

Technical note 10/97

Heavy metal analysis of liquid waste and sediment collected from the Aliaga Petrochemicals plant, Aliaga, Izmir, Turkey. September 1996.

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Introduction

The Aliaga Petrochemicals plant, Izmir, Turkey, is a large PVC production complex. As well as PVC manufacture, the plant produces ethylene dichloride (EDC) and vinyl chloride monomer (VCM), the starting products from which PVC is made. The production of trichloroethylene and perchloroethylene, from VCM is also carried out on site, as is the production of chlorine and sodium hydroxide using mercury chlor-alkali technology.

In September 1996, six samples, 2 effluent and 4 sediment, were collected from and around two outfall pipes. On the day of sampling only one of the two outfall pipes (reference: outfall 2) was discharging waste effluent.

All samples collected were stored and transported in analytically clean glass bottles (previously rinsed with both nitric acid and pentane to remove both metallic and organic residues). They were transported for analysis to the Greenpeace Research Laboratory based at the University of Exeter, UK. They were kept cold during transit, and refrigerated immediately on arrival. All details on samples and sampling sites are given in appendix 1.

Analytical Methodology

Analytical-grade reagents and analytically clean glassware were used throughout sample preparation and analytical procedures.

1. Solid samples (MI6147-MI6151)

Samples of sediment were dried in an oven for 48 hours until dry weight readings became constant. They were then sieved through a 2 mm stainless steel mesh. 0.5g of the resulting homogenous sample was weighed into a 120 ml Teflon microwave vessel, fitted with a screw cap and pressure relief valve. To this 10 ml of deionised water was added, followed by 7.5 ml of concentrated hydrochloric acid and 2.5 ml of concentrated nitric acid. The vessels were 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.

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. Both Certified Reference Materials and blanks were prepared with the batch of samples.

Reference materials used were PACS-1 and BEST-1 (for Hg): trace elements in marine sediment, certified by the National Research Council, Canada (1996).

2. Aqueous Samples (MI6152-MI6153)

Samples were preserved in 10% v/v concentrated acid on arrival. After twenty four hours, 50 ml was transferred to a 120 ml Teflon microwave vessel and digested using the same procedure and program conditions as described above.

After cooling to ambient temperature, samples were filtered into volumetric flasks, diluted with deionised water, made up to a volume of 50 ml, and mixed. A blank and a quality control standard, containing all the metals to be determined (prepared internally at a concentration of 8 mg/l), were digested along with the samples. Identical preparation procedures were followed for both samples and standards.

Following preparation, the samples were analysed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The following metals were quantified: manganese (Mn), chromium (Cr), zinc (Zn), copper (Cu), lead (Pb), nickel (Ni), cobalt (Co) and cadmium (Cd). Instrument calibration standards were prepared (concentration of 10 mg/l matrix matched to the samples) and the calibration validated using quality control standards, prepared at 50% of the calibration range (i.e. 5 mg/l). Samples exceeding the calibration range, were diluted appropriately, in duplicate, and re-analysed. All other instrument and laboratory quality control procedures were adhered to.

Mercury (Hg) was determined using Cold Vapour Generation ICP-AES. Mercury (ii) was reduced to mercury (0) vapour using sodium borohydride (0.6% w/v) and hydrochloric acid (10 molar). Calibration standards were prepared at 10 and 100 ug/l. A quality control standard was prepared at a concentration of 50 ug/l. All samples exceeding the calibration range were diluted and re-analysed. All other instrument and laboratory quality control procedures were adhered to.

Results

See appendix 1 for full sample descriptions, results, certified reference and quality control data.

Discussion

Four samples were collected from Outfall 1. Three sediment samples, collected at varying distances from the outfall, and one waste effluent. At the time of sampling no significant discharge was observed, and thus levels of heavy metals determined in the wastewater sample (MI6152) are low. Only manganese, zinc, copper and cobalt are present at detectable levels.

Outfall 2 was operational at the time of sampling, and 255 ug/l of Hg was present in this sample. This wastewater concentration of Hg is five times greater than the maximum limit allowed by European Environmental Legislation.

All metals analysed, with the exception of Cd, were detected in all sediment samples. Analysis of sediment provides an excellent picture of the extent of pollution within a defined area. Water, due to fluctuations in emissions and flow, follows a less well defined pattern. Heavy metals will bind predominantly to suspended material, and finally accumulate in the sediment. Thus providing a reliable history of pollution.

Sediments will always contain some level of heavy metal ions, levels very much dependent on the geology of the area as well as anthropogenic inputs. Analysis of the Aliaga sediments shows that levels of Zn, Cu, Pb, Ni and Co are slightly elevated above background concentrations (Salomons and Forstner, 1984), however Hg levels are anomalously high. Background concentrations of Hg are cited as ranging from 0.2 to 0.4 mg/kg. Levels determined in these sediments range from 403 mg/kg (MI6150 20-25 m away from outfall 2) to 1137 mg/kg (MI6147, closest to outfall 1). The anthropogenic source of this Hg is the chlor-alkali process waste at Aliaga.

The chlor-alkali process makes use of Hg in the simultaneous production of chlorine and caustic soda from a brine solution. The process is electrolytic, employing metallic Hg as the flowing cathode.

EC Directive 85/613/EEC states that when Hg is used in the chlor-alkali industry, effluents discharged must not contain more than 50 ug/l (parts per billion) of Hg. Although this standard does not apply to Turkey, the fact that such a low permissible limit is set for Europe should indicate how toxic, persistent and bioaccumulative this metal is. 255 ug/l of Hg is being discharged from Outfall 2, and sediments, collected over 20 m away from this discharge point, contain levels of Hg 1000 times greater than published background concentrations. Although no significant discharge was observed from Outfall 1 at the time of sampling, levels of Hg retained in the sediments surrounding the outfall are so high (over 2000 times greater than background) that one can only assume levels far in excess of 50 ug/l have been discharged from this point.

It is well known that retention of Hg by sediments may delay the elimination of contamination for many years (Bryan and Langston, 1991). Ten years after Hg discharges ceased in Minimata Bay, Japan, sediment levels as high as 100 mg/kg were still present. The fate of Hg, once discharged into the aquatic environment, is dominated by the rapid adsorption to soluble and particulate carbon compounds. Because of the strength with which Hg is bound to the sediment, exchange of metal back to the water column is generally slight. Accumulation from the sediment may thus be a dominant pathway for uptake in aquatic organisms and account for relatively high concentrations in deposit feeders inhabiting Hg contaminated sites (Balogh, 1987).

The implications of this chemical behaviour are numerous. Hg is the only metal widely accepted to biomagnify through the food chain, so aquatic invertebrates, fish and birds feeding from polluted sights are all at risk. Fish especially (including shellfish) can accumulate high levels of Hg compared with other aquatic species (USPHS, 1989). Biomagnification of Hg is due to the bacterial methylation of inorganic Hg. The product formed, methylmercury, can readily pass across cell

membranes, where it accumulates. The bioconcentration factor of methylmercury in fish to that in water is usually between 10000 and 100000 (WHO, 1990), and it is through eating fish (including shellfish and fish products) that humans are likely to accumulate methylmercury from the environment. For the chlor-alkali process workers, there is likely to be another accumulation route. There is the potential for workers to be exposed occupationally to inorganic compounds of Hg (including elemental Hg vapour) within the factory.

Both elemental and methylmercury are highly toxic to the central nervous system and the kidneys, especially in children. Brain damage can also be observed in the developing foetus if the mother is exposed (USPHS, 1989). Hg is a highly toxic metal, it has no beneficial effects in humans, and there is no known homeostasis mechanism for it. Any long term exposure may therefore be expected to progressively cause severe disruptions in the normal functioning of the organ where accumulation is occurring (Nriagu, 1988).

From the level of Hg found in the effluent discharged from Aliaga Petrochemicals, and the levels of Hg found in the sediments surrounding the plant, it can be concluded that treatment of the chlor-alkali process wastes is minimal, if not non-existent. Such unregulated discharge of Hg containing wastewater should cease, if more widespread contamination of the Aliaga area, is to be avoided.. Furthermore, the current effects of this contamination, on human and aquatic life should be subject to a full investigation.

References

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INORGANIC ANALYTICAL RESULTS

Aliaga Petrochemicals, Izmir, Turkey, 1996

Sample type: Sediment
Sample name: Petkim 1
Sampling date: 23.9.96
Lab. code: MI6147

Other information: Sediment collected from outfall 1. Collected from the bank of an open canal, 5-10 m from the sea.

Analysis method: ICP-AES

METAL	CONCENTRATION (mg/kg)
Manganese	182.4
Chromium	35.2
Zinc	437.0
Copper	158.3
Lead	26.9
Nickel	48.2
Cobalt	87.0
Cadmium	n/d
Mercury	1137.0

INORGANIC ANALYTICAL RESULTS

Petkim, Aliaga, Izmir, Turkey, 1996

Sample type: Sediment
Sample name: Petkim 2
Sampling date: 23.9.96
Lab. code: MI6148

Other information: Sediment collected 10-15 m away from the mouth of outfall 1 (see enclosed map).

Analysis method: ICP-AES

METAL	CONCENTRATION (mg/kg)
Manganese	870.8
Chromium	91.5
Zinc	560.4
Copper	297.2
Lead	26.4
Nickel	94.3
Cobalt	200.0
Cadmium	n/d
Mercury	513.9

INORGANIC ANALYTICAL RESULTS

Petkim, Aliaga, Izmir, Turkey, 1996

Sample type: Sediment
Sample name: Petkim 3
Sampling date: 23.9.96
Lab. code: MI6149

Other information: Sediment collected 10-15 m away from the mouth of outfall 1 (see enclosed map).

Analysis method: ICP-AES

METAL	CONCENTRATION (mg/kg)
Manganese	1160.7
Chromium	59.82
Zinc	737.5
Copper	141.1
Lead	35.7
Nickel	46.4
Cobalt	284.8
Cadmium	n/d
Mercury	459.2

INORGANIC ANALYTICAL RESULTS

Petkim, Aliaga, Izmir, Turkey, 1996

Sample type: Sediment
Sample name: Petkim 4
Sampling date: 23.9.96
Lab. code: MI6150

Other information: Sediment collected 20-25 m away from the mouth of outfall 2 (see enclosed map).

Analysis method: ICP-AES

METAL	CONCENTRATION (mg/kg)
Manganese	420.0
Chromium	28.0
Zinc	105.0
Copper	26.0
Lead	25.0
Nickel	26.0
Cobalt	8.0
Cadmium	n/d
Mercury	403.4

INORGANIC ANALYTICAL RESULTS

Petkim, Aliaga, Izmir, Turkey, 1996

Sample type: Sediment
Sample name: Petkim 5
Sampling date: 23.9.96
Lab. code: MI6151

Other information: Sediment collected 20-25 m away from the mouth of outfall 2 (see enclosed map).

Analysis method: ICP-AES

METAL	CONCENTRATION (mg/kg)
Manganese	300.8
Chromium	19.4
Zinc	88.7
Copper	22.6
Lead	39.5
Nickel	19.4
Cobalt	5.7
Cadmium	n/d
Mercury	409.8

INORGANIC ANALYTICAL RESULTS

Petkim, Aliaga, Izmir, Turkey, 1996

Sample type: Industrial waste water / seawater
Sample name: Petkim 6
Sampling date: 24.9.96
Lab. code: MI6152

Other information: Effluent collected from outfall 1 (see enclosed map). There was no significant discharge at the time of sampling.

Analysis method: ICP-AES

METAL	CONCENTRATION (ug/l)
Manganese	450
Chromium	<10
Zinc	330
Copper	60
Lead	<30
Nickel	<10
Cobalt	10
Cadmium	<10
Mercury	<2

INORGANIC ANALYTICAL RESULTS

Petkim, Aliaga, Izmir, Turkey, 1996

Sample type: Industrial waste water / seawater
Sample name: Petkim 7
Sampling date: 24.9.96
Lab. code: MI6153

Other information: Effluent collected from outfall 2 (see enclosed map). There was significant discharge at the time of sampling.

Analysis method: ICP-AES

METAL	CONCENTRATION (ug/l)
Manganese	10
Chromium	<10
Zinc	70
Copper	50
Lead	<30
Nickel	<10
Cobalt	<10
Cadmium	<10
Mercury	255