Identification of organic pollutants discharged from the Shell Petrochemicals Plant. Avellaneda (Dock Sud), Argentina, 1998.

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Sample description

In May 1998, one sample of industrial wastewater (LA8033) was collected from the discharge channel of Shell Petrochemicals. The company is situated in the Avellaneda (Dock Sud) district of Argentina, and discharges its liquid wastes into the Rio de la Plata.

Sampling Methodology

Sample LA8033 was collected and stored in a 1-litre glass Duran bottle previously rinsed with pentane, to remove all organic residues. The bottle was rinsed three times with the sample before the final collection, and filled completely, thus ensuring no air bubbles were present. The sample was then transported to the Greenpeace Research Laboratory, kept cold during transit, and refrigerated immediately on arrival. Organic compounds were identified qualitatively using Gas Chromatography Mass Spectrometry (GC-MS).

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 105^0C, and rinsed three times with low haloform pentane.

Prior to the sample extraction 10ml of the cool sample were transferred into 20ml Head-Space sampler for volatile organic compounds (VOC) analysis. The rest of sample was spiked with deuterated (d8) naphthalene (an internal standard) at a concentration of 150ug/l. 20ml of pentane was 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 hydrophobic phase separator filter and collected in pre-cleaned reagent tube. The sample was acidified to pH 2 with 10% nitric acid, a second portion of 20ml pentane was added and the extraction procedure repeated. Finally, both extracts from the sample were combined and evaporated to a volume about 3ml.

The concentrated extract was cleaned through Florisil column, eluted with 95:5 mixture of pentane:toluene, and evaporated down to a volume 2ml under a stream of clean nitrogen. 1-bromonaphthalene was then added as a marker.

Chromatographic Analysis

Samples were analysed using 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 270,000 mass spectra. 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.

Volatile organic compounds (VOC) were analysed using a Hewlett Packard (HP) 5890 Series II gas chromatograph with HP 19395A Head-Space Sampler, interfaced with a HP Chem-Station data system, and linked to a HP 5970 Mass Selective Detector operated in scan mode.

Results and Discussion

A total of 88 compounds were isolated in sample LA8003, with 24 (27%) being reliably identified. The compounds found fell into three broad groups: alkylbenzenes (mainly methyl and ethyl derivatives), polycyclic aromatic hydrocarbons (methyl derivatives of naphthalene and phenanthrene), and long chain aliphatic hydrocarbons. When these groups of compounds are found together, their presence is often indicative of petroleum contamination (Overton 1994).

<u>Petroleum hydrocarbons</u>

Petroleum is a complex mixture of hydrocarbons that is formed from the partial decomposition of biogenic material, over geological time-scales. Petroleum hydrocarbons are released into the environment through natural seeps, non-point source urban runoffs, and by large quantities of accidentally released oil. Petroleum substances can also be found, albeit at low concentrations, in sewage (Connel, 1974), however the total amount discharged is relatively high due to the large volumes involved. Refined petroleum products principally contain the alkanes. It is often difficult to distinguish the origin of the hydrocarbons found in environmental samples. In cases of anthropogenic pollution, i.e. crude oil or petrol spills, alkanes are present together with monoaromatic hydrocarbons (benzenes) and polyaromatic hydrocarbons (naphthalene and others) (Overton 1994).

<u>Alkylbenzenes</u>

The occurrence of these compounds in the environment is largely due to their presence in crude oil and petroleum products, although they are also produced following the degradation of the linear alkylbenzene sulphonate (LAS) detergents. The alkylbenzenes themselves are highly resistant to degradation and may accumulate in sediments (Preston & Raymundo 1993). Alkylbenzenes are useful sewage markers (Chalaux *et al.* 1995) and due to their stability in sediments, they are very useful in tracing the transport of contaminants from their point sources.

In terms of toxicity, acute exposure can cause central nervous system (CNS) depression. With impaired reaction times and impaired speech the two most commonly noted CNS effects (Klaassen *et al.* 1996). All alkylbenzenes can be irritating to the eyes and mucous membranes and can cause irritation and burning of the skin. All are narcotics at high concentrations (Budavari *et al.* 1989).

Polycyclic aromatic hydrocarbons (PAHs)

PAHs are a group of compounds found in coal and oil. They are also formed during the combustion of coal, oil and gas. More than 100 different PAHs are known, however only a few have industrial / domestic applications.

Monoaromatic and polyaromatic hydrocarbons are considered to be the most toxic, and are known to be present at the highest concentrations during the initial phase of a crude oil spill (Overton 1994). The PAHs which were found in these samples were mainly naphthalene and its alkyl derivatives, along with phenanthrene.

Once PAHs are released into the aquatic environment, degradation by microorganisms is often slow, leading to their accumulation in exposed sediments, soils, aquatic and terrestrial plants, fish and invertebrates. PAHs can have a deleterious effect on human health, and individuals exposed to mixtures of PAHs, through inhalation or skin contact, for long periods of time, have been shown to develop cancer (ATSDR 1997).

Many of the carcinogenic polycyclic aromatic hydrocarbons are derived from an angular benz[a]anthracene skeleton. Anthracene itself is not carcinogenic, but benz[a]anthracene appears to have weak carcinogenicity. Addition of another benzene ring in select positions result in agents with powerful carcinogenicity such as dibenz[a,h]anthracene or benzo[a]pyrene. In addition, substitution of methyl groups on specific carbons of the ring also enhances carcinogenicity. Thus, 7,12-dimethylbenz[a]anthracene (DMBA) is one of the most powerful synthetic, polycyclic aromatic hydrocarbon carcinogens known (Klaassen *et al.* 1996).

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