HEAVY METALS IN RIVERS AND SOILS OF CENTRAL CHILE

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ABSTRACT

Industrial and domestic waste waters in Chile are discharged without previous treatment into rivers and other inland waters which are used to irrigate agricultural lands. The present study reports on results obtained when analyzing inland waters for Cd, Cu,Zn, Hg and As. Copper content was found to be high in most of the rivers studied and its sources were identifiable copper mining wastewaters. Cadmium and Zn levels are above accepted levels in some instances, whereas Hg and As content of river waters studied were found to be within accepted levels.

The more reactive chemical forms of heavy metals in soils irrigated with polluted waters, as determined by sequential extraction, were found to be the most abundant ones. These forms are easily bio-available.

KEYWORDS

Heavy Metals, Copper, wastewaters, water pollution, soil pollution

INTRODUCTION

Chile occupies an area of approximately 850000 km² in the southern cone of South America. It is a long (appr. 4200 km) and narrow (average 120 Km) strip of land between 18° and 56° south. More than 50% of its 14 million population live in the 200 km long semi-arid area of the central part of the country between 32° and 34° south, limited by an up to 6000 m high Andean mountain range and an up to 2000 m high coastal range of mountains that fall abruptly into the Pacific ocean. Average width of this part of the country is less than 100 km. Average rainfall is between 350 and 400 mm per year with practically no rain between November and April. This area is crossed from east to west by three main river systems. The capital of the country, Santiago, with a 4.5 million population, is located in this area.

In Santiago, sewage and industrial wastewaters are not subjected to any treatment. Moreover, around 85% of the untreated waters are collected by a partially open ditch canal, the Zanjon de la Aguada (ZA), the rest being discharged into the Mapocho river. Both streams cross the central part of the city in an east-west direction. Untreated ZA waters are used to irrigate vegetable crops and surplus waters flow into the Mapocho river whose waters are in turn used to irrigate agricultural areas. The Mapocho is a tributary of the Maipo rivers. Thus domestic and industrial pollutants contained in these untreated wastewaters are transferred to soils and eventually may enter the food chain (Moon et. al, 1994; Lehman and Mills, 1994).

In this study we will be referring to pollution with some heavy metals, i.e. Cu, Cd, Zn and Hg and also As, of three river systems: the Aconcagua R. and Cachapoal R, north and south of Santiago respectively and the ZA-Mapocho-Maipo R. system in Santiago itself. These streams, excepting the Maipo river, are also subjected to pollution by wastewaters from three major copper mining activities.

The presence of microbial pathogens in the ZA-Mapocho R. system has been established (Castillo and Cordano, 1975) and is responsible for endemic entheric diseases and hepatitis, common in the Santiago Metropolitan are where vegetable crops irrigated with these waters are consumed. A first effort to treat these wastewaters has been made by installing a small deep-lagoon type treatment plant that can take care of sewage waters from a population of 80,000 and additional treatment plants are at the planning stage.

EXPERIMENTAL

Sampling sites were chosen according to the purpose of the evaluation. In the case of the 32 km long ZA canal four sites 0, 6, 12 and 18 km from the canal origin were selected, the last one at the point where the ZA enters the agricultural area where its waters are the only ones used to irrigate about 5000 hectares. Special attention was paid to the day of the week and the time of the day samples were collected, and sampling was repeated three times during the irrigation period (spring to fall seasons). Averages are reported, fluctuations from the mean being plus/minus 20% (Dixon and Chiswell, 1996).

River water samples were obtained from the center of the flow by inmersing acid washed polyethylene bottles to a depth of 50 cm, from locations where these are used to irrigate agricultural areas. The samples were passed through 0.45 um cellulose nitrate filters (APHA, 1989). Heavy metals in the filtrate were complexed with APDC (ammonium pyrrolidin dithiocarbamate) and the complex formed was extracted with a xylene-methyl isobutyl ketone mixture (Fawzy et al, 1979). After separating phases and mineralizing the organic phase, heavy metals were determined by Atomic Absorption Spectrometry (AAS) using a Perkin Elmer Model 1001B instrument. Heavy metals in the suspended matter fraction were also determined by AAS after treating the filters with a HCl/HNO_3 mixture at 80°C, cooling and filtering (Sabri et al., 1993).

Soils samples were obtained from: 1) areas irrigated exclusively with ZA waters and 2) similar soils irrigated with non polluted waters. Total metals in soils were determined by AAS after acid treatment (Baker and Amacher, 1982). Sequential extraction of heavy metals was performed using the procedure proposed by Elliot et al. (1990) extracting successively with 1M MgCl2 at pH7 (Exchangeable fraction); 1M sodium acetate at pH5 (Carbonate fraction); then a 1M oxalic acid -0.175 M ammonium oxalate mixture (Occluded fraction) and finally with a 0.1 M pyrophosphate solution (Organic fraction).

RESULTS

The data contained in the different tables show heavy metal pollution of river waters of central Chile. This is specially the case with the ZA canal (Table 1), which collects domestic sewage and industrial waste waters from Santiago. Figures show up to 8 ppb of Cd, 500 ppb of Cu, 200 ppb Zn. The amount of, e.g., Cu found at different times of the day at the same site may vary more than 30%, the lowest amount being detected at early hours of the day. There is a marked increase between sampling sites, indicating point sources of pollutants.

Table 1. Cadmium, copper and zinc in the ZA canal (ug/L)

Distance, Km downstream	Time of day	Cadmium sol.*	Cadmium susp.*	Copper sol.	Copper susp.	Zinc sol.	Zinc susp.
0	08:00	-	3.1	9.5	30.2	22	74
6	08:30	0.2	3.1	15.5	52.0	10	101
	12:00	1.1	4.2	31.0	57.1	20	143
	17:00	0.6	3.3	29.0	63.3	0	180
12	09:00	2.1	6.5	19.2	160.5	20	160
	17:00	0.7	5.7	29.6	106.0	0	200
18	10:00	0.7	4.0	18.2	410.0	20	180
	14:00	0.5	5.2	31.0	520.3	10	400
	19:00	0.2	1.1	27.0	430.4	30	190

*in solution *in suspended particles

Copper content in the ZA has decreased over the last 10 years, whereas Cd, Zn, Hg As remain practically the same. (Table 2).

Table 2. Heavy metals in the ZA canal Km 18, in different years (ug/L).

Year	Cadmium		Copper		Zinc		Mercury		Arsenic	
	sol.	susp.	sol.	susp.	sol.	susp.	sol.	susp.	sol.	susp.
1984	0.7	4.0	18	410	20	180	ne	ne	ne	ne
1989	0.5	1.1	32	205	18	176	1.9	0.6	0.3	2.9
1994	1.5	2.3	21	277	6	106	0.4	1.0	4.3	3.5

ne: not determined

Analyzing heavy metal content in the three river systems under study (Table 3), high copper concentrations were found in some of them, due to wastes from copper mining activities in the high mountains.

Table 3. Heavy metals in rivers of central Chile (ug/L)

	Cadmium		Copper		Mercury		Arsenic	
	sol.	susp.	sol.	susp.	sol.	susp.	sol.	susp.
ACONCAGUA	<0.1	0.6	21.8	286.2	0.4	0.7	3.3	2.4
MAPOCHO	<0.1	2.4	28.1	412.5	0.2	0.8	4.8	3.5
MAIPO	0.3	1.8	10.3	13.1	0.8	1.1	4.2	8.5
CACHAPOAL	<0.1	<0.1	27.6	543.1	0.7	0.4	11.1	16.1

During the last 5 years the copper mining industry has taken actions to reduce pollution of river waters by installing sedimentation lagoons. The results are visible (Table 4) as shown by a more than 50% reduction of Cu levels in the Cachapoal river.

Table 4. Heavy metals in the Cachapoal river. (ug/L)

	Copper	Cadmium	Mercury	Arsenic
1988	1070	<0.1	<0.1	27
1993	590	<0.1	1.1	29
1995	301	<0.1	0.8	25

As to soils, it can be observed (Table 5) that those irrigated with the polluted ZA waters contain substantially higher amounts of the heavy metals under study than those irrigated with non-polluted water sources.

Table 5. Some properties and total heavy metal content of soils under study

Soil	depth cm	pH	Org-C %	Cd	Cu	Zn	Hg	As
				mmol/kg				
ENCINA	0-30	7.59	2.70	0.071	7.40	3.44	0.002	0.024
	30-60	7.30	0.65	0.060	8.72	3.03	0.003	0.030
LAGUNA	0-30	7.00	2.01	0.043	5.46	2.56	0.002	0.028
	30-60	6.80	1.20	0.046	3.03	2.21	0.002	0.029

When sequentially extracting Cu, Cd and Zn, a higher carbonate bound copper form is observable in the ZA irrigated soil, while the occluded, organic and exchangeable forms are proportionally the same (Table 6).

Table 6. Sequentially extracted heavy metals from two soils. (umol/kg)

Metal	Soil	Exchangeable 0-30	Exchangeable 30-60	Carbonate 0-30	Carbonate 30-60	Occluded 0-30	Occluded 30-60	Organic 0-30	Organic 30-60
Cadmium	Encina	10	10	10	10	0	0	20	30
	Laguna	10	10	10	10	10	10	20	20
Copper	Encina	110	100	510	560	2710	2740	670	760
	Laguna	70	70	210	160	1990	1730	680	750
Zinc	Encina	40	30	150	120	1890	1640	90	80
	Laguna	30	30	110	100	310	300	130	120

DISCUSSION

The data obtained for all the systems under study show substantial pollution with heavy metals. The most obvious cases are the canal (ZA) and river (Mapocho) which cross the city of Santiago both collecting all of its liquid and semi-liquid domestic and industrial residues. The resulting heavy metal pollution could probably be reduced if proper decontamination facilities were installed by each contaminating industry, and adequate legislation and control of their effluents were enforced. Small manufacturer wastewaters as well as domestic sewage waters would have to be collected and treated accordingly at appropriate plants.

Copper-mining enterprises located in the high Andean mountain range where the river systems under study are born, traditionally polluted these waters and, e.g., very high copper contents were quite common. The gradual increase in environmental awareness resulted in an increase in the measures taken by the involved copper enterprises to control their liquid wastes. The success of these measures are clearly visible as shown in this study and it is to be hoped that additional measures will be introduced to further limit stream pollution.

Wastewater irrigated soils were found to contain higher amounts of heavy metals than those not irrigated with them. The accumulation and persistence of heavy metals in these soils may produce potentially serious hazards in the food chain. Knowledge of the chemical forms of these metals in soils provides some information about their reactivity and eventual plant availability. Assuming that chemical reactivity decreases with the succesive extractions in the sequential procedure and comparing the waste-water irrigated soil metal content with the one irrigated with non-wastewater sources, an increase in the reactivity of copper and zinc, and thus in their bio-availability, was observable in the first three extracts. This confirms the hazards involved in regard to heavy metals when irrigating with these untreated wastewaters.

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