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Abstract

Trace metals in a marine bird food chain were investigated in the Chañaral area, downstream from the El Salvador copper mine, Chile. Beach deposits, algae and marine invertebrates showed a decreasing residue gradient for arsenic, copper, iron, lead, titanium and vanadium from the tailings discharge site on the edge of the visible tailing deposits. Cadmium was found in high levels in marine organisms at some reference sites. Observed metal levels in birds, except cadmium, were thought to be close to background levels and may reflect the presence of little contaminated prey for birds to feed upon in the tailing deposit area. Cadmium levels of some concern (40-90 ppm) were observed in Whimbrels (Numenius hudsonicus) and in sand crabs (Emerita analoga) (5-6 ppm). It is suggested that the cadmium pathway should be further investigated in the Whimbrel food chain.

Résumé

Nous avons investigué la présence de métaux lourds dans une chaine alimentaire du milieu marin dans la région de Chañaral, en aval de la mine de cuivre El Salvador au Chile. Les sédiments de la baie, les algues et les invertébrés marins avaient des taux d'arsenic, de cruivre, de fer, de plomb, de titanium et de vanadium décroissant du site de décharge des résidus miniers jusqu'à la limite visible des résidus. Nous avons décelé des taux élevés de cadmium dans les organismes marins de certains sites de référence. Les taux de métaux (à l'exception du cadmium) dans les oiseaux étaient près des niveaux présent dans l'environment, suggérant que dans les environs de dépot miniers, la plupart des proies étaient peu contaminéés. Des niveaux de cadmium inquiétants (40-90ppm) furent détectés dans le Courlis Corlieu (Numenius hudsonicus) et dans le crabe sable (Emerita analoga) (5-6ppm). La chaine alimentaire menant au Courlis Corlieu devrait être examinée afin de déterminer le chemin du cadmium.

Introduction

Untreated mining wastes, at the rate of 39,000 tons per day, are discharged through a semi-artificial canal directly to the marine shore from the El Salvador copper mine in northern Chile (Castilla and Nealler 1978). The tailings were deposited on a sandy beach near Chañaral between 1938 and 1974 and since 1975 at Caleta Palito, 8 km north of Chañaral (Fig. 1). Total biological loss at the sandy beach macrofauna occurred at the latter site as a result of smothering by tailing sediments (Castilla 1983). Massive fish and mollusc mortality was observed by local inhabitants at the new discharge site a few days after its establishment in 1975 (Castilla and Nealler 1978).

Since no chemical analyses of marine organisms have been conducted along the 20 km beach area contaminated with tailings, a pilot study was initiated in the last weeks of November 1981 and March 1982 to determine trace metal residues in beach deposits, algae, marine invertebrates, marine birds and prey from their stomachs. The results of the analyses are presented here.

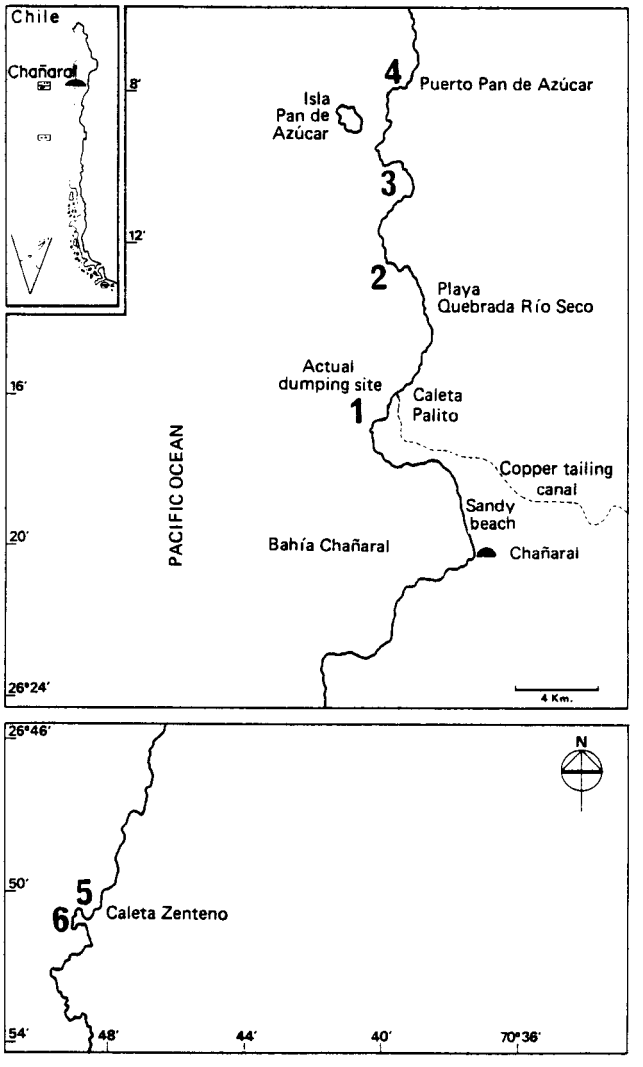

Figure 1. Shoreline between Puerto Pan de Azúcar and Caleta Zenteno showing the sampling stations (numbers 1 to 6 and sandy beach near Chañaral).

Methods

Beach deposit samples were collected at beach sites north of Chanaral, and were located at 1) the tailings discharge site, 2) the northern edge of the visible contaminated area, 3) a bay, 4 km north of station 2, 4) Puerto Pan de Azúcar, another bay 8 km north of station 2, and 5) an accessible beach locality about 60 km south of Chañaral (Fig. 1). Algae (Enteromorpha sp.) were sampled at stations 1, 2, 4 and at station 6, a small beach about 62 km south of Chañaral. Limpets (Collisella spp.) grazing on Enteromorpha and snails (Littorina peruviana), sand crabs (Emerita analoga) and locos (Concholepas concholepas) were also sampled. Enteromorpha and L. peruviana are upper and mid rocky intertidal organisms, C. concholepas is found in the lower rocky intertidal and adjacent subtidal zone, and the sand crab (E. analoga) is mainly a lower intertidal sandy beach organism.

Marine birds were collected with a shotgun (under permit) at the above mentioned stations, as well as at Chañaral beach and at a beach near Concepción, 1200 km to the south of Chañaral. The Concepción site was chosen as a previous study showed mercury residue levels to be present in the marine organisms (Hoffmann 1979). Concepción samples were for determining mercury residues in marine bird tissues as well as serving as a reference sampling station. Birds collected for analysis were the Dominion or Kelp Gull (Larus dominicanus), the most abundant resident gull in the area, the Grey Gull (Larus modestus), which nests in the Chilean desert but feeds on the coast, the Franklin's Gull (Larus pipixcan), a migrant from the North American prairies, the Whimbrel (Numenius hudsonicus) and the Sanderling (Calidris alba), two shorebird species from arctic North America, a resident oystercatcher (Haematopus ostralegus), the Humboldt Penguin (Spheniscus humboldti), which nests in the thousands with the Kelp Gull on an island near Puerto Pan de Azúcar, and the Turkey Vulture (Cathartes aura), which is

predominantly a beach scavenger. All birds were collected in November except Whimbrels and Sanderlings which were sampled both in November and March for comparative purposes.

Bird livers and stomachs were removed immediately after collection, and these tissues were examined to ensure that no shot fragments remained in the samples for analyses. Bird livers, stomachs, invertebrates and fishes were frozen within two hours after collection. In the laboratory, bird livers, beach deposit, Enteromorpha, whole marine invertebrates, and identifiable food items of the birds were analyzed for silver, arsenic, aluminium, beryllium, calcium, cadmium, cobalt, chromium, copper, iron, potassium, magnesium, manganese, molybdenum, sodium, nickel, phosphorus, lead, titanium, zinc and zirconium by Barringer Magenta Ltd. of Rexdale, Ontario. Only arsenic, cadmium, copper, iron, lead, titanium and vanadium residues will be shown here, as residue levels of those elements were generally higher (except titanium) in deposits at the tailings discharge site than anywhere else. Cobalt and molybdenum residue levels were also higher in beach deposit at the discharge site, but are not included here as levels of those elements were mostly below 0.5 ppm levels in the marine invertebrates, marine birds and their food. Besides the above elements, mercury residue levels are shown in birds and their food. Trace metals were analyzed by flameless atomic absorption and are shown in parts per million (ppm) wet weight. The accuracy of the analytical procedures were checked against multi-element analyses of NBS bovine liver, NBS oyster, NBS tuna and NBS spinach leaves, and Canadian rock standard, Sy-2. The results were accurate except for chromium, molybdenum, lead and vanadium at levels less than 1 ppm (R.J. Norstrom, correspondence).

Results

Metal residues in beach deposits, algae and marine invertebrates

Arsenic, cadmium, copper, iron, lead, titanium and vanadium residue show a decreasing residue gradient in beach deposit from the discharge site (1) to the nearest reference station (3), but those metals became elevated again at Puerto Pan de Azúcar (4). Cadmium, iron, titanium and vanadium residues were similarly elevated at the reference site (5) 50 km south of Chañaral. The elevated metal levels at Puerto Pan de Azúcar can perhaps be attributed to an ore processing plant which ceased operation about 50 years ago. Elevated cadmium, iron, titanium and vanadium levels in beach deposit at site 5 are not understood, unless the above elements have naturally high residue levels at that beach.

Entromorpha, and limpets grazing on that algae, show a decrease in some metal residues, except cadmium, from the discharge to reference sites (Table 1). Enteromorpha was the only visible aquatic organism inhabiting the discharge site suggesting tolerance to high metal levels and smothering. Littorina peruviana and Emerita analoga indicate a similar residue trend as Enteromorpha and limpets, except for elevated titanium residues at control site 5. Higher titanium and cadmium levels in some organisms at site 5 are in agreement with elevated residues of those elements in beach deposits at that location.

Metal residues in the bird diets

Fishes obtained from Larus dominicanus indicated relatively low cadmium, copper and iron levels compared to those in crabs and snails obtained from Larus modestus, Haematopus ostralegus and Numenius hudsonicus (Table 2). Emerita analoga from birds at Puerto Pan de Azúcar had the highest cadmium and copper levels which are in agreement with residue levels in crabs collected

Table 1. Comparison of residues of seven metals in beach deposit, Enteromorpha, limpets, snails, crabs and "locos" along the coastline downstream of El Salvador copper mine, Chile. Sampling stations are shown in Figure 1.

Beach deposit and organisms analyzed, and sampling stations		Metal residues in ppm wet weight						
		As	Cd	Cu	Fe	Pb	Ti	V
Beach deposit	1	57.6	10	5000	10300	50	5670	222
	2	17.7	<1	813	6430	20	1490	58.8
	3	1.4	3	8.4	4580	<0.5	1290	16.6
	4	5.1	3	231	25050	5	1955	58.3
	5	0.8	6	5.8	30450	<0.5	9045	103
Enteromorpha	1	1.4	<1	1260	3370	47.3	35.6	8.2
	2	2.1	<1	197	1700	5.5	20.4	2.9
	4	0.3	<1	13.2	625	<0.5	23.0	2.2
	6	-	0.6	0.8	121	<0.3	8.5	<0.02
Collisella spp.	2	0.07	2.2	245	228	7.7	0.8	0.35
grazing on	4	0.05	3.7	4.9	78.6	<0.5	0.3	0.20
Enteromorpha	5	0.03	8.0	0.9	26.2	<0.5	0.14	0.13
Littorina	2	0.08	1.1	834	73.3	2.5	0.8	0.13
peruviana	4	0.09	1.3	395	48	<0.5	0.4	<0.05
	5	0.06	4.4	86	80	1.0	4.6	0.35
Concholepas	3	0.07	0.9	17	59.4	<0.5	1.6	0.5
concholepas	4	0.02	2.2	4.6	7.1	<0.5	1.2	0.1
Emerita analoga	3	1.1	2.2	65.8	122	<0.3	0.6	<0.02
	4	1.1	5.4	35.5	100	<0.3	1.5	<0.02

directly from the beach (Table 2). Emerita analoga from birds at Concepción showed elevated mercury levels (Table 2). Lead is not shown in Table 2 as residue levels in birds and their food were generally less than 0.5 ppm.

Metal residues in birds

The most outstanding residue differences in birds concern cadmium (Table 3). Cadmium levels were particularly elevated in Larus modestus (22.8 ppm), Numenius hudsonicus from Puerto Pan de Azúcar (49.3 ppm in November, 89.7 ppm in March) and Whimbrels collected between the discharge site and Puerto Pan de Azúcar (32.2 ppm) and reference site 5 (38 ppm). The high cadmium levels encountered in those birds may relate to their diet consisting of Emerita analoga which in turn had elevated cadmium levels compared to other marine organisms (Tables 1 and 2). Since the highest cadmium residues in birds and marine organisms occurred at Puerto Pan de Azúcar and reference site 5, most cadmium contamination does not appear to be related to the present tailings discharge from the El Salvador copper mine, but may relate to former handling of ore at those locations or to naturally occurring high background levels of cadmium. High cadmium levels mostly occur in birds feeding on intertidal marine organisms rather than on fishes.

Arsenic, copper and iron residues in Numenius hudsonicus and arsenic in Calidris alba were somewhat elevated in March compared to November which suggests further contamination of those North American shorebirds with those metals while wintering on the Chilean coast.

Highest mercury residues in Numenius hudsonicus were from Concepción, which may relate to elevated mercury levels in Emerita analoga, on which the birds feed (Table 2). Mercury residue levels in Cathartes aura, collected from the tailing discharge site, were also higher than in other birds from the Chanaral region, and may relate to the Turkey Vulture's high trophic level in

Table 2. Comparison of arsenic, cadmium, copper, iron and mercury residues in fishes, crabs, and snails from stomachs of marine birds collected downstream from the El Salvador copper mine and at Concepción, Chile. Samples are from November 1981 except where indicated from March 1982. Dash indicates sample unanalyzed for mercury.

Food and sampling stations		Bird species	Metal residues in ppm wet weight				
			As	Cd	Cu	Fe	Hg
FISHES							
Clupea benticki	4	Larus dominicanus	0.05	0.9	2.1	47	-
Scombersox saurus stolatus	4	"	0.7	1.3	3.4	103	-
"	4	"	0.7	1.3	3.4	43	-
"	5	"	0.4	1.2	1.8	90	-
Isacia conceptionensis	4	"	0.7	0.8	0.8	47	-
CRABS							
Emerita analoga	4	Larus modestus	0.3	5.3	46.7	254	<1
"	4	"	0.8	5.7	30.0	403	<1
"	4	Haematopus ostralegus	0.8	5.7	24.4	489	<1
"	4	"	0.4	4.8	27.2	393	-
"	Concepción	Numenius hudsonicus	0.5	1.4	15.8	1880	4.3
"	Concepción	Larus pipixcan	0.1	1.0	12.2	630	4.5
SNAILS							
Littorina peruviana (March)	3	Numenius hudsonicus	0.6	2.6	86.4	31	-
Eatonina atacamae (March)	3	"	3.9	4.8	6.1	2530	-

Table 3. Comparison of residues of arsenic, cadmium, copper, iron and mercury in livers of marine and shore birds and Turkey Vultures feeding along the coastline downstream of the El Salvador copper mine and at Concepción, Chile. Residue range in parentheses. Samples are from November 1981 except where indicated from March 1982.

Bird species	Sampling locations	No. birds sampled	Average metal residues in ppm wet weight									
			As		Cd		Cu		Fe		Hg	
Larus dominicanus	2	2*	0.01		2.8	(2.8-2.9)	4.1	(3.8-4.3)	185	(75.296)	0.6	(0.58-0.64)
"	4	5	0.01		4.8	(2.6-7.9)	5.4	(3.8-4.3)	189	(59-312)	—	
"	5	5	0.01		9.1	(5.4-13.7)	5.1	(4.2-5.9)	202	(36-374)	0.7	(0.6-0.9)
"	Concepcion	3	0.01		4.1	(0.7-2.1)	3.6	(3.5-5.7)	283	(262-304)	0.5	(0.3-0.8)
Larus modestus	4	4	<0.01		22.8	(12-14)	6.2	(4-7.4)	160	(65-368)	0.2	(0.17-0.22)
Larus pipixcan	Chanaral beach	2	0.02	(0.01-0.03)	1.5	(1-2)	4.8	(4.7-4.8)	990	(879-1110)	0.2	(0.16-0.27)
"	5	1	0.01		3.6		5.5		652		0.7	
"	7	2	0.01		3.7	(3-4.4)	4.6	(4.3-4.9)	581	(563-599)	0.9	
Numenius P. hudsonicus	2	1	<0.01		1.0		7.8		360		0.7	
"	4	3	0.01		49.3	(24.6-65.7)	5.0	(3.9-5.7)	438	(251-665)	0.3	(0.2-0.4)
"	Concepcion	2	0.01		1.4	(0.8-2.1)	4.1	(3.6-4.6)	413	(371-456)	1.9	(1.9-2.0)
" (March)	1	1	0.07		7.9		7.5		1010		0.5	
" (March)	3	2	1.9	(1.1-2.7)	32.2	(7.3-57.1)	10.3	(7.1-13.5)	487	(391-582)	—	
" (March)	4	1	0.06		89.7		9.4		676		0.15	
" (March)	5	2	6.8		38.0	(20.7-55.3)	13.2	(8.7-17.8)	720	(370-1070)	—	
Calidris alba	2	2	0.02	(0.01-0.03)	4.2	(1-7.4)	10.0	(7.8-12.2)	331	(282-381)	0.7	(0.5-0.9)
"	5	1	0.04		0.8		9.2		330		0.9	
" (March)	3	4(pooled)	0.4		7.9		11.1		362		0.09	
" (March)	3	4(pooled)	0.3		7.6		11.5		528		0.08	
" (March)	3	4(pooled)	0.4		6.5		9.2		274		0.5	
Haematopus ostralegus	Chanaral beach	3	0.01		13.7	(8.4-19.9)	8.0	(6.8-8.6)	84.5	(81-86)	0.16	(0.13-0.22)
Spheniscus humboldti	4	1	0.01		0.08		25.1		41		0.08	
Cathartes aura	1	3	0.01		2.8	(1.6-4.3)	7.9	(7.6-10.1)	217	(185-322)	2.2	(1.2-4.2)

* Livers analyzed individually, except where indicated that they were pooled.

the coastal food chain. Turkey Vultures were observed to scavenge on dead birds and other vertebrates on the beaches.

Discussion

No gross ill effects were observed in birds during our investigation in the Chañaral region. Observed metal levels in birds, except cadmium, may represent normal background levels. Observed mercury levels were generally below those associated with mercury poisoning (Borg et al. 1969) and considerably lower than those reported for livers of ducks from contaminated areas of northwestern Ontario (Vermeer et al. 1973). The relatively low copper levels in birds in or near the tailing area, compared to high copper levels in beach deposit and Enteromorpha suggest low dietary uptake of this metal. Low copper residues in marine birds from the Chañaral area may be explained by the observation that most of the intertidal macrofauna died off during the establishment of the new discharge site in 1975 (Castilla and Nealler 1979), and left therefore little contaminated prey for the birds to feed upon.

Relatively high cadmium levels in birds, feeding on intertidal invertebrates, may derive from prey such as Emerita analoga. Although elevated, observed cadmium levels may not be acutely toxic to birds. Adult drake Mallards (Anas platyrhynchos) fed up to 200 ppm cadmium in the diet for three months survived with no loss of body weight, while laying hen Mallards fed 200 ppm cadmium also survived, but egg laying was suppressed at that concentration (White and Finley 1978). Bull et al. (1977) reported 290 ppm cadmium in the kidney of a single Northern Fulmar (Fulmarus glacialis) that was healthy and reproductively active. Although not acutely toxic, sublethal effects of cadmium in birds include growth retardation, anemia, and testicular damage (Hammons et al. 1978). Japanese Quail fed 75 ppm cadmium developed

bone marrow hypoplasia, anemia, and hypertrophy of heart ventricles at 6 weeks (Richardson et al. 1974). In Mallard ducklings fed 20 ppm dietary cadmium for 12 weeks, blood chemistry was altered, and mild to severe kidney lesions developed (Cain et al. 1983).

It is well known that bird livers and kidneys retain the highest percentage of cadmium in tissues (Anderson and Van Hook 1973, Dyer and Born 1974, White and Finley 1978, and Jacobs et al 1978). Cadmium residues in other tissues are relatively low compared to those in kidneys and livers (Dyer and Born 1974, White and Finley 1978). Most cadmium ingested by birds is not absorbed. For example, hens excreted 70-80 percent of a single oral dose of cadmium during the first 24 h and 90-93 percent by 96 h (Sell 1975). Cadmium retention varies with exposure time. Hens contaminated on a diet of 60 ppm cadmium for 20 days retained a significantly higher percentage of total cadmium intake (4%) than hens fed a single oral dose (2%) (Sell 1975). Cadmium, however, is retained much longer in the kidney, where it is deposited in the renal cortex and can result in patchy necrosis (Nicholson et al. 1983).

Cadmium levels in kidneys of seabirds and shorebirds appear to be about 3 times that found in their livers (Bull et al. 1977, Blomqvist et al. 1987). Blomqvist et al. (1987) found that cadmium concentrations in the kidney versus the liver tissues of Dunlins (Calidris alpina) and Curlew Sandpipers (C. ferruginea) were strongly linearly related. The highest observed cadmium level of 89.7 ppm in the liver of a Whimbrel in our study might correspond to a 270 ppm level in the kidney of the bird.

Although observed cadmium levels in this study may not be acutely toxic to birds, our sample is small, and the accumulation of cadmium in the marine bird food chain in northern Chile needs further investigation. It also should be determined if the birds acquired cadmium from background levels from beach

deposits, mining ore, phosphate deposits or from particles deposited by upwelling, a well known phenomenon occurring along the coasts of northern Chile and Peru. Cadmium levels in marine sediments from the Atlantic and Pacific Oceans range from 0.1 to 1.0 ppm with some marine phosphate deposits having cadmium levels ranging from 50 to 170 pmm (Caro 1964). The Chañaral coastal region may be ideal for further investigation of the cadmium pathway in the marine bird food chain, since shore feeding birds with high cadmium levels are accessible for observation. From other studies it appears that mostly pelagic seabirds, which are generally less accessible than shoreline foragers, accumulate high cadmium residue levels (Anderlini et al. 1973, Ottaway and Campbell 1976, Bull et al. 1971, Torwer et al. 1978). Emerita analoga, a common food item of avian intertidal foragers (see also Blokpoel et al. 1989), is widely distributed along the Pacific coast of North and South America and could be used as an indicator of dietary cadmium utilized by birds.

A study of cadmium in Whimbrels may have some urgency from the public health point as these birds are used for human consumption. A few birds with high cadmium levels may have no adverse effect, however, Whimbrels are commonly hunted in northern Chile and extensive consumption could have negative consequences.

Since the relatively high levels of cadmium observed in birds in this pilot study were completely unexpected, only bird livers were collected for analyses. In future research at these study sites, bird kidneys should also be analysed for cadmium residues, as these tissues retain the highest percentage of cadmium. Secondly, as during our brief investigation several selected reference sampling stations proved to be highly contaminated with metal residues from either industrial or natural sources, we suggest that in

future studies more reference stations be used for comparison with known contamination sites.

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