Identification of heavy metals discharged from the SULFACID S.A. chemical plant, Fray Luis Beltran, Santa Fe Province, Argentina 1998.

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Sample Description

Two samples of effluent were collected from a channel discharging from the Sulfacid treatment plant into the Parana River. Sample LA8038 was collected in May 1998, sample LA8073 in September 1998. The plant is known to produce a range of sulphur compounds, along with zinc and cadmium electrodes. Due to the recent flooding of the Parana River, no sediment samples were collected.

Sampling Methodology

Both samples were collected and stored in a 1-litre glass Duran bottle previously rinsed with nitric acid to remove all heavy metal residues. The bottles were rinsed three times with the sample before the final collection, and filled completely, thus ensuring no air bubbles were present. They were then transported to the Greenpeace Research Laboratory, kept cold during transit, and refrigerated immediately on arrival. Heavy metals were determined quantitatively using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES).

Analytical Methodology

Both samples were preserved in 5% v/v nitric acid on arrival. After 24 hours, 50 ml was transferred to a 120 ml Teflon microwave vessel microwave vessel fitted with a screw cap and pressure relief valve. The vessels were then sealed, placed on a rotating table in a microwave oven (model MDS-2000, CEM Corp.), and allowed to digest for one hour at full power (630 W).

After cooling to ambient temperature, the digests were filtered into volumetric flasks, diluted with deionised water, made up to a volume of 50 ml and mixed. A blank sample, and an internal prepared quality control (8mg/l, 0.8 mg/l for mercury) were also prepared, matrix matched to the samples.

ICP-AES Analysis

Following preparation, the samples were analysed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), using a Varian Liberty-100 Sequential Spectrometer. The following metals were quantified directly: manganese (Mn), chromium (Cr), zinc (Zn), copper (Cu), lead (Pb), nickel (Ni), cobalt (Co) and cadmium (Cd). A multi-element instrument calibration standard was prepared at a concentration of 10 mg/l (matrix matched to the samples). The calibration was validated using a quality control standard, prepared from different reagent stocks, at 8 mg/l. Samples exceeding the calibration range were diluted appropriately, in duplicate, and re-analysed.

Mercury (Hg) was determined using Cold Vapour Generation ICP-AES. Hg (ii) was reduced to Hg (0) i.e. a vapour, following reduction of the samples with sodium borohydride (0.6% w/v), sodium hydroxide (0.5% w/v) and hydrochloric acid (10 molar). The vapour was carried in a stream of argon into the spectrometer. Two calibration standards were prepared, at 10 ug/l and 100 ug/l (matrix matched to the samples). Samples exceeding this range were diluted and re-analysed. The quality control standard was again prepared from a different reagent stock at 80% of the calibration range (i.e. 80 ug/l). The spectrometer was re-calibrated after every 10 samples.

Reporting limits of 0.01 mg/l were used for all metals with the exception of lead (0.03 mg/l) and mercury (0.002 mg/l). These were calculated using statistical methods supplied by the UK Water Research Centre (1989).

Results

Are expressed in mg/l (parts per million)

Sample number	Mn (mg/l)	Cr (mg/l)	Zn (mg/l)	Cu (mg/l)	Pb (mg/l)	Ni (mg/l)	Co (mg/l)	Cd (mg/l)	Hg (mg/l)
LA8038	0.24	<0.01	1.70	<0.01	0.04	<0.01	<0.01	0.03	<0.002
LA8073	0.17	<0.01	1.48	0.03	0.04	<0.01	<0.01	0.03	0.003

Results of Heavy Metals Analysis, Sulfacid, Argentina 1998

Discussion

Detectable levels of manganese, zinc, lead and cadmium were found in both samples of effluent. With copper and mercury also detected in sample LA8073. Of these, zinc and cadmium are of greatest importance. Zinc is present at mg/l levels in both samples, and although cadmium is only present at 0.03 mg/l in both samples, its high toxicity, persistence and bioaccumulation potential, mean that all anthropogenic inputs to the aquatic environment warrant concern and require investigation.

The source of these metals is the SULFACID chemical plant, which manufactures zinc and cadmium electrodes. Wastewaters from the plant are treated and then discharged to the Parana River. However as is evident form our analysis, the treatment processes used are not capable of removing all of the cadmium and zinc.

Zinc

Environmental releases of zinc from anthropogenic sources far exceed the releases from natural sources (ATSDR 1997). Such anthropogenic releases include those resulting from electroplating, smelting and ore processing, as well as acid mine drainage, effluents from chemical processes (textiles, pigment and paint, fertiliser production), and discharges of untreated domestic sewage.

Although zinc is not regarded as being especially toxic, it is sometimes released into the environment in appreciable quantities, and can thus have deleterious effects on certain species at specific concentrations. For example, effects on fertilisation and embryonic development have been observed in species of fish and harpacticoid copepods (Ojaveer *et al.* 1980, Verriopoulos and Hardouvelis 1988).

Once discharged into the environment, zinc, along with most other heavy metals, will bind predominantly to suspended material, and finally accumulate in the sediment. As concentrations in sediment can exceed those of the overlying water by between three and five orders of magnitude (Schuhmacher *et al.* 1995, Bryan and Langston 1992), the bioavailability of even a minute fraction of the total sediment metal assumes considerable importance.

Evidence for the bioavailability of zinc in sediments comes from research on plants and deposit feeding invertebrates. Schuhmacher (1995) found that zinc in molluscs and algae collected from the Ebro River reflected sediment concentrations. Another study by Fishbein (1981) concluded that crustaceans and fish can accumulate zinc from both water and food. A BCF of 1,000 was reported for both aquatic plants and fish, and a value of 10,000 was reported for aquatic invertebrates. Ramelow *et al.* (1989) found a high enrichment of zinc in oysters (BCF of 3,300) and other particulate feeders. Particulate matter containing higher concentrations of zinc than ambient water. Other investigators have also indicated that organisms associated with sediments have higher zinc concentrations than organisms living in the aqueous layer (Biddinger and Gloss 1984).

A study investigating levels of heavy metals in biota from the Rio de la Plata, which provides the freshwater supply for Buenos Aires (Verrengia-Guerrero and Kesten 1993) showed the accumulation of zinc in fish and benthic organisms associated with polluted sediments.

In terms of human health, most of the studies relating to the effects of zinc concentrate on exposure via inhalation (which can cause a specific short-term disease called metal fume fever). Less is known about the long-term effects of ingesting too much zinc, through food, water or dietary supplements. It is an essential trace element, but ingestion of higher than recommended levels can have adverse effects on health. The recommended Dietary Allowances for zinc are 15 mg/day for men and 12 mg/day for women. If doses 10 –15 times higher than these recommendations are taken by mouth, even for a short time, stomach cramps, nausea and vomiting may occur (ATSDR 1997). Ingesting high levels for several months may cause anaemia, damage to the pancreas, and decreased levels of high-density lipoprotein (HDL) cholesterol (ATSDR 1997).

Clearly the two most direct potential routes of exposure to humans following discharges of zinc to the Parana River would be consumption of the water or of fish or other food derived from the river. It is not, however, possible to estimate the magnitude of the hazard, which may be presented by the discharge in question in this study.

Cadmium

Cadmium has no biological function, and is highly toxic to both animals and plants even at low concentrations. It is also persistent in the environment and has the potential to bioaccumulate through the food chain (ATSDR 1997). Concentrations of cadmium usually encountered in the environment do not cause acute toxicity, however elevations above background concentrations can have deleterious effects on plant and animal health (Bryan and Langston 1992, Alloway 1990).

Once discharged to the environment, cadmium, along with most other heavy metals, will bind predominantly to suspended material, and finally accumulate in the sediment. There is evidence to show that cadmium can be absorbed from surface sediments, suspended particular matter and water (Bryan and Langston 1992, Bryan and Humberstone 1973, Ray *et al.* 1980, Schwartz *et al.* 1985). It is known to be one of the more mobile, and hence bioavailable, trace metals (Jensen and Bro-Rasmussen 1990).

Toxic effects on exposure biota include observed correlations between increased levels of cadmium found in limpets and a reduced ability to utilise glucose (Shore *et al.* 1975, Bryan and Langston 1992). Reductions in reproduction rates and thus population numbers in copepods and isopods (Giudici and Guarino 1989) have also been observed. The toxicity of low sediment-cadmium concentrations was also suggested by observations showing that in San Francisco Bay, the condition of certain species of clam declined as cadmium concentrations rose from 0.1 to 0.4 mg/kg (Luoma *et al.* 1990).

Regarding potential human exposure, food, water and cigarette smoke will be the largest sources of cadmium for members of the general population. Eating food or drinking water with very high cadmium levels can severely irritate the stomach, leading to vomiting and diarrhoea (ATSDR 1997). Eating lower levels of cadmium over a long period of time can lead to a build up in the kidneys. This cadmium build-up causes kidney damage, and also leads to the weakening of bone (Nriagu 1988). Studies concerned with the effects of eating and drinking high levels of cadmium are not strong enough to show that such exposure can lead to an increased rate of cancer. However the U.S. Department of Health and Human Services and the U.S. Environment Protection Agency have both determined that cadmium and cadmium compounds may reasonably be anticipated to be carcinogens (ATSDR 1997).

As mentioned above in the case of zinc discharges, the two most direct potential routes of exposure to humans following discharge of cadmium to the Parana River would be consumption of the water or of fish or other food derived from the river. Again however, although any discharges of cadmium warrant concern, it is not possible in this case to estimate the magnitude of the hazard, which may be presented by the discharge.

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