

# **Identification and environmental significance of organic pollutants found in industrial wastewater and river sediments associated with Dow Quimica Company, Guaruja, SP, Brazil, 1998.**

Technical Note 19/98

Prepared by Iryna Labunska, Ruth Stringer, David Santillo & Angela Stephenson  
Greenpeace Research Laboratories,  
December 1998.

## **Summary**

Three samples of sediment and one sample of wastewater were collected in the vicinity of Dow Quimica Co., Guaruja, Brazil between April and August 1998. All samples contained a number of organic compounds, only a fraction of which could be identified. Of those, which could be identified, tetrachloromethane and chloroform were of particular interest. The presence of these organochlorines in both wastewater and receiving sediments indicates that the Dow plant could be acting as a significant source of volatile organochlorines to the surrounding environment. Metals were present both in the sediments of the river and in the wastewater. It is not clear to what extent these may derive from natural or industrial sources.

## **Introduction**

Dow Quimica Company is the fifth largest chemical company in the world, with annual sales of more than \$20 billion. The company operates 114 manufacturing sites in 33 countries and employs more than 42,900 people. The Brazilian branch of Dow Quimica Company, situated in Guaruja, SP, produces epoxy resins using bisphenol A and epichlorohydrin. The plant also produces polyols, which are used as raw materials for the production of polyurethane foam.

Three samples of river sediment and one sample of wastewater associated with Dow Quimica Company were collected in April and August 1998. On both occasions the samples were collected from an area beside the Dow boundary wall where approximately 15 discharge pipes are situated by the river. At the time of the first sampling, in April, there was no discharge observed from any of the pipes. Therefore, only two sediment samples (LA8012 and LA8013) were collected. On the second occasion, in August, one of the pipes was found to be discharging and an effluent sample (LA8067) was collected from it. The sediment LA8068 was collected beneath the same pipe. Locations of the sampling points and sample descriptions are presented in Table 1.

| Location   | Sample type | Sample code |
|--|-------------|-------------|
| Rio da Pouca Saude, close to Dow Quimica discharge pipes | Sediment    | LA8012      |
|  | Sediment    | LA8013      |
| Pipe discharging into Rio da Pouca Saude                 | Wastewater  | LA8067      |
| Beneath pipe from which sample LA8067 was collected      | Sediment    | LA8068      |

*Table 1. Locations and description of the samples LA8012, LA8013, LA8067, and LA8068*

## Materials and Methods

All samples were collected and stored in glass bottles that had been rinsed with pentane and nitric acid to remove all organic and heavy metal residues. Aqueous samples were collected in 1-litre bottles, rinsed three times with the sample before filling with sample. Bottles were filled completely, ensuring no air bubbles were present. They were stored cold, kept cold during transit, and refrigerated immediately on arrival at the Greenpeace Research Laboratories.

### 1. Organic Screen Analysis

All solvents were of High Purity Grade (PRAG or low haloform). Glassware used in extraction and cleaning up procedures was cleaned in detergent, rinsed with tap water and deionised water, dried in the oven overnight at 105<sup>0</sup>C, and rinsed three times with low haloform pentane.

#### Solid Samples

Solid samples were analysed separately for volatile and extractable organic compounds.

For volatile organic compound analysis, no sample preparation was required. Approximately 2g of sample were transferred to a 20ml headspace vial for analysis as described below.

In preparation for analysis of extractable organic compounds, approximately 30g (wet weight) was weighed and transferred to a clean 100 ml glass bottle. Samples were spiked with deuterated (d8) naphthalene (an internal standard) at a concentration of 4.7 mg/kg. 15 ml of pentane was added, followed by 5 ml of acetone. All samples were then sonicated for 2 hours.

Extracts were decanted, filtered through a pre-cleaned hydrophobic phase separator filter and collected in reagent tubes. They were then acidified to pH 2 with 10% nitric acid. Following this, a second portion of 20 ml pentane was added and the extraction procedure repeated. Finally, both extracts obtained for each sample were combined and evaporated to a volume of approximately 3 ml. The concentrated extract was cleaned through Florisil column, eluted with a 95:5 mixture of pentane:toluene, and evaporated

down to a volume 2 ml under a stream of analytical grade nitrogen. 1-bromonaphthalene was then added to provide an indication of GC/MS performance.

### **Aqueous Samples**

Aqueous samples were analysed separately for extractable and volatile organic compounds.

10ml of the original sample were transferred to a 20ml Headspace vial for volatile organic compound (VOC) analysis. The rest of the sample was extracted with pentane. Prior to the extraction, samples were spiked with deuterated (d8) naphthalene (an internal standard) at a concentration of 150 ug/l. 20 ml of pentane were added, and the sample agitated for 2 hours on a bottle roller to maximise contact between solvent and sample.

After separation of the phases, the solvent extract was filtered through a hydrophobic phase separator filter and collected in pre-cleaned reagent tube. The aqueous sample was acidified to pH 2 with 10% nitric acid, a second portion of 20 ml pentane was added and the extraction procedure repeated. The cleanup procedure employed was as described above for solid samples.

### **Chromatographic Analysis**

Organic compounds were identified qualitatively using Gas Chromatography Mass Spectrometry (GC-MS). Instrumentation was a Hewlett Packard (HP) 5890 Series II gas chromatograph, interfaced with a HP Chem-Station data system, and linked to a HP 5972 Mass Selective Detector operated in scan mode. The identification of compounds was carried out by computer matching against a HP Wiley 275 library of 275,000 mass spectra combined with expert interpretation.

Instrumentation for the analysis of volatile organic compounds was a Hewlett Packard (HP) 5890 Series II gas chromatograph with HP 19395-A headspace sampler, interfaced with a HP Chem-Station data system, and linked to a HP 5970 Mass Selective Detector operated in scan mode. Again, the identification of compounds was carried out using a combination of computer matching (against a HP Wiley 138 library of 138 000 mass spectra) and expert interpretation.

Results are reported as a list of those compounds reliably and tentatively identified. Match qualities of 90% or greater are assumed to give reliable identifications; tentative identification refers to qualities between 51% and 90%. Analytes yielding match qualities of 50% or less are assumed to be unidentified.

## **2. Metals analysis**

### **Solid samples**

Samples were dried in an oven until weight readings became constant. They were then homogenised using a pestle and mortar and passed through a 2mm sieve to exclude stones and other large debris. A portion of sample (0.5g) was placed in a 120ml Teflon microwave vessel fitted with a screw cap and pressure relief valve. Deionised water (10ml), concentrated hydrochloric acid (7.5ml) and concentrated nitric acid (2.5ml) were then added to the pressure vessel. The vessel was then sealed and the sample digested in a microwave oven (model MDS-2000, CEM Corp.) at full power (630 watts) for 1 hour.

The digests were allowed to cool to room temperature, filtered and diluted to a final volume of 50ml.

Standard reference materials (PACS-1; trace elements in marine sediments) and blank samples were prepared alongside the environmental samples. All samples were analysed by ICP-AES as described below.

### **Aqueous samples**

Water samples were preserved in 5% v/v nitric acid on arrival. 50 ml was transferred to a 120 ml Teflon microwave vessel and digested using the same procedure and programming conditions 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 quality control standard (internally prepared at a concentration of 8.0 mg/l) and a blank sample were prepared with the batch of samples. Both were prepared in 5% v/v nitric acid.

### **ICP-AES Analysis**

Analysis was carried out using an inductively coupled plasma atomic emission spectrometer (Varian Liberty-100 sequential spectrometer). The following metals were quantified directly: cadmium (Cd); chromium (Cr); cobalt (Co); copper (Cu); lead (Pb); manganese (Mn); nickel (Ni) and zinc (Zn).

Mercury was determined separately using the same instrumentation operating in cold vapour generation mode. Digests prepared as described above were reacted with sodium borohydride (0.6% w/v); sodium hydroxide (0.5% w/v) and hydrochloric acid (10 molar) to reduce the dissolved mercury (II) to mercury (0) vapour. The mercury vapour was drawn through the spectrometer in a stream of argon.

For all metals, calibration was by comparison with matrix matched calibration samples. Concentrations of 10ug/l and 100ug/l were used for mercury analysis; a multi-element standard at 10mg/l was used for all other metals. A quality control sample prepared from different stock standards was also analysed; concentrations were 80ug/l for mercury and

8mg/L for each of the other metals analysed. Any samples falling outside the calibration range were diluted and reanalysed.

## Results and Discussion

### 1. Organic compounds

A large number of compounds were isolated from these samples but few could be reliably identified. Some compounds, most notably the straight chain hydrocarbons, were present at such low concentrations that reliable identification of specific compounds could not be achieved. The results of organic screening analysis and the list of compounds identified to a high degree of reliability are presented in the Table 2. The sediment sample LA8012, which was collected at the time when no discharge was observed from the pipes, contained only long chain straight hydrocarbons that normally present in the river sediments. In comparison, two other samples (sediment LA8068 and wastewater LA8067) collected during wastewater discharge contained chloroorganic compounds – tetrachloromethane, which was found in both samples, and chloroform, which was present only in the wastewater sample.

| Sample code | Compounds isolated | Reliably identified | Name of compounds reliably identified   |
|-------------|--------------------|---------------------|---|
| LA8012      | 49                 | 2(4%)               | Heptacosane<br>Pentacosane  |
| LA8013      | 37                 | 4(11%)              | cis-benzene, 1,1'-(1,2-cyclobutanediyl)bis-Phenol<br>2,6-Bis(1,1-dimethylethyl)-4-methylphenol<br>4-methyl phenol |
| LA8067      | 30                 | 2(7%)               | Chloroform<br>Tetrachloromethane  |
| LA8068      | 11                 | 2(18%)              | Pentacosane<br>Tetrachloromethane   |

Table 2. List of compounds reliably identified in the sediment samples LA8012, LA8012, LA8068 and in the wastewater samples LA8067.

Tetrachloromethane, also known as carbon tetrachloride, and chloroform are volatile compounds, such that a large proportion of the quantities of these compounds released to the environment will rapidly partition to the air.

Tetrachloromethane does not occur naturally but has been produced in large quantities to make refrigeration fluid and propellants for aerosol cans (ATSDR 1997). Tetrachloromethane can remain in air for several years before it is broken down and can cause depletion of the ozone layer. Consequently, it is controlled by the Montreal Protocol on substances that deplete the ozone layer. Under this legislation, use and production of carbon tetrachloride has been banned since the 1<sup>st</sup> January 1996 apart from special cases (Montreal Protocol 1997).

Small amounts of tetrachloromethane are often found contaminating surface water. Tetrachloromethane is not expected to adhere to soil particles (ATSDR 1997) or persist in the sediments for long periods. The presence of this compound in the sediment LA8068 might therefore indicate recent introduction of tetrachloromethane into the river.

Although chloroform can be generated through natural processes, the majority of chloroform (also known as trichloromethane, methane chloride, or methyltrichloride) found in the environment arises from industrial sources. It was formerly widely used as an anaesthetic (Budavari *et al.* 1989) and its primary toxic impact is on the nervous system. It can enter the environment when wastewater that contains chlorine is released into water or soil. It may enter water and soil from spills and by leaks from storage and waste sites. In addition to its industrial production and use, small amounts of chloroform are formed as an unwanted product during the process of chlorination of drinking water or effluents (ATSDR 1997).

Both tetrachloromethane and chloroform have been widely used as solvents for resins, oils, fats, lacquer, varnishes, and rubber waxes (Budavari 1989). Continuous use of these chemicals in those applications at this plant might explain the presence of these compounds in the wastewater. Nevertheless, it is clearly not possible from the current study to determine whether these organochlorines were being manufactured or used on site, or simply generated as unintentional by-products of other processes.

Both tetrachloromethane and chloroform are toxic compounds. Both are listed in group 2B by the International Agency for Research on Cancer (possible carcinogen to humans) (IARC 1998 & 1999).

Sample LA8013 contained phenol together with two derivatives, 4-methylphenol and 2,6-bis(1,1-dimethylethyl)-4-methylphenol. As mentioned above, the Dow Quimica plant is using phenolic compounds in the production cycle. Hence it may be expected that those compounds might be found in the wastewater from the plant or in the vicinity of the discharge. The compound 2,6-bis(1,1-dimethylethyl)-4-methylphenol, also known as butylated hydroxytoluene (BHT), is frequently employed as an antioxidant in different products including rubbers and polymer materials (Jobling *et al.* 1995). It is also used as an antiskinning agent in paints, varnishes and other surface finishes. There is some evidence that BHT can act as a promoter of liver cancer, in combination with carcinogenic substances, through induction of abnormal liver metabolism (Williams & Weisburger 1986).

## **2. Metals analysis results**

Results of metals analysis are given in tables 3 and 4 below.

All metals analysed for were detected in at least one of the sediment samples. There are no consistent concentration gradients between samples. Given their proximity and the possible influence of tidal flows and multiple inputs, this is not surprising. The

background concentrations of metals in freshwater sediments have been determined by various researchers (see eg Salomons and Forstner 1984, Bryan and Langston 1992, Palanques 1993, Palanques *et al.* 1995). Concentrations that might be expected in

| Sample             | Cd (ppm)       | Cr (ppm)      | Co (ppm)      | Cu (ppm)      | Pb (ppm)      | Mn (ppm)        | Hg (ppm)       | Ni (ppm)      | Zn (ppm)       |
|--------------------|----------------|---------------|---------------|---------------|---------------|-----------------|----------------|---------------|----------------|
| LA8012             | 1.02           | 17.86         | 2.55          | n/d           | 20.41         | 98.98           | 1.22           | 7.14          | 128.06         |
| LA8013             | 0.89           | 29.02         | 2.68          | 16.07         | 58.48         | 82.14           | 0.36           | 8.48          | 209.38         |
| LA8068             | n/d            | 10.00         | 6.00          | 6.00          | 22.00         | 130.00          | 0.50           | 7.00          | 113.00         |
| <b>back-ground</b> | <b>&lt;0.5</b> | <b>&lt;50</b> | <b>&lt;50</b> | <b>&lt;50</b> | <b>&lt;50</b> | <b>&lt;1000</b> | <b>&lt;0.5</b> | <b>&lt;50</b> | <b>&lt;100</b> |

Table 3. Concentrations of metals in sediment samples LA8012, LA8013 and LA8068 and for a typical uncontaminated sediment.

| Sample | Cd (ppm) | Cr (ppm) | Co (ppm) | Cu (ppm) | Pb (ppm) | Mn (ppm) | Hg (ppm) | Ni (ppm) | Zn (ppm) |
|--------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| LA8067 | n/d      | 0.04     | n/d      | 0.24     | 0.05     | 0.48     | 0.004    | n/d      | 0.14     |

Table 4. Concentrations of metals in discharged water sample LA8067.

uncontaminated sediments have been incorporated into table 3 for comparative purposes. Although background concentrations of heavy metals are governed by local geological conditions, these can be a useful indicator of contributions from anthropogenic sources. From the data given, it is apparent that concentrations of cadmium, chromium, cobalt, copper, manganese and nickel are well within ranges that might be found naturally. Lead, mercury and zinc were present in one or more sample at concentrations at the higher end of this “normal” range. This suggests the possibility of some slight influence from anthropogenic inputs, although more data would be required to come to firm conclusions.

The water sample LA8067 contained low (part per billion) concentrations of chromium, copper, lead, manganese, mercury and zinc. It is unlikely that a discharge containing these concentrations of metals would make any impact on the concentrations of metals in the sediments. Again, it is difficult to draw any conclusions about the source(s) of the metals in this sample. The metals detected here could also be from industrial sources, but given the concentrations of metals in the sediments at this site, runoff or other surface waters could come to contain at least some of the metals detected here through natural geochemical processes. Mixing drainage and industrial wastewaters could therefore account for the results of this sample.

## Conclusions

These analyses indicate industrial contamination of discharged water and river sediment with environmentally harmful organochlorines. The situation regarding metals is less clear; whilst there might be some industrial contamination, further data would be needed to establish whether the metals detected are from natural, industrial sources, or a mixture of both.

## References

ATSDR (1997) Toxicological Profiles. Agency for Toxic Substances and Disease Registry, U.S. Public Health Service (CD-ROM)

Bryan, G.W. and Langston, W.J. (1992) Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom Estuaries: a review. *Environmental Pollution* 76: 89-131

Budavari, S.M., O'Neil, J., Smith A. and Heckleman P.E. [Eds] (1989) *The Merck index: an encyclopaedia of chemicals, drugs and biologicals*. 11th Edn Merck and Co, Inc., New Jersey, USA

Jobling, S., Reynolds, T., White, R., Parker, M.G. & Sumpter, J.P. (1995) A variety of environmentally persistent chemicals, including some phthalate plasticizers, are weakly estrogenic. *Environmental Health Perspectives* 103(6): 582-587.

IARC (1998) Carbon tetrachloride [56-23-5]. IARC Monographs Vol.20, Suppl.7, Vol.71

IARC (1999) Chloroform [67-66-3]. IARC Monographs Vol.73

Montreal Protocol (1997) The 1987 Montreal Protocol on Substances than Deplete the Ozone Layer as adjusted and amended by the second Meeting of the Parties (London), 27-29 June 1990 and by the fourth Meeting of the Parties (Copenhagen, 23-25 November 1992 and further adjusted by the seventh Meeting of the Parties (Vienna, 5-7 December 1995) and further adjusted and amended by the ninth Meeting of the Parties (Montreal, 15-17 September 1997).

Palanques, A. (1993) Distribution and heavy metal pollution of the suspended particulate matter on the Barcelona continental shelf (North-Western Mediterranean). *Environmental Pollution* 85: 205-215

Palanques, A., Diaz, J.I. and Farran, M. (1995) Contamination of heavy metals in the suspended and surface sediment of the Gulf of Cadiz (Spain): the role of sources, currents, pathways and sinks. *Oceanologica Acta* 18(4): 469-477

Salomons, W. and Forstner, U. (1984) *Metals in the Hydrocycle*. ISBN 3-540-12755-0, Springer-Verlag, Berlin, Heidelberg, New York, Tokyo, 349pp.

Williams G.M. and Weisburger J.H. (1986) Chemical carcinogens. In *Toxicology: the basic science of poisons*. Klaasen C.D., Ambur M.O. and Doull J. [Eds], MacMillan Publishing Co., New York: 99-173.