

Trace Metals in Seabirds, Steller Sea Lion, and Forage Fish and Zooplankton from Central California

WILLIAM J. SYDEMAN* and WALTER M. JARMAN†

*Point Reyes Bird Observatory, 4990 Shoreline Highway, Stinson Beach, CA 94970, USA

†Energy and Geoscience Institute, Civil and Environmental Engineering, University of Utah, Salt Lake City, UT 84106, USA

We studied concentrations of the trace metals, aluminum (Al), chromium (Cr), iron (Fe), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), silver (Ag), cadmium (Cd), and mercury (Hg), in krill (*Euphausia pacifica* and *Thysanoessa spinifera*), two species of fish (short-bellied rockfish *Sebastes jordani* and northern anchovy *Engraulis mordax*), four species of marine bird (Common Murre *Uria aalge*, Brandt's Cormorant *Phalacrocorax penicillatus*, Rhinoceros Auklet *Cerorhinca monocerata*, and Pigeon Guillemot *Cepphus columba*) and a pinniped, (Steller sea lion *Eumetopias jubatus*) from the Gulf of the Farallones, central California in 1993. Geometric mean levels of some trace elements in Steller sea lions were elevated (Cu, 91.0 mg/kg dry weight; Hg, 19.0 mg/kg; Se, 4.1 mg/kg). Levels of Hg in Pigeon Guillemot (3.5 mg/kg) were also elevated. Mercury increased whereas Pb decreased with increasing trophic level in the Gulf of the Farallones food web. Selenium levels were highest for krill and sea lions, and intermediate for fish and birds occupying mid trophic levels. Results indicate little to relatively high trace metal contamination of upper trophic level marine wildlife in the central California coastal marine ecosystem. © 1998 Elsevier Science Ltd. All rights reserved

Introduction

In central California, planned ocean dumping of San Francisco Bay dredge spoils has raised concerns that trace metals may pose a hazard to the marine ecosystem. To establish (i) a baseline prior to implementation of a dredge-spoil dumping program and (ii) relationships between metals and marine food web constituents, we investigated concentrations of the metals aluminum (Al), chromium (Cr), iron (Fe), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), silver (Ag), cadmium (Cd), and mercury (Hg) in seabirds, a marine mammal and some of their prey in the Gulf of the Farallones National Marine Sanctuary (see also Jarman *et al.*, 1996, 1997; Sydeman *et al.*,

1997). Four species of seabird and one species of pinniped were studied: Common Murre (*Uria aalge*), Brandt's Cormorant (*Phalacrocorax penicillatus*), Rhinoceros Auklet (*Cerorhinca monocerata*), and Pigeon Guillemot (*Cepphus columba*), and Steller sea lion (*Eumetopias jubatus*). Based on previous studies of seabird and marine mammal diet (Jones, 1982; Briggs *et al.*, 1988; Ainley *et al.*, 1990), the following prey species were selected: krill (a combination of *Euphausia pacifica*, *Thysanoessa spinifera*, and *T. gregaria*), juvenile (0 age-class) short-bellied rockfish (*Sebastes jordani*) and adult northern anchovy (*Engraulis mordax*). We compared results with other studies on similar organisms in this and other marine ecosystems.

Materials and Methods

Sample collection

During the seabird breeding season (April–June) of 1993, we collected seabird eggs from Southeast Farallon Island, California (SEFI: 37°N, 123°W). Sea lion tissue samples were from dead pups collected at either Año Nuevo Island, California (ANI: 36°N, 123°W; $n = 6$) or SEFI ($n = 2$); ANI is located ~90 km south of SEFI. Samples of fish were obtained by capturing Rhinoceros Auklets on SEFI as they returned with prey at dusk to feed their chicks. We obtained five krill samples from National Marine Fisheries Service during rockfish stock recruitment surveys conducted in the Gulf of the Farallones, February 1994. One krill sample was also obtained from a fresh Western Gull regurgitation collected on SEFI in June 1993.

Data analysis

Owing to relatively small sample sizes, samples from different collection locations were pooled. In the text, concentrations are reported as geometric means (GM) on a mg/kg dry weight basis. All data were normally distributed, except Hg and Pb, which were log trans-

formed prior to statistical tests. We tested for differences between species using ANOVA followed by pairwise contrasts (Tukey's test) using Minitab: Release 9 for Windows (Minitab Inc., 1993). Statistical significance was assumed when $P < 0.05$.

Trace metal analysis

We analyzed individual seabird eggs and sea lion liver tissue. Generally, only Hg, Se, and possibly Pb are passed from the laying female to eggs (Leonzio and Massi, 1989), therefore, we limited our analyses to Hg, Se, and Pb for seabird eggs. Whole bodies (> 5) of short-bellied rockfish, northern anchovy, and krill were combined and homogenized to prepare composite samples for analyses. Laboratory analyses were performed by Analytical Service Laboratories, Ltd, Vancouver, British Columbia, Canada. Samples were prepared for analysis by nitric acid/hydrogen peroxide digestion. Extracts were bulked to volume using deionized/distilled water and analyzed by the following techniques:

1. Aluminum, copper, and iron were analyzed using a Thermo Jarrel Ash Model ICAP61 simultaneous inductively coupled argon plasma spectrophotometer interfaced with an IBM PS/2 286 data acquisition system (U.S. EPA Method 6010).
2. Arsenic and selenium were analyzed using a Perkin-Elmer Model 5000 dual-beam atomic absorption spectrophotometer coupled to a Perkin-Elmer Model MHS-20 automated hydride generation system (U.S. EPA Method 7000).

3. Cadmium, chromium, and lead were analyzed using a Varian Model Spectra AA-300 single-beam atomic absorption spectrophotometer equipped with an automatic Zeeman background-corrected electrothermal atomizer (U.S. EPA Method 7000).
4. Mercury was analyzed using a Pharmacia Model U.V. mercury monitor equipped with a 30-cm absorption cell (U.S. EPA Method 7000).
5. Silver was analyzed using a Perkin-Elmer Model 2380 dual-beam atomic absorption spectrophotometer flame model equipped with an automatic deuterium background correction (U.S. EPA Method 7000).

Results

Concentrations of trace metals in marine birds, Steller sea lions and some of their prey from the Gulf of the Farallones, central California are summarized in Table 1. Aluminum concentrations differed significantly between krill, fish, and sea lions (ANOVA: $F_{3,23} = 5.44$, $P = 0.007$), but pairwise comparisons established that only krill and sea lions were statistically different (Tukey's test, $P < 0.05$). Arsenic levels were also significantly different between species (ANOVA: $F_{3,23} = 25.0$, $P < 0.001$); as with Al, As was found in greater abundance at lower trophic levels. Cadmium and chromium levels were not statistically different between krill, fish, and sea lions (ANOVA: $F_{3,23} = 0.41$, $P = 0.747$ and $F_{3,23} = 2.03$, $P = 0.142$, respectively). Copper levels were statistically different between species (ANOVA: $F_{3,23} = 6.75$, $P = 0.003$).

TABLE 1

Metal concentrations for samples of zooplankton, fish, birds and marine mammals in the Gulf of the Farallones food web. Values are reported in mg/kg dry weight (NM = not measured)

	Krill		Short-bellied rockfish		Northern anchovy	
	GM ± SD	N	GM ± SD	N	GM ± SD	N
Aluminium (Al)	62.0 (42-92)	6	52.0 (32-84)	5	36.0 (20-63)	5
Arsenic (As)	2.6 (1.8-3.8)	6	2.3 (2.2-2.4)	5	3.5 (2.8-4.4)	5
Cadmium (Cd)	2.4 (2.2-2.7)	6	0.7 (0.52-1)	5	0.9 (0.73-0.99)	5
Chromium (Cr)	0.2 (0.1-0.26)	6	4.7 (1.2-18)	5	5.8 (1.1-30)	5
Copper (Cu)	46.0 (32-65)	6	4.9 (4-6)	5	4.8 (3.8-6)	5
Iron (Fe)	17.0 (11-26)	6	230.0 (150-360)	5	140.0 (82-220)	5
Lead (Pb)	0.6 (0.31-1.3)	6	0.4 (0.24-0.74)	5	0.4 (0.08-1.6)	5
Mercury (Hg)	0.0 (0.03-0.03)	6	0.04 (0.04-0.04)	5	0.1 (0.04-0.05)	5
Selenium (Se)	3.2 (2.9-3.5)	6	1.6 (1.5-1.7)	5	0.9 (0.76-1.1)	5
Silver (Ag)		0		0		0
	Rhinoceros Auklet	N	Brandt's Cormorant	N	Pigeon Guillemot	N
Aluminium (Al)	NM		NM		NM	
Arsenic (As)	NM		NM		NM	
Cadmium (Cd)	NM		NM		NM	
Chromium (Cr)	NM		NM		NM	
Copper (Cu)	NM		NM		NM	
Iron (Fe)	NM		NM		NM	
Lead (Pb)	0.25 (0.14-0.44)	9	0.33 (0.11-0.97)	11	0.21 (0.11-0.42)	11
Mercury (Hg)	1.6 (1.2-2.1)	15	1.3 (0.61-2.6)	15	3.5 (2.2-5.5)	15
Selenium (Se)	2 (1.7-2.3)	15	2.3 (1.8-3)	15	2.3 (1.9-2.7)	15
Silver (Ag)	NM		NM		NM	

continued overleaf

TABLE 1 continued

	Common Murre	N	Steller Sea Lion	N
Aluminium (Al)	NM		24.0 (16–35)	2
Arsenic (As)	NM		0.4 (0.27–0.6)	8
Cadmium (Cd)	NM		15.0	1
Chromium (Cr)	NM		0.2 (0.14–0.4)	4
Copper (Cu)	NM		91.0 (34–240)	8
Iron (Fe)	NM		1800.0 (1100–2800)	8
Lead (Pb)	0.1 (0.07–0.12)	7	0.2 (0.11–0.36)	2
Mercury (Hg)	0.7 (0.45–0.95)	15	19.0(4.8–73)	8
Selenium (Se)	2.1 (1.7–2.6)	15	4.1 (1.1–16)	8
Silver (Ag)	NM		0.3 (0.19–0.62)	7

This was due to the extremely high levels of Cu found in sea lions; levels between krill and fish were not different (Tukey's test, $P > 0.05$). Iron levels also were statistically different (ANOVA: $F_{3,23} = 25.0$, $P < 0.001$), but, as with Cu, only the sea lion concentrations were significantly different from krill and fish. Silver was only detected in sea lions.

Lead, mercury and selenium were measured in all species, including seabirds. Lead showed significant differences between species (Table 1; ANOVA: $F_{7,83} = 6.14$, $P < 0.001$). Lead was detected in 63% of the seabird eggs and Pb levels differed significantly among bird species (Table 2; ANOVA: $F_{3,33} = 4.21$, $P = 0.013$). Pair-wise comparisons showed that levels of Pb in Common Murre eggs were significantly lower than levels in other bird species (Tukey's test, $P < 0.05$). Lead was detected in only 25% of the sea lion samples. Mercury also differed significantly between species (ANOVA: $F_{7,83} = 108.0$, $P < 0.001$), with concentrations increasing with increasing trophic level. Mercury was found in all seabird eggs and also differed significantly among the bird species (Table 2; ANOVA: $F_{3,44} = 21.06$, $P < 0.001$). Pairwise comparisons revealed similar values in Brandt's Cormorant and Common Murre eggs, but significant differences were found between these species and Rhinoceros Auklet and Pigeon Guillemot. Additionally, values from auklet and guillemot eggs differed (Tukey's test, $P < 0.05$). Relatively high levels of Hg were detected in all sea lion samples: one fetus measured 307 mg/kg, a significantly elevated value. Concentrations of Se were high in krill and sea lions and lower in seabirds, with levels differing significantly between species (ANOVA: $F_{7,83} = 6.93$, $P < 0.001$). Se was detected in all seabird eggs, but levels did not differ significantly between bird species ($P > 0.05$). Elevated Se levels were found in sea lion liver samples. In the fetus containing highly elevated Hg, the Se level also was very high (83.5 mg/kg).

Discussion

In krill, Al and Cu concentrations in our study were higher than levels reported by Martin and Knauer (1973) based on samples from Monterey Bay in the early 1970s, but were below 100 mg/kg dry weight

(GM), a level at which Bruland *et al.* (1991) suspected cross-contamination. Concentrations of Cd, Fe, Hg, and Pb in krill were similar or lower than those reported elsewhere (Martin and Knauer, 1973; Rideout *et al.*, 1989; Rainbow, 1989). Due to automobile emissions and industrial effluent (Veron *et al.*, 1994), Pb levels in the north Atlantic Ocean are typically higher than concentrations in the Pacific Ocean (Fowler, 1990); this may explain why Pb levels in krill from the Pacific Ocean (Martin and Knauer, 1973; this study) were lower than those from the north Atlantic Ocean (Rideout *et al.*, 1989).

We found no comparative information on Al from marine fish. Previously reported levels of As, Cd, and Cu in fish were within the ranges found in this study (Eisler, 1981a; Thompson, 1990). Iron concentrations in fish in this study were considerably higher and showed a wider range of values than has been found in other studies (Thompson, 1990; Sharif *et al.*, 1991). Concentrations of Pb were well below the 2 mg/kg dry weight typically associated with fish in unpolluted waters (Thompson, 1990) and levels of Hg and Se were also low (Eisler, 1981a; Thompson, 1990).

Seabirds

Concentrations of Pb and Se from the seabird eggs in this study were comparable to other studies (Eisler, 1981b; Thompson, 1990). Selenium values obtained in this study were orders of magnitude lower than levels found in waterfowl experiencing selenium toxicosis at Kesterson Reservoir, California (Ohlendorf *et al.*, 1990); however, this comparison is problematic because the relative concentrations of Se in livers versus eggs is unknown in these species. Mercury concentrations in seabird eggs in the Gulf of the Farallones, however, are worthy of additional examination. Thompson (1990) suggested that levels of Hg in seabird eggs rarely exceed 2.5 mg/kg dry weight, but levels of Hg in this study ranged from 1.6–3.5 mg/kg. In particular, the value obtained for Pigeon Guillemot is of interest and deserves further investigation and monitoring.

Steller sea lion

An important finding in this study concerns Cu and Hg in Steller sea lions. In California, Steller sea lions are a threatened species protected under the Endangered Species Act. Generally, copper is found in low abundance in marine mammals (Eisler, 1981c), but elevated levels have been associated with premature parturition in other sea lion species (Martin *et al.*, 1976). In this study, high Cu levels were detected in all samples (Table 2), and one premature fetus contained a level of 309 mg/kg. Hg concentrations were also elevated. On SEFI, the Steller sea lion population is declining (Sydeman and Allen, in press). The population suffers from generally low natality rates and premature parturition (Hasting and Sydeman, 1998).

Both the population decline and irregular reproductive activities remain unexplained. The high levels of Cu and Hg found in this study warrant further research to determine if there is an association between elevated trace metal concentrations and decline in this population.

Aluminum was detected in only 25% of the sea lion samples; reports of Al in marine mammals are scarce so it is not possible to provide comparisons with this study. Levels of As in marine mammals rarely exceed 5 mg/kg (Eisler, 1981c; Thompson, 1990) and As levels in sea lions in this study were within this range. In Steller sea lions from Japan, levels of Cd ranged from 0.5 to 6.5 mg/kg in young (1–9 year-old) animals (Thompson, 1990). In California sea lion (*Zalophus californianus*), Cd ranged from 5.7 to 90 (GM = 15) mg/kg in animals over 10 years old (Thompson, 1990). We detected Cd in only one sea lion liver sample (Table 2), and the level was relatively low in comparison to previous reports. In our study, Cr was detected in 50% of the sea lion samples, but in low concentrations. Levels of Fe in sea lion in this study were similar to levels reported for California sea lions (Thompson, 1990); iron levels in marine mammals can be high (up to 1000 mg/kg), which is apparently a physiological adaptation associated with deep-diving in these species.

Trophic level relationships

Cadmium has been reported to biomagnify in some ecosystems (Hawker, 1990), but this pattern was not established in this study. There are no other published reports on biomagnification or depletion of chromium in marine food webs. Concentrations of Pb apparently decreased with increasing trophic level in the Gulf of the Farallones. However, we sampled different tissues in each species (e.g. whole bodies of krill and fish, eggs of seabirds, and liver tissue of sea lions), which makes interpretation difficult. Levels of Pb in eggs are generally lower than in liver (Leonzio and Massi, 1989), therefore, the trend of decreasing Pb concentrations from krill to birds may be an artifact of changing the sample matrix from bodies to eggs. However, there was a significant decline in Pb levels between krill and sea lions, thereby reflecting bio-depletion of Pb. Mercury increased with increasing trophic level in the Gulf of the Farallones coastal marine ecosystem, as has been found elsewhere (Furness, 1993).

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