively high concentrations of metals detected at the nearshore stations along the US–Mexican border and at Punta Banda (Stations 1, 2, and 4; Fig. 1, Table 1) are the same as those measured earlier in coastal upwelled waters along the California coast (Table 3). The elemental levels measured at the central Baja California stations (Punta Colonet and San Quintin; Stations 6–11; Fig. 1, Table 1) were within the range of values characteristic of the California Current (Table 3). The similarity of this coastal water composition with that observed in surface waters of the northeast Pacific suggests that anthropogenic metal discharges from adjacent land masses have relatively little effect on the coastal water concentrations. The metal distributions off the Baja California coast indicate that the area was primarily affected by two physical oceanographic processes: local upwelling in the north and the intrusion of the California Current in the south.

Mass balance estimates

The preceding arguments, which indicated that the wastewater discharges from the urban areas of San Diego in the USA and Tijuana in Mexico had little effect on the metal concentrations in surface waters, were substantiated by mass balance estimates. The total metal input rates calculated for the study area were compared with the known input rates of trace elements from the wastewater discharges (San Diego and Tijuana) (Table 4).

TABLE 4

Comparison of metal input rates to the area of study by advection (total input) and from wastewater discharges

Metal	Seawater concentration (ng kg ⁻¹)	Total input rate ^a into the area of study (kg day ⁻¹)	Input rate from wastewater discharges (kg day ⁻¹)	
			Point Loma ^b	Tijuana ^c
Cadmium	19	114	0.85	0.08
Zinc	124	745	49	15
Lead	12	72	14	7

^aBased on a residence time for water of 2 days (15 cm s⁻¹) (Godinez-Sandoval, 1986; SCCWRP, 1987), the total volume of water in the study area (12 km³), and the seawater concentration of a given metal.

^bMichael Stewart (personal communication, 1988); Point Loma wastewater treatment plant, City of San Diego.

^cNishikawa-Kinomura et al. (1988).

The total metal input rates were determined for a volume of 12 km^3 (based on a surface area of 200 km^2 ; 20 km between the municipal discharges from the cities of San Diego and Tijuana, and 10 km width of the coastal zone), a discharge depth of 60 m, and a water residence time of 2 days (based on the average current velocity along the US–Mexican border for the summer conditions of 15 cm s^{-1} (Godinez-Sandoval, 1986; SCCWRP, 1987)).

These calculations indicated that about 1% (1 kg day^{-1}) of the cadmium, 9% (64 kg day^{-1}) of the zinc, and 29% (21 kg day^{-1}) of the lead could be derived from wastewater discharges. This substantiated earlier results which suggested that levels of metals in the Southern California Bight were largely controlled by natural transport processes, and that only a few areas (primarily adjacent to sewage outfalls) had elevated concentrations attributable to anthropogenic inputs (Martin et al., 1976; Bruland and Franks, 1978, 1979).

At present, insufficient information is available to make mass balance calculations for all the metals analyzed. However, we can make some preliminary estimates for the advection and upwelling introduction of Cd into waters at the US–Mexican border. Advective transport of metals into the study area results from the nearshore counterflow, which is a prevalent feature of the CCS. The volume transport of this shallow countercurrent is about $12 \times 10^4 \text{ m}^3 \text{ s}^{-1}$ (Wooster and Reid, 1963; Martin et al., 1976). Based on a Cd concentration typical of the California Current of 5 ng kg^{-1} (0.4 nmol kg^{-1}) (Table 3), this surface advective transport introduces 50 kg day^{-1} of Cd into the area (45% of the total input).

Upwelling is another important mechanism of metal transport in coastal waters. Bruland (1980) and Bruland et al., (1978a) showed a 300-fold variation of Cd in surface waters along the California coast, which varied with intensity of upwelling. Subsurface waters are upwelled from a depth of 50–100 m (Gomez-Valdez, 1983) along the Baja California coast, at a rate of about 3 m day^{-1} (Roden, 1972). This process transports about 40 kg day^{-1} of Cd (approximately 40% of the total input), assuming a Cd concentration for upwelled water of 70 ng kg^{-1} ($0.62 \text{ nmol kg}^{-1}$), based on a phosphate content of $1.98 \text{ } \mu\text{mol l}^{-1}$. This flux is the same order of magnitude as that introduced via lateral advection from the California Current.

These preliminary estimates of the relative significance of anthropogenic inputs of trace elements in coastal waters may be conservatively low, because non-point sources have not been quantified. For example, additional Cd input (about 14%) into the area may occur through atmospheric deposition. Hodge et al. (1978) reported that aerosol input may supply up to 25% of Cd in surface waters off the Baja California coast.

Cluster and MDS comparison of trace elements

Multivariate statistical comparisons were used to describe the geochemical covariation of trace elements along the Baja California coast. The similarity

matrix (Pearson correlation coefficients) between the 10 parameters obtained from the log transformation ($1 + \log X_i$) of the data is tabulated in Table 5, and the dendrogram and two-dimensional plot from the MDS are shown in Fig. 3. Both techniques produced similar results. With the exception of lead, all the trace metals and nutrients formed one well-defined group (Mn, Zn, Fe, Cd, Si, and PO_4). Other parameters, such as pH and temperature, separated individually.

Identification of the cluster of the chemical components provided important geochemical information on the behavior of trace metals in these coastal waters. The similarity between Cd, Zn, Fe, Si, and PO_4 distributions in seawater is well documented (Bruland et al., 1978a,b; Gordon et al., 1982; Knauer and Martin, 1981). Their oceanic profiles are similar and all of them are affected by similar remineralization and transport processes. Because there are no major rivers and little rainfall ($25\text{--}40 \text{ cm year}^{-1}$; Petersen et al., 1986) in the Southern California Bight, the association of trace metals with manganese hydroxides proposed by several authors (Jones and Murray, 1985; Martin et al., 1985) suggests a sedimentary source of trace metals in this area. This is consistent with the observation of Jones and Murray (1985), who noted that the manganese enrichment in coastal waters could be caused by the resuspension of manganese-rich sediments.

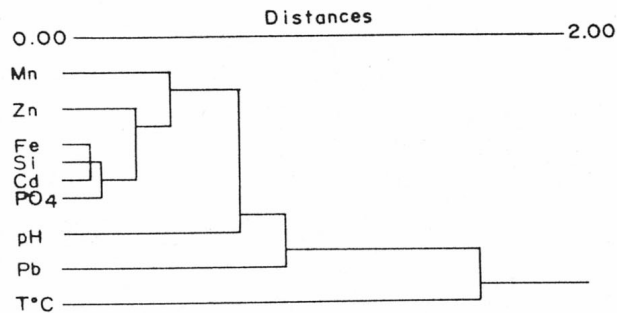
The separation of lead from the cluster of nutrients and other trace metals indicates that the source and transport processes affecting the distribution of lead are very different from those for the other metals. Pb distributions are most likely to be dominated by atmospheric inputs, whereas distributions of the other metals are mainly dominated by upwelling and advection. This result is in agreement with earlier estimates by Patterson et al. (1976), who suggested that coastal waters from the Southern California Bight are contaminated with lead from three major sources of approximately equal magnitude:

TABLE 5

Correlation coefficients for trace element concentrations and hydrographic data after the log-transformation

	Pb	Cd	Mn	Fe	Zn	PO_4	Si	pH	T
Pb	1								
Cd	0.59	1							
Mn	0.58	0.92	1						
Fe	0.45	0.94	0.82	1					
Zn	0.58	0.87	0.79	0.86	1				
PO_4	0.25	0.77	0.60	0.87	0.59	1			
Si	0.40	0.91	0.76	0.88	0.79	0.84	1		
pH	0.08	0.40	0.18	0.43	0.57	0.37	0.41	1	
T	0.36	0.27	0.06	0.41	0.22	0.54	0.42	0.26	1

a) Cluster analysis



b) MDS ordination

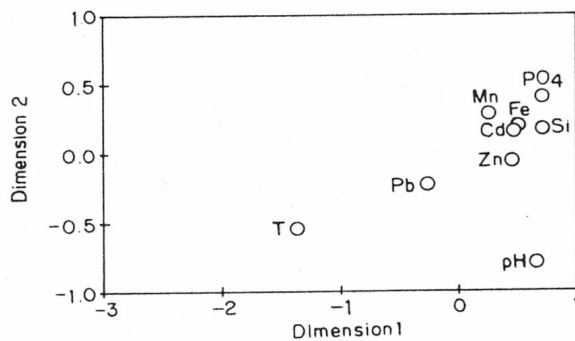


Fig. 3. Cluster and MDS ordination analyses for trace metals in surface waters off the Baja California coast.

dry deposition of atmospheric aerosols, surface runoff, and wastewater discharges.

Factor analysis

The principal mechanisms affecting the distribution of trace metals were characterized by factor analysis. This analysis was performed from the correlation matrix of the log-transformation (Table 5), using quartimax rotation. The rotated factor matrix, shown in Table 6, presents a three-factor solution which represents 95% of the total variance.

The first factor represents the effect of physical transport (upwelling and advection), which influences the levels of trace metals in surface waters. It accounts for 76.6% of the total variance among the variables. This relatively high percentage indicates that this is the principal factor influencing the distributions of Fe, Cd, Mn, Zn, Si, and PO₄. As the factor loading for Pb is also

TABLE 6

Factor loading, with the cumulative proportion of variance explained by each factor (quartimax rotated component loading matrix)

	1	2	3
Pb	0.509	0.860	0.044
PO ₄	0.804	-0.151	-0.554
Mn	0.905	0.130	0.200
Zn	0.912	0.127	0.248
Si	0.934	-0.082	-0.216
Cd	0.980	0.109	-0.011
Fe	0.989	0.071	0.039
% of total variance explained	76.64	11.69	6.56

relatively high in this group (0.509), its distribution is also affected by the same oceanographic process.

The second factor accounts for 11.7% of the total variance of components, and is almost exclusively influenced by the independent variance of lead (0.860). We attributed this to the relative predominance of anthropogenic inputs of lead in the North Pacific (Flegal and Patterson, 1983). It includes both aeolian inputs of lead ($15 \text{ ng cm}^{-2} \text{ year}^{-1}$), which accounts for over 95% of the lead flux entering the northeast Pacific surface waters (Maring et al., 1989) and wastewater discharges (about 63 tonnes in 1987) in the Southern California Bight (SCCWRP, 1987).

The third factor represents 6.6% of the total variance. It is characterized by the association of Fe, Zn, and Mn, and the inverse association of nutrients and Cd. The high loading of PO₄ (-0.554) vs. Cd (-0.011) may represent the preferential uptake of PO₄ over Cd as noted above in the metal-nutrient relationship for some of our nearshore stations. The lack of inverse correlation between Zn and nutrients, as detected for Cd, may indicate differences of the net internal reaction rates of these two elements in the upper ocean (Fanning et al., 1988). Furthermore, comparable deviations of the metal-nutrient relationships in surface waters have been reported elsewhere (Boyle et al., 1981; Kremling, 1985).

Hydrographic conditions of the study area

The dominance of natural inputs from physical oceanographic processes over anthropogenic sources affecting trace metal distributions along the Baja California coast was substantiated by the hydrographic characteristics of the study area. Trace metal enrichments detected in coastal waters off northern Baja California were associated with the inshore transport of subsurface waters which were upwelled and advected offshore. Offshore salinity transects (Fig.

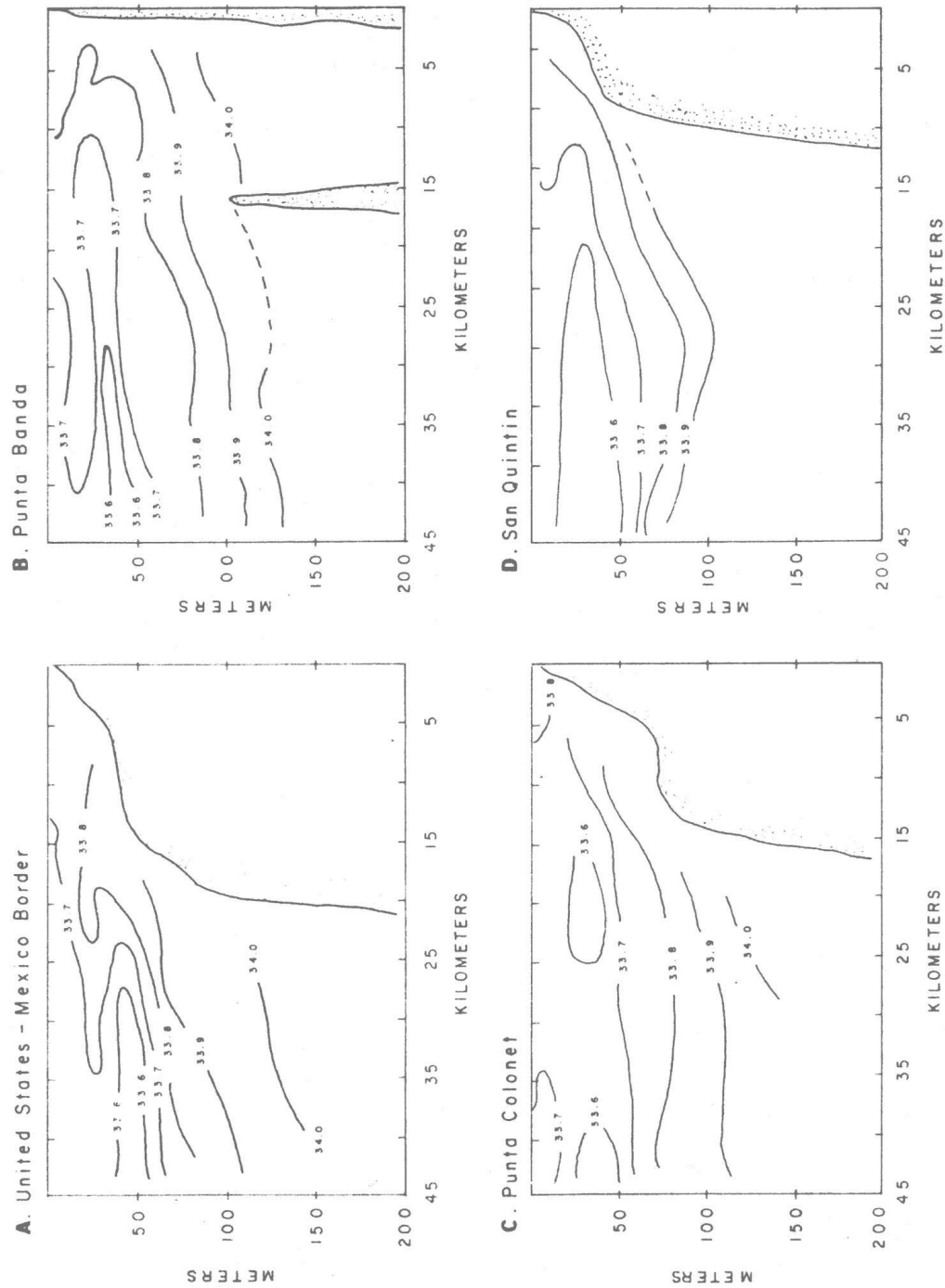


Fig. 4. Cross-shelf sections of salinity along four transects off the Baja California coast: 22-28 June 1988.

TRACE ELEMENT DISTRIBUTIONS IN COASTAL WATERS

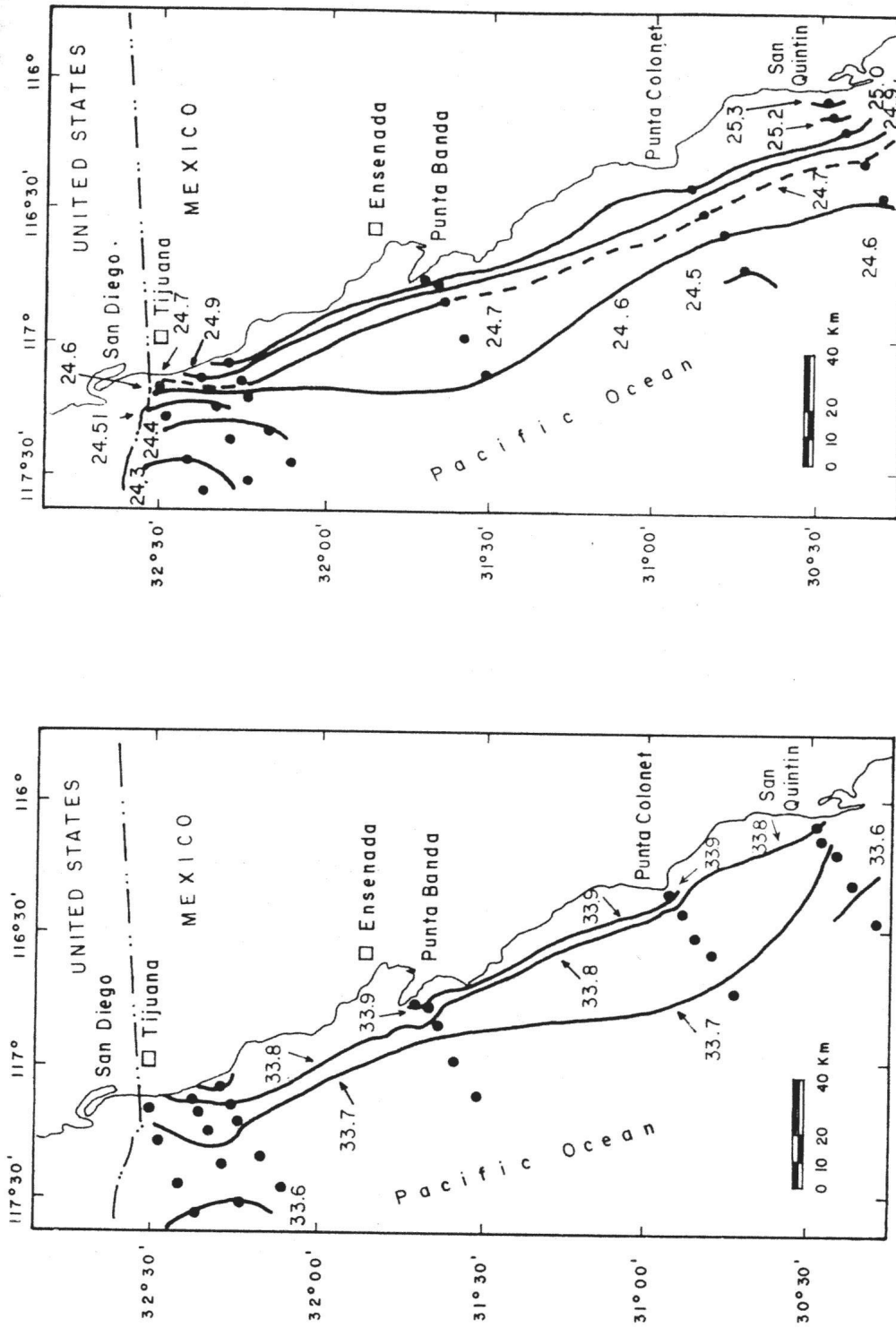


Fig. 5. Surface salinity and density (σ_t) fronts detected off the Baja California coast: 22-28 June 1988.

4) showed evidence of strong advective processes at the US–Mexican border and at Punta Banda (tránsects I and II, respectively). For the other transects, advective transport of water was not as apparent in the salinity distributions. Although the intrusion of a salinity minimum at mid-depth was present in all the transects, this was most pronounced in transect IV (San Quintin). This subsurface salinity minimum is a typical feature of the CCS. It originates in high-latitude surface waters which are low in salinity, high in oxygen concentration (Reid, 1973) and low in trace metal concentrations in comparison with coastal upwelled waters (Bruland, 1980).

Formation of fronts, parallel to the coastline, can be seen in the horizontal (surface) sections of salinity and sigma- t presented in Fig. 5. These conditions were similar to those reported by Lynn et al. (1982) for the same area. The surface water near the coast is cooler, more saline, and denser, indicating that the region was influenced by a nearshore upwelling event within 10 km of the coastline. Similar nearshore upwelling events have been reported for other areas along the California coast (Peterson et al., 1986).

The salinity and sigma- t fronts (Fig. 5) also help to identify the source of the water mass in the study area. Water masses with salinities between 33.60 and 33.75‰ and with a sigma- t value of 24.3 are generally found 700 km from shore and are associated with the North Pacific Central Water Mass (Lynn et al., 1982; Simpson et al., 1984). This indicates that a large amount of low-salinity water enters the system by horizontal advection from the north. Intrusion of open ocean waters into the coastal environment has been reported by Hickey (1979).

The nearshore upwelling transport present along the Baja California coast appears to be limited to a zone within 10 km of shore. Several studies have provided evidence that these coastal processes can enhance trace metal concentrations in coastal waters (Bruland, 1980; Jones and Murray, 1984). The central and western parts of the study area were also affected by a horizontal intrusion of metal-depleted gyre waters coming from the north.

SUMMARY

Trace metal levels measured along the Baja California coast showed both onshore and longshore gradients associated with high salinities and high nutrient concentrations. Nearshore stations located along the US–Mexican border were relatively enriched with trace metals compared with more southerly locations, but the values were oceanographically consistent with levels previously reported for the northeast Pacific (upwelled waters). This indicates that, although that area receives high loading of trace metals through wastewater discharges, this was not the predominant factor affecting trace metal distributions. Metal–nutrient relationships, and cluster and MDS analyses, indicated that the magnitude of these discharges was not pronounced enough to

alter the natural geochemical covariation of trace metals substantially. This was corroborated by mass balance calculations, which showed that only 1% of Cd, 9% of Zn, and 29% of Pb in those surface waters might originate from point source discharges. These estimates of the relative contribution of anthropogenic inputs of trace elements to the CCS may be conservatively low, because they have not incorporated inputs from non-point sources or anthropogenic inputs from point sources outside the Southern California Bight.

The principal factors affecting trace metal distributions along the Baja California coast were physical oceanographic processes. Hydrographic data indicated that the relative enrichment of trace metals detected at the northern stations was associated with upwelling, and that the depletion measured in the southern locations was associated with the intrusion of the California Current. The importance of upwelling as the principal factor influencing the metal concentrations was also indicated by factor analysis. These results provide additional evidence of the importance of circulation patterns on the distribution of trace metals in coastal waters.

ACKNOWLEDGMENTS

We thank Ken Bruland, Peggy Delaney, Gary Gill, John Donat, Don Smith, and Linda Anderson for their helpful comments on the manuscript. We are grateful to Oc. Jose A. Segovia-Zavala and the Instituto de Investigaciones Oceanologicas of the Autonomous University of Baja California (UABC) for allowing our participation on their cruise ECOBAC I. We also express our appreciation to the crew and officers of the 'Alejandro de Humboldt' and to Geoffrey J. Smith for laboratory help. This work was supported by grants from the National Science Foundation (OCE-H612113), University of California Toxic Substances Research and Teaching Program, Minerals Management Service, and UCMEXUS.

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Pergamon

Geochimica et Cosmochimica Acta, Vol. 58, No. 15, pp. 3315–3320, 1994
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 0016-7037/94 \$6.00 + .00

0016-7037(94)00128-6

Temporal variations in lead concentrations and isotopic composition in the Southern California Bight*

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(Received June 15, 1993; accepted in revised form April 8, 1994)

Abstract—Lead concentrations in surface waters of the Southern California Bight appear to have decreased threefold (from >170 to <60 pM) since they were initially measured by Clair Patterson and his associates in the 1970s. The decrease parallels a threefold decline in anthropogenic inputs of industrial lead to the bight over the past two decades. Moreover, mass balance calculations indicate that the primary source of lead to the bight now is upwelling. This is evidenced by the isotopic compositions of surface waters in the bight, which are most characteristic of Asian industrial lead aerosols ($0.4793 \leq {}^{206}\text{Pb}/{}^{208}\text{Pb} \leq 0.4833$) deposited in oceanic waters of the North Pacific. While the decrease in surface water lead concentrations in the bight reflects the reduction in industrial lead emissions from the United States, the isotopic compositions of surface waters in the southern reach of the bight reflect a concurrent increase in industrial lead emissions from Mexico ($0.4852 \leq {}^{206}\text{Pb}/{}^{208}\text{Pb} \leq 0.4877$). The isotopic composition (${}^{208}\text{Pb}/{}^{210}\text{Pb} \approx 2.427$) of elevated lead concentrations of surface waters in San Diego Bay indicate that lead is being remobilized from contaminated sediments within that bay.

INTRODUCTION

THE INITIAL STUDY OF LEAD contamination in surface waters of the Southern California Bight was conducted by PATTERSON et al. (1976) with samples collected in the mid-1970s. They measured lead concentrations and stable lead isotopic compositions in coastal waters in the bight when about 680 tonnes y^{-1} of industrial lead were delivered to the bight through three major pathways of comparable magnitude: aeolian deposition, surface runoff, and wastewater discharges (PATTERSON and SETTLE, 1974). Anthropogenic lead fluxes to the bight have declined dramatically since then as a result of both improvements in waste water treatment technologies and the phased elimination of leaded gasolines in the United States.

In order to quantify the impact of those reductions in anthropogenic lead inputs to the Southern California Bight, we measured lead concentrations and stable lead isotopic compositions of surface water samples collected in 1988–1989. We then estimated the decline of lead contamination within the area by comparing our data with those of PATTERSON et al. (1976). We also measured the lead isotopic composition of sewage, aerosols, and gasolines in southern California (USA) and Baja California (Mexico) to identify the major contemporary sources of lead contamination to the bight.

METHODS

Surface water, aerosol, wastewater, and gasoline samples were collected with trace metal clean techniques in the Southern California Bight (Fig. 1) from San Diego (32°N), California (USA) to San Quintin

(30°N), Baja California (Mexico) in 1988 and 1989 (SAÑUDO-WILHELMY and FLEGAL, 1991, 1992; Table 1). Lead concentrations were measured by graphite furnace atomic absorption spectrometry, as previously reported (SAÑUDO-WILHELMY and FLEGAL, 1991). The analytical detection limit was 0.1 pM, and the sum of contaminant lead introduced during sampling, storage, and analysis was ≤ 1 pM. Subsequent analyses of stable lead isotopic compositions (${}^{210}\text{Pb}$, ${}^{206}\text{Pb}$, ${}^{207}\text{Pb}$, and ${}^{208}\text{Pb}$) were made by thermal ionization mass spectrometry, using procedures developed to measure the isotopic composition of lead in oceanic surface waters (FLEGAL et al., 1986; FLEGAL and PATTERSON, 1983) and neritic upwelling waters (FLEGAL et al., 1989) in the North Pacific. The isotopic composition analyses were calibrated with concurrent analyses of NIST SRM 981 with a fractionation correction of 0.12 ± 0.02 per amu.

RESULTS AND DISCUSSION

The analyses revealed a threefold decrease in surface water lead concentrations from 174 pM to ≤ 57 pM over a period of thirteen years, when compared to the initial measurements of lead in the Southern California Bight by PATTERSON et al. (1976). An equivalent decline was observed when lead concentrations were normalized to ${}^{210}\text{Pb}$ activities in the bight (from 1832 to 713 pM dpm^{-1}) that were measured during those sampling periods in the 1970s (BRULAND et al., 1974) and the 1980s (WONG et al., 1992). The normalizations were made to correct for any natural perturbations in the lead cycle during the different sampling periods (BOYLE et al., 1986).

Our estimate of the decrease in lead concentrations of those surface waters paralleled the threefold decrease of lead fluxes measured in neritic sediments (from 0.45 to 0.16 $\mu\text{g cm}^{-2} \text{y}^{-1}$) in the Southern California Bight over the past two decades (FINNEY and HUH, 1989), which occurred in spite of a 42% increase in the surrounding population to ≈ 16 million (California State Census Data Center, 1985; CCSCE, 1989) and a 21% increase in wastewater discharges to $\approx 4 \cdot 10^6 \text{m}^3 \text{day}^{-1}$ to the bight during that period (SCCWRP, 1991). The

* Paper presented at the symposium "Topics in Global Geochemistry" in honor of Clair C. Patterson on 3–4 December 1993 in Pasadena, California, USA.

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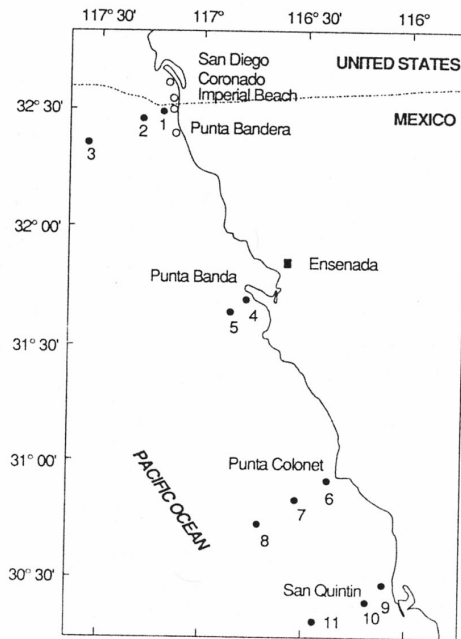


FIG. 1. Locations of surface coastal (●) and nearshore (○) stations in the Southern California Bight.

estimated decrease was similar to the decrease in lead fluxes reported for other surface waters, which have been primarily attributed to the reduction in aeolian inputs of industrial lead aerosols (e.g., TREFRY et al., 1985; BOYLE et al., 1986; BOUTRON et al., 1991; VÉRON et al., 1993). The decline in lead contamination within the Bight also appeared to reflect a decrease in the atmospheric deposition of industrial lead associated with the elimination of lead additives in gasoline throughout the USA (from 189 to $55 \cdot 10^3$ tonnes y^{-1} ; US Department of the Interior, 1977, 1990).

The impact of that decrease in lead inputs was indicated by mass balance calculations, which were based on the model developed by VAN GEEN et al. (1991; Table 2). The lead mass balance expression for the coastal area was

$$C_{\text{sew}} \cdot Q_{\text{sew}} + C_{\text{up}} \cdot Q_{\text{up}} + f \cdot Q_{\text{adv}} \cdot (C_c - C_o) + \text{Atm} = C_c \cdot Q_{\text{adv}}$$

where C is the concentration and Q is the water flux of sewage, upwelling, and advection. The upwelling water flux ($2.4 \cdot 10^{10}$ m^3 day^{-1}) was derived from a mean upwelling rate of 1–3 m day^{-1} (RODEN, 1972) and a surface area of 12,000 km^2 for the Southern California Bight (PATTERSON et al., 1976). Sewage water fluxes were $4.5 \cdot 10^6$ m^3 day^{-1} in 1988 and $3.6 \cdot 10^6$ m^3 day^{-1} in 1975; SCCWRP, 1991). C_c and C_o were lead concentrations in coastal waters and open ocean; for the mid-1970s (174 and 97 pM, respectively; PATTERSON et al., 1976), and for 1988 (57 and 36 pM; SAÑUDO-WILHELMY and FLEGAL, 1991). Lead concentrations in sewage (C_{sew}) were obtained from regional monitoring reports

100 dilution (BASCOM, 1982). An upwelling concentration (C_{up}) of 26 pM (SHAULE and PATTERSON, 1981) was used for all calculations. A 100% trapping efficiency ($f = 1$) was assumed, because a shelf trapping efficiency of >1 was calculated from the mass balance equation, indicating that an additional input was required to satisfy the mass balance. Atmospheric deposition (atm) was calculated by the difference between inputs and outputs, assuming steady state. Inputs from surface runoff were excluded because the samples were collected during arid periods of a protracted drought when such fluxes were negligible.

The model calculations indicated that atmospheric deposition of industrial lead was the primary (40%) anthropogenic source of lead in the bight during the 1970s (Table 2). Atmospheric deposition has declined substantially (17%) by the end of the 1980s, when upwelling (46%) became the predominant source of lead to the bight. This represented a threefold increase in the relative amount of lead associated with upwelling, which corresponded with the threefold decrease in the total lead flux to the bight over the thirteen year period. While the lead fluxes from sewage have also decreased threefold, the relative contribution from wastewater discharges was minimal (Table 2). Consequently, this estimate contrasts with our previous mass balance calculations, which indicated that about 29% of the lead along the USA-Mexico border (200 km^2) could still be derived from local outfalls (SAÑUDO-WILHELMY and FLEGAL, 1991).

The predominance of lead derived from remote sources was evidenced by the isotopic composition of surface waters in the bight, which indicated that most of the lead was now derived from aeolian depositions of industrial lead aerosols to oceanic surface waters in the North Pacific. This is illustrated in Fig. 2, which shows two contrasting isotopic gradients for coastal waters off southern California and Baja California. The isotopic compositions reflect a mixture of lead in upwelled waters from the North Pacific ($0.4793 \leq ^{206}\text{Pb}/^{208}\text{Pb} \leq 0.4833$; FLEGAL et al., 1989) and contemporary (1988–1989) USA industrial lead aerosols ($0.4893 \leq ^{206}\text{Pb}/^{208}\text{Pb} \leq 0.4945$) in the northern reach of the bight, and they reflect a mixture of lead in southern California coastal waters and Mexican industrial lead aerosols ($0.4852 \leq ^{206}\text{Pb}/^{208}\text{Pb} \leq 0.4877$) in the southern reach of the bight. For example, the isotopic composition of nearshore (<100 m offshore) water ≈ 10 km north of the USA-Mexico border at Coronado ($^{206}\text{Pb}/^{208}\text{Pb} = 0.4894$) fits the North Pacific (upwelling)-USA (California) mixing line, the isotopic composition of nearshore water ≈ 5 km north of the USA-Mexico border at Imperial Beach ($^{206}\text{Pb}/^{208}\text{Pb} = 0.4868$) indicates an addition of some Mexican industrial lead, and the isotopic composition of nearshore water collected at the USA-Mexico border ($^{206}\text{Pb}/^{208}\text{Pb} = 0.4859$) indicates the predominance of Mexican industrial lead (Fig. 2 and 3).

The longshore gradient in lead isotopic compositions (Fig. 3) can be partially attributed to a net equatorward flow of coastal surface currents in the Southern California Bight during the sampling periods. The gradient shows that local inputs of USA industrial lead were advected toward the border (Coronado and Imperial Beach) and that local inputs of Mexican industrial lead were advected south from the border

Table 1. Concentrations (pM) and isotopic composition of lead ($\bar{x} \pm 2\sigma$) in surface waters, aerosols, sewage, and gasolines collected along the Southern California Bight.

Station number	Location	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	[Pb]
Coastal stations (2-45 km offshore; June 1988)					
1	32°30.4'N; 117°10.4'W	18.502 ± 0.009	0.8433 ± 0.0002	2.0654 ± 0.0006	57
2	32°28.5'N; 117°17.2'W	18.406 ± 0.091	0.8481 ± 0.0016	2.0660 ± 0.0009	42
3	32°21.3'N; 117°33.1'W	18.528 ± 0.009	0.8423 ± 0.0002	2.0669 ± 0.0007	36
4	31°43.0'N; 116°45.1'W	18.614 ± 0.018	0.8397 ± 0.0002	2.0639 ± 0.0004	28
5	31°38.4'N; 116°50.7'W	18.351 ± 0.033	0.8484 ± 0.0009	2.0683 ± 0.0009	34
6	30°55.8'N; 116°22.1'W	18.406 ± 0.013	0.8482 ± 0.0002	2.0782 ± 0.0006	21
7	30°51.3'N; 116°30.0'W	18.433 ± 0.022	0.8464 ± 0.0002	2.0703 ± 0.0005	20
8	30°43.4'N; 116°42.7'W	18.608 ± 0.013	0.8381 ± 0.0002	2.0632 ± 0.0005	25
9	30°28.9'N; 116°04.6'W	-----	0.8460 ± 0.0016	2.0649 ± 0.0009	18
10	30°25.8'N; 116°11.0'W	18.365 ± 0.030	0.8480 ± 0.0003	2.0748 ± 0.0004	25
11	30°17.9'N; 116°27.0'W	18.472 ± 0.011	0.8444 ± 0.0003	2.0687 ± 0.0006	26
Nearshore stations (<0.1 km offshore; June 1989)					
	Coronado	18.709 ± 0.031	0.8350 ± 0.0298	2.0434 ± 0.0324	59
	Imperial Beach	18.622 ± 0.094	0.8371 ± 0.0403	2.0541 ± 0.0298	44
	US-Mexico Border	18.779 ± 0.016	0.8331 ± 0.0185	2.0579 ± 0.0128	129
	Punta Bandera	18.756 ± 0.030	0.8330 ± 0.0030	2.0569 ± 0.0033	290
	San Diego Bay	18.730 ± 0.032	0.8388 ± 0.0324	2.0361 ± 0.0371	120
Aerosols					
	Los Angeles, CA (March, 1990)				
		18.903 ± 0.078	0.8255 ± 0.0082	2.0285 ± 0.0086	----
		18.911 ± 0.170	0.8334 ± 0.0062	2.0436 ± 0.0066	----
	Santa Barbara, CA (November, 1990)				
		18.980 ± 0.041	0.8227 ± 0.0058	2.0221 ± 0.0113	----
		18.832 ± 0.013	0.8298 ± 0.0029	2.0362 ± 0.0029	----
		18.810 ± 0.007	0.8311 ± 0.0014	2.0393 ± 0.0013	
	Mexico City, Mexico (June, 1989)				
		18.755 ± 0.008	0.8336 ± 0.0001	2.0611 ± 0.0003	----
		18.754 ± 0.009	0.8338 ± 0.0001	2.0610 ± 0.0003	----
		18.614 ± 0.019	0.8321 ± 0.0004	2.0504 ± 0.0011	----
	Ensenada, Mexico (June, 1989)				
		18.766 ± 0.006	0.8320 ± 0.0011	2.0542 ± 0.0025	----
		18.752 ± 0.006	0.8318 ± 0.0010	2.0531 ± 0.0025	----
Sewage					
	San Diego, CA	18.856 ± 0.017	0.8283 ± 0.0020	2.0335 ± 0.0095	----
	Tijuana, Mexico	18.797 ± 0.004	0.8308 ± 0.0015	2.0455 ± 0.0031	----
Mexican Gasolines					
	EXTRA	18.731 ± 0.009	0.8306 ± 0.0016	2.0488 ± 0.0033	----
	NOVA	18.689 ± 0.003	0.8318 ± 0.0008	2.0547 ± 0.0013	----

Table 2. Lead fluxes in moles day⁻¹ and percentages (in parentheses) into the Southern California Bight.

Year	Sewage	Upwelling	Particle flux	Atmospheric	Advection
1975	21	624	1848	1683	4176
	(< 1)	(15)	(44)	(40)	
1988	6	624	504	234	1368
	(< 1)	(46)	(37)	(17)	

surface waters in the bight (WINANT and BRATKOVICH, 1981; LYNN and SIMPSON, 1990) and it corroborates recent measurements of the southward dispersion of industrial silver in nearshore surface waters in the bight (SAÑUDO-WILHELMY and FLEGAL, 1992). Some northerly flow may have also occurred during those periods, as indicated by the isotopic composition gradients of nearshore waters along the USA-Mexico border.

The longshore gradient in lead isotopic composition is partially attributable to the rapid scavenging of lead within

the bight. The residence time of lead in the bight is ≤ 60 days (SAÑUDO-WILHELMY and FLEGAL, 1992), and mass balance calculations indicate that the particulate lead flux accounts for 37% of the lead input into the area (Table 2). That flux estimate is consistent with calculations of the primary productivity required to sustain the particulate lead flux in the bight, based on the lead content of plankton relative to phosphorous (MARTIN et al., 1976; MICHAELS and FLEGAL, 1990) and POC production in the bight (HOLM-HANSEN et al., 1966). The POC production ($0.95 \text{ g m}^{-2} \text{ day}^{-1}$) required to

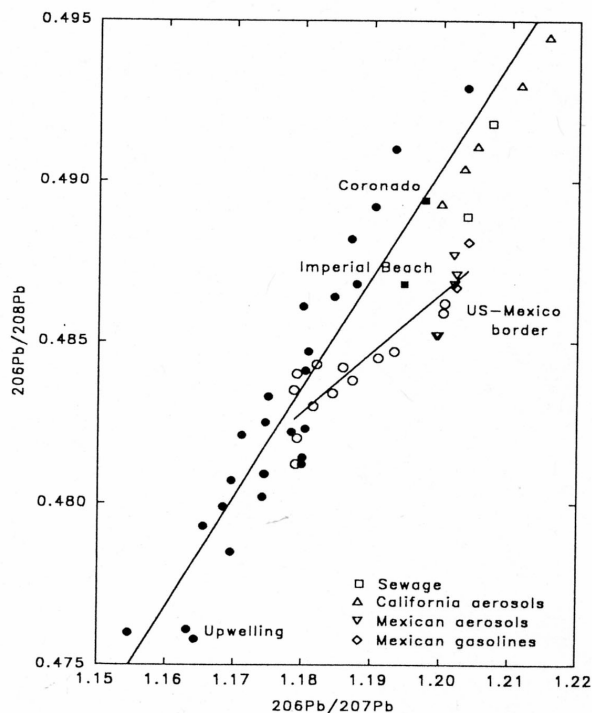


FIG. 2. $^{206}\text{Pb}/^{208}\text{Pb}$ vs. $^{206}\text{Pb}/^{207}\text{Pb}$ of surface waters collected north (■) and south (○) of the USA-Mexico border (Table 1). Stable lead isotopic composition (●) measured in coastal waters of California (USA) are from FLEGAL et al. (1989). Lead isotopic composition of anthropogenic sources (Table 1) are plotted for comparison.

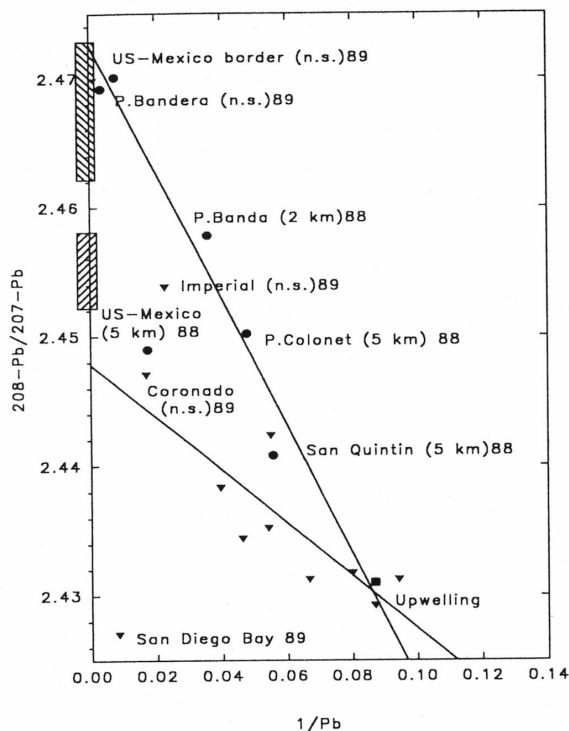


FIG. 3. $^{208}\text{Pb}/^{207}\text{Pb}$ vs $1/[\text{Pb}]$ of surface nearshore (n.s.) and coastal (5 km) waters collected north (\blacktriangledown) and south (\bullet) of the USA-Mexico border from FLEGAL et al. (1989) and (Table 1). Lead isotopic composition of anthropogenic sources from California (\square) and Mexico (\square) (Table 1) are shown by the hatched areas.

sustain the particulate lead flux is very close to the high primary production ($\approx 1.0 \text{ g C m}^{-2} \text{ day}^{-1}$) measured in early summer in the bight (EPPLEY, 1992). Therefore, the variation in lead isotopic composition of surface waters appears to be due, in part, to the efficiency of natural scavenging processes within the bight.

Finally, the anomalous isotopic composition ($^{208}\text{Pb}/^{207}\text{Pb} = 2.427$) of surface waters collected from San Diego Bay in 1989 (Table 1; Fig. 3) evidences the persistent cycling of contaminant lead within that embayment. The lead appears to be primarily derived from previous industrial inputs to San Diego Bay ($^{208}\text{Pb}/^{207}\text{Pb} = 2.431$; PATTERSON et al., 1976) prior to the elimination of wastewater discharges to the bay, which occurred in 1964 (P. MICHAEL, pers. commun.). This is consistent with the proposed remobilization of lead from estuarine sediments that appears to occur in San Francisco Bay (RIVERA-DUARTE and FLEGAL, 1993), as well as with the apparent remobilization of copper from contaminated sediments in San Diego Bay (FLEGAL and SAÑUDO-WILHELMY, 1993). However, the distinct isotopic composition of lead in San Diego Bay shows that it was not a source of

lead to surface waters of the bight during our sampling periods (Fig. 3).

CONCLUSIONS

The initial analyses of lead concentrations and isotopic compositions of surface waters in the Southern California Bight by Patterson and his associates in the 1970s established a benchmark for future studies of the biogeochemical cycling of lead within that area. Those data were used in this study to document a threefold decrease in lead concentrations within the bight over thirteen years. That estimated decline was corroborated by mass balance calculations, which also indicated that upwelling is now the primary source of anthropogenic lead to the bight. The isotopic analyses indicated that surface waters in the southern reach of the bight are now being contaminated by contemporary emissions of industrial lead from Mexico and that surface waters in San Diego Bay are now being contaminated by industrial lead previously deposited in the bay nearly three decades ago. These analyses suggest that lead concentrations in semi-enclosed bays and estuaries may remain elevated for protracted periods (e.g., decades) in spite of reductions in wastewater discharges to those areas, while lead concentrations in coastal waters may be rapidly reduced within a period of months.

Acknowledgments—We thank P. Ritson and D. Smith for their support with the isotopic analyses. We are grateful to J. P. Gallo-Reynoso (Universidad Nacional Autónoma de México) for collecting aerosols in Mexico City and to J. A. Segovia-Zavala (Universidad Autónoma de Baja California) for allowing our participation on the cruise ECOBAC I. Constructive comments were provided by M. Kretzmann, E. Boyle, and two anonymous reviewers. The research was supported by grants from the NSF (OCE-H612113), University of California Toxic Substances Research and Teaching Program, Mineral Management Service.

Editorial handling: T. M. Church

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The Department of the Interior Mission

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering sound use of our land and water resources; protecting our fish, wildlife, and biological diversity; preserving the environmental and cultural values of our national parks and historical places; and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to ensure that their development is in the best interests of all our people by encouraging stewardship and citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in island territories under U.S. administration.



The Minerals Management Service Mission

As a bureau of the Department of the Interior, the Minerals Management Service's (MMS) primary responsibilities are to manage the mineral resources located on the Nation's Outer Continental Shelf (OCS), collect revenue from the Federal OCS and onshore Federal and Indian lands, and distribute those revenues.

Moreover, in working to meet its responsibilities, the **Offshore Minerals Management Program** administers the OCS competitive leasing program and oversees the safe and environmentally sound exploration and production of our Nation's offshore natural gas, oil and other mineral resources. The **MMS Royalty Management Program** meets its responsibilities by ensuring the efficient, timely and accurate collection and disbursement of revenue from mineral leasing and production due to Indian tribes and allottees, States and the U.S. Treasury.

The MMS strives to fulfill its responsibilities through the general guiding principles of: (1) being responsive to the public's concerns and interests by maintaining a dialogue with all potentially affected parties and (2) carrying out its programs with an emphasis on working to enhance the quality of life for all Americans by lending MMS assistance and expertise to economic development and environmental protection.