# TOXIC HOTSPOTS:

## A Greenpeace Investigation of

## GUJARAT INDUSTRIAL ESTATES

## Organic and heavy metal contaminants in samples taken at three industrial estates in Gujarat, India.

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## Executive summary

Following a sampling and analysis programme carried out in 1996, in May 1999, Greenpeace International carried out a further programme at industrial estates located at Ankleshwar, Nandesari and Vapi in Gujarat, India. These estates consist of an estimated 3,000, 300 and nearly 2,000 industrial units respectively. The industries utilise common effluent treatment plants (CETPs) to varying degrees to treat process waste streams. Considered individually (and in aggregate) the diverse chemical manufacturing processes involved generate highly complex waste streams for which techniques to deal with them either do not exist or are unproven in practical application (Englande 1994). Common effluent treatment plants have been promoted in the region as a long-term solution to the environmental problems arising from contaminated wastewater disposal. This report utilises data from samples taken from the open waste-water channels and common effluent treatment plants (CETPs) associated with these industrial estates and from the surrounding environment to demonstrate that in a large majority of cases, such plants do not adequately treat industrial effluents generated by these industries. Accordingly, environmentally significant chemical contaminants, rather than being treated and degraded are still being discharged to the wider environment.

Comparison of sample results obtained in 1996 with those obtained from the current programme in 1999 revealed that similar profiles of persistent organic pollutants and heavy metals to be present in samples. The CETPs were brought on line subsequent to the 1996 programme and presumably were intended to address the diverse chemical mixtures being discharged. This strategy has demonstrably failed. In one instance wider range of organic contaminants was found and included, specifically, brominated compounds and the insecticide chlorpyrifos. In both 1996 and 1999 the Greenpeace International programmatic studies in the vicinity of the Ankleshwar estate demonstrated the widespread occurrence of *inter alia* chlorinated benzenes, chlorinated benzenamines, certain polychlorinated biphenyls, chlorinated toluenes and brominated organic compounds. Moreover, the widespread contamination of the Ankleshwar area with elevated levels of copper is indicative of the generally inadequate process control and waste management practices employed on this estate.

Common Effluent Treatment Plants are known to concentrate heavy metal contamination in solid residues, which far from providing a solution, is merely the transfer of contamination from one environmental medium to another and is associated with specific waste disposal problems. Notwithstanding this cadmium levels in the effluent from the CETP on the Vapi industrial estate clearly demonstrate that not all the heavy metals are removed from the liquid phase, resulting in significant, direct, discharges to aquatic systems outside the plant. Further confirmation of the relative inefficiency of CETPS in degrading chemicals present in the influent stream is provided by sludge/sediment samples taken at Ankleshwar. In this case, samples of sludge collected adjacent to the final settling lagoon of the CETP on Ankleshwar were found to contain the same organic contaminants as sediment samples taken from the Amlakhadi channel into which this plant discharges. The influence of historical discharges may be largely discounted. The presence of chlorinated and brominated benzamines, which are generally accepted as having a short environemental half-life indicates that recent discharges to the channel are responsible for this contamination.

The widespread impact of poor management and control practices is illustrated by groundwater samples taken in the vicinity of Sarigam. This is located a few kilometres south of the Vapi industrial estate. Upon analysis, this groundwater was found to contain trichloroethene, benzene, chlorobenzene, 1,3- and 1,4-dichlorobenzenes. The concentration of trichloroethene present exceeded the US EPA permissible levels set for drinking water by a factor of four. Benzene is a known human carcinogen and dichlorobenzene is a persistent organic contaminant that is itself resistant to microbial breakdown and is suspected to inhibit the microbial degradation of other chemicals.

This report highlights the complexity of the chemical mixtures that continue to be discharged and to persist in the environment in the Gujarat region. In this context it also discusses the limited utility and effectiveness of current treatment plants and outlines the need for an overall waste treatment strategy with a long-term goal of elimination of priority pollutants at source.

## Introduction

The "Golden Corridor" of the Indian State of Gujarat is an industrial belt that runs along the main north-south highway, linking the southern town of Vapi, with northern State capital of Ahmedabad. It is so called because of the wealth that has been generated by rapid industrial development. However the price of this economic success has been, and continues to be, widespread and in many regions, severe environmental damage. This area includes the large industrial estates in Ankleshwar, Nandesari and Vapi (see Figure 1).

These industrial areas contain thousands of individual industrial units, including dye factories, textile, rubber, pesticide and paint manufacturers, pulp and paper producers, pharmaceutical, engineering and chemical companies (CPCB 1996, Bruno 1995, Nagar 1995). Visual surveys of the sites reveal industrial development that is haphazardly organised and poorly controlled, with facilities for waste management generally inadequate, and in many cases, non-existent. Widespread contamination of the industrial sites and surrounding areas is clearly observed. Poor health and safety, and waste management practices may pose serious health hazards, not only to the workers, but also to the communities within and around the sites, and the villages downstream from the effluent discharges.

In all three industrial estates, piles of sludge and solid waste are dumped indiscriminately on open ground, and open roadside ditches are used to carry mixed effluent to pumping stations and rivers. Where waste treatment facilities do exist (often in the form of common effluent treatment plants, CETPs), only a limited range of physical, biological and simple chemical variables are addressed (e.g. pH, conductivity, dissolved and suspended solids, BOD, COD, nitrogen and phosphorus, along with certain other major ions). This is a common feature of CETPs (Hadjivassilis *et al.* 1994), since treatment facilities are fundamentally unable to deal adequately with persistent organic compounds and heavy metals. Indeed, their operation may well be severely hindered by the presence of such contaminants, which can exert toxic effects on the micro-organisms responsible for biological waste treatment.

At best, therefore, CETPs serve to concentrate persistent pollutants from liquid waste

streams into highly contaminated sludges. Far from solving a problem, this simply creates another hazardous waste stream. In addition, by combining wastewaters from a large


*Fig. 1 Location of Ankleshwar, Nandesari and Vapi Industrial Estates, Gujarat, India*

number of industrial units, often engaged in very different manufacturing processes, highly complex effluents and wastes, with wholly unpredictable toxicological properties may be generated. And as existing pollution-control legislation does not demand detailed

chemical characterisation of effluents, many components of wastes are overlooked, including persistent organic compounds. Consequently wastewaters that meet these limited legislative requirements are considered acceptable for discharge to surface water, despite the fact that high concentrations of toxic and persistent chemicals may still be present.

Greenpeace International first visited the industrial estates of Gujarat in April 1996 in order to conduct a preliminary investigation of waste management practice the chemical industry and the resulting environmental contamination. Based on the results obtained from analysis of over 40 samples, this study reported high levels of contamination with persistent organic pollutants and heavy metals resulting from inadequate waste management practices, including the failure of the CETPs to degrade the persistent toxic substances present in the majority of the waste streams sampled (Santillo *et al.* 1996). Since 1996, CETPs under construction on the Ankleshwar and Vapi estates at that time have been completed and commissioned. The introduction of a CETP to treat combined wastes has also been proposed for Sarigam, a smaller industrial estate 10 kilometres South of Vapi.

In May 1999 Greenpeace returned to the industrial estates of Gujarat, with the aim of re-sampling the open waste channels, the CETPs and the surrounding environs, in order to determine:-

a) the extent to which waste management practices had changed, if at all, since 1996 and;
b) the efficacy of the CETPs at Nandesari, Ankleshwar and Vapi in addressing the complex waste streams.

The results of this follow-up study are presented here.

## Materials and Methods

A total of 18 samples were collected from the four areas in order to determine the effectiveness of the CETPs in treating the highly complex mixture of waste they receive, and to determine the nature of non-treated wastes being discharged into local river systems.

All samples were collected and stored in clean glass bottles that had been thoroughly washed with detergent, and rinsed with deionised water, analytical grade pentane and nitric acid to remove all organic and heavy metal residues. Soil samples for heavy metal determinations and organic screen analysis were collected in 100ml clear glass bottles, while aqueous samples were collected in 1-litre clear glass bottles. Aqueous samples for volatile organic compounds (VOCs) analysis were collected in 125ml amber glass bottles capped with a ground glass stopper. Bottles were filled completely, ensuring that no air bubbles were present. All samples were stored cold, kept cold during transit, and refrigerated at $4^0$C immediately on arrival at the Greenpeace Research Laboratories.

Detailed descriptions of sample preparation and analytical procedures are presented in Appendix 1.

# 1. Ankleshwar Industrial Estate

## 1.1 Introduction

The Ankleshwar industrial estate is made up of approximately 3,000 individual companies. Over half of these are chemical units, manufacturing dyes, paints, fertilisers, pharmaceuticals, industrial chemicals, pulp and paper and pesticides (Bruno 1995, CPCB 1996). The Ankleshwar Industrial Association has estimated that its members generate between 250-270 million litres a day of liquid waste, and approximately 50 thousand tonnes of solid waste annually (Bruno 1995). Of this, 58% arises from the manufacture of dyes and dyes intermediates, 19% from drugs and pharmaceuticals, and 5% from inorganic chemicals (CPCB 1996).

Many of the larger, more modern plants on the site do have their own wastewater treatment facilities (although the range of chemical parameters addressed is likely to remain limited), while many others send their waste to the common effluent treatment plant described above. It is reported that many of the medium to smaller sized units simply discharge their effluents to a chaotic system of open roadside ditches and an incomplete and broken underground pipeline network, that carry mixed effluent to pumping stations or directly to the river system for discharge.

Two creeks run through the industrial site at Ankleshwar, the Amlakhadi and the Sarangpur Khadi. According to official records, only wastewaters, having being treated at the CETP, are pumped to a common collection channel, which ultimately flows into the Amlakhadi. However in practice, untreated wastes are discharged to both the Amlakhadi and the Sarangpur, which ultimately flow into the Narmada River.

A total of eight samples were collected in the vicinity of the Ankleshwar industrial estate, including two wastewater samples, two ground water samples, and four sediment samples.

## 1.2 Description of sampling sites

**The Common Effluent Treatment Plant (CETP) and the Amlakhadi channel (IT9048, IT9049, IT9051 and IT9052)**

The Common Effluent Treatment Plant (CETP) receives a complex mixture of wastes from a large number of sources on the industrial estate. While some waste is piped directly to the CETP for treatment, the majority is brought in by tanker. A sample of sludge (IT9048) was taken from a pile adjacent to the final settling lagoon of the CETP, from where treated wastewater is discharged into the Amlakhadi. This sludge is believed to be dredged from the final settling lagoon and local sources report that it may be taken to a cement kiln where it is burned as fuel.

A combined solid wastes dump has recently been introduced on the Ankleshwar industrial estate. It was not possible to gain access to this dump area, and there was no visible surface leachate from the dump at the time of sampling.

A matrix of wastewater pipes run throughout the Ankleshwar industrial estate, some of which are used to carry wastewater from a number of sources to the CETP. Some of these pipes, however, are used to discharge untreated wastewater to the Amlakhadi, from where it flows into the Narmada River.

A sample of effluent (IT9049) was taken from a half-full 25 centimeters diameter pipe which was discharging effluent into a channel that leads to the Amlakhadi. This wastewater was pungent, and extremely acidic. It was not possible to determine the source of this effluent. This sample was not intended to be representative of other wastes entering the Amlakhadi, but merely to demonstrate the potential for contamination of the aquatic environment resulting from such discharges.

The Amlakhadi was previously sampled in 1996, at a location near to the Kadakia College. The water was found to contain many organochlorine compounds, including trichlorotoluene and chlorinated benzenes, as part of a diverse mixture of organic pollutants. Sediment collected from the same location at that time had a very high organic content, and contained oils, organic sulfur compounds and organochlorines. Sediments collected from a number of locations along the Amlakhadi contained heavy metals above levels expected for river sediments, including mercury, chromium, cadmium and copper. During monsoon the Amlakhadi overflows, submerging the surrounding lands in polluted water (Santillo *et al.* 1996).

In order to determine the current levels of pollution in the Amlakhadi, the channel was resampled. A sample of river water (IT9051) and sediment (IT9052) were taken from the Amlakhadi at the Ambroli bridge, near to the Central Industries Security Force. This location is approximately 2.5 kilometres downstream of the Ankleshwar industrial estate, and 0.5-1 kilometres downstream of the confluence of the Amlakhadi and the Panoli channel. The river contained large amounts of silt at this point.

**Sarangpur Channel (IT9043)**

A sample of sediment (IT9043) was taken from the Sarangpur channel, approximately 0.5 kilometres from the Sarangpur village, and approximately 0.5 kilometres downstream from the industrial estate. At this point, a solid wastes dump lies adjacent to the Sarangpur channel. According to official sources, the dumping of solid industrial wastes in this area has now been discontinued. It has been reported by locals, however, that the dumping continues. There appeared to be no measures in place to prevent leaching from the solid wastes dump into the Sarangpur channel. At the point of sampling, the channel was approximately 5 centimetres deep and not flowing. The channel is dammed at this point, and the channel is a dry bed upstream of the dam.

**Sarangpur Village (IT9044 and IT9046)**

Two samples of ground water were taken from the village of Sarangpur, approximately 1 kilometre from the Ankleshwar estate. One sample (IT9044) was taken from an open well located approximately 200 metres from the Sarangpur channel, and approximately 0.5 kilometres from the point at which the Sarangpur channel was sampled (IT9043). The well was approximately 25 metres deep, and the ground water was red-brown in colour,

foaming upon agitation. When used for irrigation, the water is reported, by a local farmer, to cause crops of pigeon-peas to fail, and to give a poor yield of malformed fruit from aubergine plants. Prolonged contact of unprotected skin with this water is likewise reported to result in splitting of the skin. A local farmer reported that eleven other wells in Sarangpur village contained water that appears to be of a similar quality.

A further ground water sample (IT9046) was taken from an approximately 35 metre deep bole-hole located in the village of Sarangpur, on the border of Yogi Nagar and Bapu Nagar I settlements. Freshly drawn water from this bore-hole is initially clear and colourless, though exposure to sunlight results in a slight pink colouration after only 10 minutes. Locals reported that either boiling, or exposure to sunlight for a day, results in the water becoming dark red, with a scum on the surface. Use of the water for washing was likewise reported to cause skin irritation. It was reported by locals that this type of colouration of the water has been observed since 1985, though the length of time before a new bore starts to give contaminated water has decreased over the years. A new bore would previously have given uncontaminated water for up to 4-5 years, while at the present a new bore produces contaminated water almost immediately.

**Heubach Colour Limited (sample IT9050)**

Numerous unofficial dumps of unlabelled industrial wastes can be observed throughout the industrial estate. The waste is generally lying in uncovered piles, with no visible means to prevent leaching or spreading of the wastes. A notable example of this is a large amount of blue-green solid waste that has been dumped in an area of approximately 60 metres by 60 metres, on waste ground adjacent to the Heubach Colour Limited plant. A sample of which was collected for analysis.

| Sample Number | Sample Description |
|---|---|
| **IT9043** | Sediment collected from the Sarangpur channel, prior to confluence with the Narmada River, approximately 0.5 kilometres from the Ankleshwar industrial site, and approximately 0.5 kilometres from the village of Sarangpur. |
| **IT9044** | Irrigation water from an open well in the village of Sarangpur, approximately 200 metres from the Sarangpur channel, and 1 kilometre from the Ankleshwar industrial site. |
| **IT9046** | Groundwater collected from a bore-hole in the village of Sarangpur, between the districts of Yogi Nagar and Bapu Nagar I. Used as drinking water. |
| **IT9048** | Sludge collected adjacent to the final settling lagoon of the Ankleshwar Common Effluent Treatment Plant. |
| **IT9049** | Untreated effluent collected from a pipe discharging into a channel that leads to the Amlakhadi channel. |
| **IT9050** | Blue / green solid waste collected from waste ground adjacent to Heubach Colour Limited, Ankleshwar. |
| **IT9051** | Water from the Amlakhadi channel at Ambroli bridge, approximately 2.5 kilometres downstream of the Ankleshwar industrial site, and 1 kilometre downstream of the Panoli confluence |
| **IT9052** | Sediment collected from the Amlakhadi channel (see IT9051) |

***Table 1.1 Descriptions of samples collected from Ankleshwar, Gujarat, India 1999.***

## 1.3 Results and discussion

A total of eight samples were therefore collected from this industrial area (see Table 1.1 for full sample descriptions). Water samples IT9044 and IT9046 were analysed for volatile organic compounds only (see discussion below). The other six samples (IT9043, IT9048, IT9049, IT9050, IT9051 and IT9052) have been analysed for semi-volatile organic compounds and heavy metals. Details of the analytical methods used are given in Appendix 1.

The results of organoscreen analysis are presented in Table 1.2a. Groups of organic compounds reliably identified in these samples are presented in Table 1.2b. List of all reliably identified organic compounds and groups of tentatively identified compounds are presented in Appendix 2 (Tables 1.2c and 1.2d).

Most of the samples from this area contained wide range of organic contaminants with organohalogen compounds being the major contributor. Hexachlorobenzene, chlorinated benzenamines and several isomers of PCBs were identified in five samples, di- and trichlorobenzenes in four samples, and tetra- and pentachlorobenzenes and chlorinated toluenes in three samples. Brominated organic compounds were also identified in three samples (see Table 1.2a). Very similar contaminants, typical from mixed chlorine industries, were found in samples IT9048 and IT9049 as in IT9051 and IT9052.

| Sample Code | Compounds isolated | Number Reliably identified (%) | Halogenated Compounds | PAHs | Phenolic compounds | Phthalates | Organosulphur compounds | Organonitrogen compounds | Organophosphorus compounds | Other aromatics | Aliphatics |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **IT9043** | 23 | 8(35%) | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 6 |
| **IT9048** | 164 | 74(45%) | 28 | 7 | 0 | 0 | 7 | 2 | 0 | 4 | 23 |
| **IT9049** | 135 | 68(51%) | 19 | 3 | 0 | 1 | 7 | 13 | 0 | 15 | 10 |
| **IT9050** | 74 | 28(38%) | 9 | 1 | 1 | 3 | 0 | 1 | 0 | 7 | 5 |
| **IT9051** | 96 | 49(51%) | 18 | 7 | 0 | 1 | 3 | 1 | 0 | 7 | 12 |
| **IT9052** | 170 | 55(34%) | 20 | 0 | 4 | 0 | 1 | 1 | 3 | 4 | 23 |

***Table 1.2a. Results of organoscreen analysis of sediment, solid waste, industrial waste water and river water samples collected in the vicinity of the Ankleshwar Industrial Estate, Gujarat, INDIA***

Results of the heavy metals analysis are presented in Tables 1.3a (solid samples) and 1.3b (aqueous samples). The results show that high levels of copper were found in every sample. Levels in the solid samples ranged from 11.75 g/kg in sample IT9050, collected from a pile of blue / green waste close to the Huebach Colour Limited (dye manufacturers) plant, to 112.5 mg/kg found in the sediment of the Sarangpur. Aqueous samples also contained significant copper levels, with over 6 mg/l present in the unidentified effluent (IT9049), and nearly 600 ug/l present in the river water of the Amlakhadi (IT9051). Sample IT9051 also contained extremely high levels of manganese, and significant levels of cadmium, chromium, nickel and zinc. Sediment sample IT9052, also collected from the Amlakhadi channel, contained elevated levels of chromium, mercury and zinc.

| Groups of compounds reliably identified | Number of samples | Sample Codes |
|---|---|---|
| **ORGANOHALOGEN COMPOUNDS** | | |
| Dichlorobenzenes | 4 | IT9048, IT9049, IT9051, IT9052 |
| Trichlorobenzenes | 4 | IT9048, IT9049, IT9051, IT9052 |
| Tetrachlorobenzenes | 3 | IT9048, IT9051, IT9052 |
| Pentachlorobenzene | 3 | IT9048, IT9049, IT9052 |
| Hexachlorobenzene | 5 | IT9043, IT9048, IT9049, IT9050, IT9052 |
| Chlorinated benzenamines | 5 | IT9048, IT9049, IT9050, IT9051, IT9052 |
| Brominated benzenamines | 2 | IT9048, IT9051 |
| Brominated benzenes | 1 | IT9048 |
| Chlorinated toluenes | 3 | IT9048, IT9051, IT9052 |
| Brominated toluenes | 1 | IT9048, |
| Chlorinated xylenes | 1 | IT9050 |
| Brominated xylenes | 1 | IT9050 |
| Brominated methoxybenzenes | 1 | IT9048 |
| Polychlorinated benzonitriles | 1 | IT9050 |
| Polychlorinated pyridine derivatives | 2 | IT9051, IT9052 |
| Polychlorinated butadienes | 1 | IT9049 |
| PCBs | 5 | IT9043, IT9048, IT9049, IT9051, IT9052 |
| **POLYCYCLIC AROMATIC HYDROCARBONS** | | |
| Naphthalene and its derivatives | 3 | IT9048, IT9049, IT9051 |
| Phenanthrene and its derivatives | 1 | IT9050 |
| **PHENOLIC COMPOUNDS** | | |
| Octyl phenol | 1 | IT9050 |
| Cresols | 1 | IT9052 |
| Phenol | 1 | IT9052 |
| Dichlorophenol | 1 | IT9052 |
| **PHTHALATES** | | |
| DEHP | 3 | IT9049, IT9050, IT9051 |
| DiBP | 1 | IT9050 |
| DBP | 1 | IT9050 |
| **OTHER AROMATICS** | | |
| Biphenyl and its derivatives | 4 | IT9048, IT9049, IT9050, IT9051 |
| Alkylated benzene derivatives | 5 | IT9048, IT9049, IT9050, IT9051, IT9052 |
| Dibenzothiophene and its derivatives | 2 | IT9048, IT9051 |
| Other organosulphur compounds | 4 | IT9048, IT9049, IT9051, IT9052 |
| Benzenamine and its derivatives | 2 | IT9049, IT9052 |
| Azobenzene derivatives | 3 | IT9048, IT9049, IT9051 |
| Other organonitrogen compounds | 1 | IT9049 |
| Organophosphorus compounds | 1 | IT9052 |
| Benzyl benzoate | 1 | IT9052 |
| **ALIPHATICS** | | |
| Linear alkanes and alkenes | 6 | IT9043, IT9048, IT9049, IT9050 IT9051,IT9052 |
| Cyclic alkanes and alkenes | 2 | IT9043, IT9052 |

***Table 1.2b. Groups of organic compounds reliably identified in sediment, solid waste, industrial wastewater and river water samples collected in the vicinity of the Ankleshwar Industrial Estate, Gujarat, INDIA***

Background information on the metals and organic compounds found in these samples, including common sources, environmental behaviour and toxicological properties, are presented in the Appendix 3 and Appendix 4 at the end of this report. Possible sources of these metals and organic compounds in these samples are discussed below.

| Sample Number | Cd (mg/kg) | Cr (mg/kg) | Co (mg/kg) | Cu (mg/kg) | Pb (mg/kg) | Mn (mg/kg) | Hg (mg/kg) | Ni (mg/kg) | Zn (mg/kg) |
|---|---|---|---|---|---|---|---|---|---|
| **IT9043** | n/d | 69.1 | 25.0 | 112.5 | 2.2 | 1009.6 | 1.4 | 50.7 | 62.5 |
| **IT9048** | n/d | 12.0 | 9.0 | 2933.0 | 17.0 | 104.0 | 1.2 | 18.0 | 83.0 |
| **IT9050** | n/d | 33.0 | n/d | 11750.0 | 29.0 | 98.0 | 0.2 | 23.0 | 147.0 |
| **IT9052** | 1.9 | 137.7 | 6.6 | 1434.9 | 67.0 | 219.8 | 3.7 | 30.2 | 159.4 |

***Table 1.3a Results of heavy metals analysis (expressed as mg/kg dry weight), Ankleshwar, Gujarat, India 1999***

| Sample Number | Cd (ug/l) | Cr (ug/l) | Co (ug/l) | Cu (ug/l) | Pb (ug/l) | Mn (ug/l) | Hg (ug/l) | Ni (ug/l) | Zn (ug/l) |
|---|---|---|---|---|---|---|---|---|---|
| **IT9049** | <10 | 540 | <10 | 6360 | 140 | 420 | <2 | 100 | 160 |
| **IT9051** | 20 | 90 | <10 | 580 | <30 | 15610 | <2 | 270 | 280 |

***Table 1.3b Results of heavy metals analysis (expressed as ug/l), Ankleshwar, Gujarat, India 1999***

**The common effluent treatment plant (CETP) and the Amlakhadi channel (IT9048, IT9049, IT9051 and IT9052)**

Four samples were taken in and around this area.

Sludge sample IT9048 was collected adjacent to the CETP lagoon. 164 organic compounds were isolated from this sample. 74 compounds (45%) were reliably identified, 28 of those being organohalogen compounds including di-, tri-, tetra-, penta- and hexachlorobenzenes, tribromobenzene, chlorinated and brominated benzenamines, chlorinated and brominated toluenes, and two PCBs (PCB-135 and PCB-136). Other aromatic compounds found in this sample included naphthalene derivatives, biphenyl and its derivatives, alkylbenzenes, organosulphur and organonitrogen compounds, and linear alkanes and alkenes.

This sample contained high levels of copper, therefore illustrating that even if the CETPs are capable of removing heavy metals from the in-coming waste stream, metals are still left in concentrated solid residues. Possible sources of copper are numerous, as the metal and its compounds are extensively used as alloys and electrical conductors, dyes, printing inks, catalysts, pesticides, disinfectants and fertilisers (ATSDR 1997). Production and use of any of these could release high levels of copper into the environment, and as effluent streams are mixed in the CETP and the open ditches, it is impossible to trace individual waste streams and sources.

Effluent sample IT9049 was collected from an unidentified pipe discharging directly to the Amlakhadi. 135 organic compounds were isolated from this sample. 68 compounds (51%) were reliably identified. Among those, 19 compounds were organohalogens including di-, tri-, penta- and hexachlorobenzenes, chlorinated benzenamines, tetra- and penta-butadiene, and five PCBs (PCB-3, PCB-10, PCB-13, PCB-19 and PCB-24). Other organic compounds found in this samples were naphthalene and its derivatives, one phthalate ester (DEHP), biphenyl and its derivatives, alkylbenzenes, organosulphur compounds, benzenamine and several alkylated benzenamines, aliphatic hydrocarbons, and several

organonitrogen compounds including benzonitrile, nitrobenzene, carbazole, phenazine and a pyridine derivative.

This sample also contained high levels of copper, along with significant levels of chromium. Chromium and its compounds are used in alloys, tanning agents, textile pigments and preservatives, pesticides, catalysts and corrosion inhibitors (ATSDR 1997). Again due to the industrial diversity of the estate and the mixing of waste streams prior to discharge, individual sources of chromium cannot be traced.

Two samples (water sample IT9051 and sediment sample IT9052) were collected from the Amlakhadi channel. 96 and 170 organic compounds were isolated from the samples IT9051 and IT9052 respectively. 49 compounds (51%) and 55 compounds (34%) were reliably identified. Both water and sediment samples contained wide range of compounds similar to those isolated from the CETP-related samples including chlorinated benzenes, chlorinated benzenamines, chlorinated toluenes, chlorinated pyridines, alkylbenzenes, PCBs, organosulphur compounds and linear aliphatics. Only sample IT9051 contained brominated benzenamines, naphthalene and its derivatives, biphenyl and its derivatives, DEHP, dibenzothiphenes, and azobenzene derivatives. At the same time, sample IT9052 also contained penta- and hexachlorobenzenes, which were not present in the sample IT9051, as well as phenolic compounds (phenol, cresols and dichlorophenol), alkylated benzenamine, benzyl benzoate, and organophosphorus compounds including insecticide chlorpyrifos and two relative compounds.

All four samples (IT9048, IT9049, IT9051 and IT9052) indicate contamination of this site by a wide range of organic compounds, the majority of which are toxic to both the environment and humans, and may persist for a long time. In the previous study conducted by Greenpeace (Santillo *et al.* 1996), water and sediment samples from the Amlakhadi channel showed very similar patterns of organic contaminants to the current study. Additionally, however in the current study a wider range of organic contaminants was found, including brominated compounds and the insecticide chlorpyrifos.

It is clear that the operation of the CETP is not effective because the same organic compounds were found in both sediment sample from CETP lagoon (sample IT9048) and in sediment and water from Amlakhadi channel which supposedly receives treated wastes (samples IT9052 and IT9051 respectively). Additionally, toxic chemicals are undoubtedly entering the Amlakhadi channel from the pipes carrying untreated wastewater. Some of the organic compounds found in the Amlakhadi channel samples may represent past contamination because they are persistent (for example, chlorinated benzenes). However, the presence of other halogenated compounds, such as chlorinated and brominated benzenamines, is a sign of current input, because these compounds are likely to break down more rapidly when released to the environment (Kosson & Byrne 1995). More information on toxicological profiles, uses, production and environmental behaviour of key organic compounds identified in these samples is presented in Appendix 3.

Water sample IT9051 contained high levels of cadmium, chromium, copper, manganese, nickel and zinc. Whilst sediment sample IT9052, collected from the same sampling point, contained high levels of copper, and elevated levels of chromium, mercury and zinc. Possible sources of copper and chromium are described above. Possible sources of the other metals include the following (ATSDR 1997):

Cadmium and its compounds are used in metal plating, nickel-cadmium batteries, pigments and PVC stabilisers. Nickel and its compounds are used in alloys, batteries, and catalysts. Mercury and its compounds are used in batteries, catalysts, thermometers, pharmaceuticals, pesticides and in the manufacture of chlorine. Zinc and its compounds are used as alloys, pesticides, catalysts, PVC stabilisers, fertilisers, paints, pigments and dyes. Manganese and its compounds are used in alloys, batteries, catalysts, fertilisers, pesticides and disinfectants.

Levels of these metals found naturally in unpolluted freshwater ecosystems are low. For example, river water levels of cadmium and chromium are usually less than 1 ug/l (ATSDR 1997, WHO 1992), yet 20 ug/l of cadmium and 90 ug/l of chromium were detected in sample IT9051. Similarly river water levels of copper, manganese, nickel and zinc usually range from 20-50 ug/l (ATSDR 1997). Therefore, depending on the reference value used, copper levels in IT9051 exceeded background concentrations by approximately 12-30 times, manganese by 310-780 times, nickel by 5-13 times and zinc by 5-14 times.

Levels of mercury in uncontaminated sediments are extremely low, with usual concentrations ranging from 0.2-0.35 mg/kg (Salomons and Forstner 1984). Therefore in sample IT9052, levels approximately 10-18 times background concentrations are present. Background levels of copper, zinc and chromium are usually less than 100 mg/kg, and again these levels are exceeded in sample IT9052.

The environmental behaviour and toxicological properties of these metals are discussed in the Appendix 4 at the end of this report.

**Sarangpur channel (IT9043)**

One sample of sediment was collected from the Sarangpur channel. 23 organic compounds were isolated from this sample. 35% of those were reliably identified, with linear and cyclic aliphatic hydrocarbons being dominant. Additionally, two organochlorine compounds, hexachlorobenzene and one isomer of PCBs (PCB-9) were also reliably identified in this sample.

Hexachlorobenzene strongly adsorbs to soil particles (Bahnick & Doucette 1988). If discharged into water, it can be transported for long distances attached to the particles and finally deposit. It may persist in the soil, air, surface and ground water for many years (Howard 1991). It is known that hexachlorobenzene is commonly used as an intermediate in organic syntheses (Budavari et al. 1989) and may be formed as an unwanted by-product in the synthesis of other organochlorine compounds (Newhook & Meek 1994, Sala et al. 1999). Thus, the presence of hexachlorobenzene in this sediment sample may be associated with wastes generated from Ankleshwar Industrial Estate, which includes such industries.

PCB-9, or 2,5-dichlobiphenyl, is a representative of a large group of polychlorinated biphenyls. The PCBs have been used widely in different applications, including transformer oils, hydraulic fluids, plasticisers, 'kiss-proof' lipsticks and carbonless copy papers. They were also used in capacitor dielectrics, heat transfer fluids, lubricating and cutting oils, and in paints and printing inks (ATSDR 1997). PCBs were always marketed as technical mixes rather than individual chemicals (de Voogt & Brinkman 1989).

Additionally, PCBs used in transformer oils were usually mixed with chlorobenzenes (mainly trichlorobenzenes and tetrachlorobenzenes) as solvents (Swami *et al.* 1992, de Voogt & Brinkman 1989). Tri- and tetrachlorobenzenes were not found in this sample. Therefore the presence of PCB-9 in this sample may be associated with an alternative source. For example, it may have been formed as a by-product of the chlorine chemical industry. Such industries include the PVC industry. Waste EDC tars, together with aqueous effluents, are known to be contaminated by dichlorobiphenyls (see: US EPA 1994).

Levels of heavy metals in this sediment sample were significantly lower than those found in a similar sample collected from the Amlakhadi channel. However the level of copper found was higher than that usually associated with uncontaminated sediments. Background levels of copper are usually quoted as less than 50 mg/kg (Salomons and Forstner 1984), twice this concentration was detected in sample IT9043.

It is clear, based on our other results (from both 1996 and 1999), and our knowledge of the types of industries located in Ankleshwar, that copper contamination in this area is widespread. Such generally elevated levels of copper are again indicative of the inadequate process control and waste management practices employed by many industries of the Ankleshwar estate.

**Sarangpur Village (IT9044 and IT9046)**

Only one volatile organic compound, 1,2,4-trichlorobenzene, was found in the sample IT9044 at a concentration of 15ug/l. Environmental releases of this compound may result from industrial discharges and from spillage of dielectric fluids. 1,2,4-trichlorobenzene may be found in all environmental media. In groundwater, it may persist for several years (Howard 1991). Trichlorobenzenes have also been found in drinking water, but rarely above 1ug/l (WHO 1993). This compound may be used as a solvent and an intermediate in organic synthesis (Giddings *et al.* 1994). Additionally, 1,2,4-trichlorobenzene may be formed through the dehydrohalogenation of the unwanted isomers of the production of the pesticide 1,2,3,4,5,6-hexachlorocyclohexane (HCH).

No volatile organic compounds were found in the drinking water sample IT9046. It was not possible to determine the agents responsible for the colour change reported upon exposure to sunlight or heat.

**Heubach Colour Limited (sample IT9050)**

One sample of blue-green waste was collected close to this dye and pigment factory. The intense colour was due to the presence of high levels of copper, which is widely used in the manufacture of dyes, pigments and printing inks (ATSDR 1997). The lack of any suitable containment facility for this waste is a concern, and may be one of the reasons why copper contamination in and around this industrial estate is so widespread. The environmental behaviour of copper and its toxicological properties are given in an appendix at the end of this report.

74 organic compounds were isolated from this sample. 28 compounds (38%) were reliably identified, including nine halogenated compounds (hexachlorobenzene, tetra- and

pentachlorinated benzenamines, chlorinated and brominated xylenes, and pentachlorobenzonitrile), three phthalate esters (DEHP, DBP and DiBP), octyl phenol, alkylated biphenyl and benzene derivatives, linear aliphatic hydrocarbons, and phenanthrene and its derivatives. The majority of these compounds is toxic and persistent and their appearance in the sample may be associated with dye and pigment manufacture. More information on toxicological profiles, uses, production and environmental behaviour of key organic compounds is presented in Appendix 3.

# 2. Nandesari Industrial Estate

## 2.1 Introduction

The Nandesari industrial estate was established in 1969, and is now made up of approximately 300 industrial units, including those that produce a wide range of chemicals, pharmaceuticals, dyes, pesticides and plastics (Tiwari and Mahapatra 1999, CPCB 1996). The main contributors to the total quantity of waste generated by the estate include dyes and dye intermediates manufacture (82%), and the production of drugs and pharmaceuticals (13%) (CPCB 1996).

Only 80 of the companies on site are known to send their effluents to the CETP (Tiwari and Mahapatra 1999), with plant operators unsure of what happens to the rest. However, as was seen in Ankleshwar, albeit on a much wider scale, indiscriminate dumping and the use of roadside ditches to carry waste are widespread and common practices.

From the CETP, effluents are carried along a communal channel (Bruno 1995). Known as the "Effluent Channel Project, this runs for 55 kilometres before discharging into the Mahi River estuary close to the point where it debouches to the Gulf of Khambat. It is likely, however, that additional untreated wastes from the site and from the surrounding area are also carried along this channel to the estuary.

A total of four samples were taken from the vicinity of the Nandesari industrial estate, including two wastewater samples, and two sediment samples.

### 2.2 Description of sampling site

**The common effluent treatment plant (CETP) (IT9054)**

The Common Effluent Treatment Plant (CETP) receives a complex mixture of wastes from a large number of different sources on the Nandesari industrial estate. A sample of sludge (IT9054) was taken from the final settling lagoon of the CETP, from which wastewater is discharged to the Mahi River estuary on the Gulf of Khambhat via the communal effluent channel.

In 1996, sludge from one of the CETP evaporation ponds was collected for analysis. This sludge was found to contain chlorinated toluenes and chlorinated naphthalenes (*Santillo* et al. 1996), none of which are efficiently degraded in standard effluent treatment plants. It is not clear whether sample IT9054 was from the same lagoon as that sampled on the previous occasion.

**Communal Effluent Channel (The Effluent Channel Project) (IT9053, IT9055, IT9056)**

Wastewaters from the CETP and from other sources are carried along a 55 kilometre long, partially covered, brick lined channel to the Mahi River Estuary close to the point where the estuary enters the Gulf of Khambhat. The discharge point is known as "Point J" and is located near to Sarod, north of Jambusar. The channel is approximately 4 metres deep, and carries wastewater to a depth of approximately 3 metres. The channel does not appear to be lined to prevent leaching of the wastewater to the surrounding land and groundwater. Along the length of the channel, small pumps can be observed removing wastewater for the irrigation of cultivated land. It has been reported, by locals, that some industries discharge untreated wastewater directly into the effluent channel at various points and that clean water is often added to the channel in order to dilute any pollutants in the wastewater.

A sample of treated wastewater (IT9053) was taken from the effluent channel at a point approximately 1 kilometre downstream of the CETP. Wastewater from other sources may discharge into the effluent channel prior to this point. It was not possible to access the effluent channel any closer to the CETP.

A further sample of wastewater (IT9056) was taken from the effluent channle approximately 2-3 kilometres downstream of the Nandesari estate, close to Koyli Point. This sample was taken to determine the nature of any additional pollutants resulting from the discharge of effluents (likely to be untreated) into the waste channel.

Located approximately 2 kilometres downstream of the Nandesari estate is an "escape" channel, to enable excess wastewater to overflow from the effluent channel into the Mini River which is a tributary to the Mahi River. It was reported by a local person that this escape channel flows for at least three months of the year.

There are a number of other chemical manufacturing plants close to the effluent channel between the Nandesari estate and the discharge point, Point J. Some of these are located close to Luna village, approximately 15-20 kilometres downstream of the Nandesari complex. It has been reported , by local people, that a number of these facilities discharge untreated or partially treated wastewaters into the effluent channel.

It was not possible to sample the wastewater from the effluent channel at the point of discharge, Point J. Three holding lagoons for wastewater from the effluent channel are located approximately 1 kilometre upstream of Point J. These lagoons are separately connected to the effluent channel via a sluice gate. All wastewater from the effluent channel flows through these holding lagoons to the discharge point, Point J. A sample of sediment (IT9055) from one of these lagoons was collected in order to give an indication of pollutants present in the wastewater flowing through the effluent channel on the basis that sediments tend to "integrate" contaminants present in the overlying water by adsorption processes.

| Sample Number | Sample Descriptions |
|---|---|
| **IT9054** | Sludge collected from the CETP final settling lagoon. |
| **IT9053** | Treated effluent collected from the effluent channel between the CETP and the Gulf of Khambhat, approximately 1 kilometre downstream of the CETP. |
| **IT9056** | Effluent collected from the effluent channel approximately 2-3 kilometres downstream of the Nandesari estate. |
| **IT9055** | Sludge collected from one of three holding lagoons adjoined to the effluent channel, close to the point of discharge into the Gulf of Khambhat. |

***Table 2.1 Description of samples collected from Nandesari, Gujarat, India 1999.***

## 2.3 Results and discussion

Four samples were collected from the Nandesari industrial area (see Table 2.1 for full sample descriptions).

Results of the organic screening analysis are presented in Tables 2.2a and 2.2b. A list of all reliably identified organic compounds and groups of tentatively identified compounds is presented in Appendix 2 (Table 2.2c).

| Groups of compounds reliably identified | Number of samples | Sample Codes |
|---|---|---|
| **ORGANOHALOGEN COMPOUNDS** | | |
| Dichlorobenzenes | 4 | IT9053, IT9054, IT9055, IT9056 |
| Trichlorobenzenes | 2 | IT9054, IT9055 |
| Tetrachlorobenzenes | 1 | IT9054 |
| Pentachlorobenzene | 1 | IT9054 |
| Hexachlorobenzene | 1 | IT9054 |
| Chlorinated benzenamines | 1 | IT9054 |
| Chlorinated toluenes | 1 | IT9054 |
| Chlorinated naphthalenes | 1 | IT9054 |
| Polychlorinated butadienes | 1 | IT9054 |
| **POLYCYCLIC AROMATIC HYDROCARBONS** | | |
| Naphthalene and its derivatives | 2 | IT9053, IT9054 |
| 9H-Fluorene | 1 | IT9056 |
| Phenanthrene and its derivatives | 2 | IT9054, IT9056 |
| **PHENOLIC COMPOUNDS** | | |
| Alkyl phenol derivatives | 2 | IT9053, IT9056 |
| **OTHER AROMATICS** | | |
| Biphenyl and its derivatives | 1 | IT9056 |
| Alkylated benzene derivatives | 2 | IT9053, IT9056 |
| Organosulphur compounds | 1 | IT9054 |
| **ALIPHATICS** | | |
| Linear alkanes and alkenes | 3 | IT9054, IT9055, IT9056 |

***Table 2.2a. Groups of organic compounds reliably identified in industrial wastewater and solid waste samples collected in the vicinity of the Nandesari Industrial estate, Baroda, Gujarat, INDIA***

| Sample Code | Compounds isolated | Number reliably identified (%) | Halogenated Compounds | PAHs | Phenolic compounds | Other aromatics | Aliphatics |
|---|---|---|---|---|---|---|---|
| **IT9053** | 43 | 14(33%) | 1 | 1 | 1 | 11 | 0 |
| **IT9054** | 169 | 49(27%) | 15 | 12 | 0 | 2 | 19 |
| **IT9055** | 34 | 6(18%) | 3 | 0 | 0 | 0 | 3 |
| **IT9056** | 65 | 20(31%) | 3 | 7 | 1 | 4 | 5 |

***Table 2.2b . Results of organoscreen analysis solid waste and industrial wastewater samples collected in the vicinity of the Nandesari Industrial estate, Baroda, Gujarat, INDIA***

Results of the heavy metals analysis are presented in Tables 2.3a (solid samples) and 2.3b (aqueous samples).

| Sample Number | Cd (mg/kg) | Cr (mg/kg) | Co (mg/kg) | Cu (kg/mg) | Pb (mg/kg) | Mn (mg/kg) | Hg (mg/kg) | Ni (mg/kg) | Zn (mg/kg) |
|---|---|---|---|---|---|---|---|---|---|
| IT9054 | n/d | 77.5 | 59.8 | 536.3 | 122.6 | 191.2 | 2.3 | 295.1 | 2762.6 |
| IT9055 | 2.9 | 65.7 | 54.9 | 99.0 | 4.9 | 435.3 | 1.5 | 67.7 | 658.8 |

***Table 2.3a Results of heavy metal analysis (expressed as mg/kg dry weight) Nandesari, Gujarat, India 1999***

| Sample Number | Cd (ug/l) | Cr (ug/l) | Co (ug/l) | Cu (ug/l) | Pb (ug/l) | Mn (ug/l) | Hg (ug/l) | Ni (ug/l) | Zn (ug/l) |
|---|---|---|---|---|---|---|---|---|---|
| IT9053 | <10 | <10 | <10 | 10 | 40 | 40 | <2 | 60 | 50 |
| IT9056 | <10 | 60 | 20 | 40 | <30 | 90 | <2 | 40 | 200 |

***Table 2.3b Results of heavy metal analysis (expressed as ug/l) Nandesari, Gujarat, India 1999***

## The common effluent treatment plant (CETP) (IT9054)

169 organic compounds were isolated from the sediment sample collected from the CETP final settling lagoon (IT9054). 49 compounds were reliably identified including 15 organochlorine compounds: di-, tri-, tetra-, penta-, and hexachlorobenzene, chlorinated benzeneamines, chlorinated toluenes, chlorinated naphthalenes and tetra-, penta- and hexachlorobutadiene.

More information on toxicity, uses, production and environmental behaviour of key organic compounds is presented in Appendix 3.

Heavy metal analysis results show that significant levels of copper, lead, mercury, nickel, and zinc were found in the sludge collected from the CETP settling lagoon (IT9054). This illustrates, once again, that the CETP is only capable of redistributing heavy metal contaminants from the liquid to the solid sludge phase. While this may reduce the immediate loading to surface waters, it also creates an additional contaminated waste stream that must be addressed.

Possible sources of heavy metals are numerous and have been, with the exception of lead, described above. Lead is widely used in alloys, solder and batteries. Lead compounds have been used in paint pigments, PVC stabilisers, in pesticides, varnishes, lubricants, glazes and petrol additives (ATSDR 1997). Due to the diversity of the industries operating on the Nandesari estate, it is not possible to reconcile sources of lead any more specifically.

**Communal Effluent Channel (The Effluent Channel Project) (IT9053, IT9055, IT9056)**

43 organic compounds were isolated from the water sample IT9053 collected from the effluent channel approximately 1 kilometre downstream of the CETP. 14 compounds (33%) were reliably identified with alkylated benzenes being the major contributor. 1,4-dichlorobenzene, naphthalene and butylated hydroxytoluene (BHT) were also found in this sample.

As noted above, both the CETP and this channel receive the combined wastes from a variety of industries. Hence, the composition of the wastewater discharging into this channel may vary on a daily basis or even change several times per day depending upon which industries are contributing qualitatively and quantitatively to the overall effluent flow at any given time. This situation may be further exacerbated by the operation of many of the small to medium-sized plants largely in a batch, rather than continuous, mode of production. The compounds associated with crude oil or petroleum products were predominant in the water sample IT9053 at the time of sampling. The wide range of persistent organochlorine compounds in the sediment sample from the CETP final settling lagoon (IT9054) indicate, however, that these compounds have been discharged to the CETP at other times.

65 organic compounds were isolated from the water sample collected from the channel approximately 2-3 kilometres downstream of the Nandesari estate (IT9056). 20 compounds (31%) were reliably identified. These consisted of three isomers of dichlorobenzene, seven polycyclic aromatic hydrocarbons (PAHs), three alkylbenzenes, biphenyl, butylated hydroxytoluene and aliphatic hydrocarbons. Organic compounds found in this sample were similar to those found in the water sample IT9053 collected near to the CETP. The major difference evident was that two more dichlorobenzenes and additionally PAHs were identified in the sample IT9056 in comparison to sample IT9053. As noted previously, chlorinated benzenes are persistent compounds, which can be expected to be detectable at considerable distances from the initial point of discharge.

In the sediment sample IT9055, which was collected from one of the holding lagoons prior to discharge at Point J, only 6 compounds (18%) could be identified with high degree of reliability. Once again di- and trichlorobenzenes and aliphatic hydrocarbons predominated.

In general, analysis of the samples collected from this area showed that majority of organochlorine compounds were retained in the settling lagoon of the CETP (sample IT9054). Nevertheless, chlorinated benzenes were still found along whole length of the channel. As noted in the description of the Nandesari sampling program, water from the channel is used for irrigation. 1,4-Dichlorobenzene has been shown to inhibit the growth of cultured plant cells (Wang *et al.* 1996). These chemicals have been found in food, breast milk and drinking water in other industrialised countries (Meek et al. 1994). Moreover, they are also toxic to higher plants, inducing abnormal mitosis (cell division) in

onions for example (Ware 1988). More information on toxicity, uses, production and environmental behaviour of these and other key organic compounds is presented in Appendix 3.

Elevated levels of metals were not detected in the wastewater sample collected from the effluent channel approximately 1 kilometre downstream of the CETP (IT9053). The wastewater sample (IT9056) collected from approximately 2-3 kilometres downstream of the Nandesari estate, however, contained a number of metals including chromium, manganese and zinc. These were elevated above the levels found in sample IT9053.

For a number of metals, including chromium and mercury, levels found in the sludge collected from the effluent channel holding lagoons (IT 9055) were comparable with those found in the sludge collected from the CETP settling lagoon (IT9054). In addition, the concentration of manganese in the holding lagoon was higher than that found in the CETP sludge (IT9054). Although cadmium was not detected in the CETP sludge (IT9054), elevated levels were detected in the sludge from the holding lagoon (IT9055). These results are indicative of the discharge of wastewaters containing heavy metals to the effluent channel from sources other than the CETP.

# 3. Vapi Industial Estate

## 3.1 Introduction

The Vapi industrial estate is made up of nearly 2000 industrial units, that produce a wide range of chemicals, pharmaceuticals, dyes, pesticides and other agrochemicals, and plastics (Tiwari and Mahapatra 1999, CPCB 1996), with dye manufacturers and dye intermediate units contributing the largest quantity of hazardous waste (CPCB 1996). The situation regarding effluent treatment is same as that seen in Ankleshwar and Nandesari. Some companies send their waste to the common effluent treatment plant (CETP), whilst others dump solids indiscriminately and discharge their effluents into open ditches and lagoons.

The CETP has been completed and commissioned since the last study conducted by Greenpeace in 1996. Effluents from the CETP are discharged into the Damanganga River. However visual surveys of the plant reveal that some wastes are also discharged into this river, carried by a channel which appears to bypass the CETP.

A total of three samples were taken from the Vapi industrial estate, including two water samples, and one sediment sample.

## 3.2 Description of sampling sites

### The Common Effluent Treatment Plant

In 1996, prior to the introduction of the Common Effluent Treatment Plant (CETP), samples of sludge collected from a common effluent channel at it's confluence with the Damanganga River contained, among other compounds, chlorinated benzenes and dichlorodiazobenzenes. Both the effluent and sediment samples collected from this channel also contained elevated levels of metals, including lead and mercury (Santillo *et*

*al.* 1996).

The now operational CETP receives a complex mixture of wastes from a large number of different sources. Treated wastewater is discharged into the Damanganga River, close to the CETP. In order to determine the effectiveness of the CETP in treating the complex mixture of wastes it receives, the discharge wastewater was of the CETP was sampled from the outfall pipe, on the bank of the Damanganga River (IT9058).

Adjacent to the outfall pipe of the CETP, a black stream of what appeared to be industrial wastewater flows from the direction of the CETP directly into the Damanganga River. This wastewater, although distinct from the CETP discharge, appeared to originate from the location of the CETP. A sample of the liquid from this flow (IT9059) and sediment from beneath the liquid (IT9060) were taken for analysis.

| Sample Number | Sample Description |
|---|---|
| **IT9058** | Treated effluent collected from the Common Effluent Treatment Plant outfall pipe, at the point of discharge to the Damanganga River. |
| **IT9059** | Effluent collected from a black stream of industrial wastewater flowing into the Damanganga adjacent to the CETP outfall pipe. |
| **IT9060** | Sediment collected from a black stream of industrial wastewater flowing into the Damanganga adjacent to the CETP outfall pipe (see IT9059). |

***Table 3.1 Descriptions of samples collected from Vapi, Gujarat, India 1999.***

## 3.3 Results and discussion

Results of the organic screening analysis are given in Tables 3.2a and 3.2b. List of all identified organic compounds are presented in Appendix 2 (Table 3.2c).

Results of the heavy metals analysis are presented in Tables 3.3a and 3.3b.

### The common effluent treatment plant and bypass channel (IT9058-IT9060)

Both treated (IT9058) and apparently untreated (IT9059) wastewater samples were found to be heavily contaminated by organochlorine compounds. 18 and 35 organic compounds were isolated from samples IT9058 and IT9059 respectively. 12 organic compounds (67%) and 22 organic compounds (63%) were reliably identified in these samples. Organochlorine compounds represented the majority of reliably identified compounds in both samples: 10 and 11 of those were found in the sample IT9058 and IT9059 respectively. The classes of detected organochlorine compounds again included di-, tri-, tetrachlorobenzenes and chlorinated benzenamines. Diphenyl ether was also reliably identified in both samples. Additionally, sample IT9058 contained chlorinated a pyridine derivative and naphthalene. Sample IT9059 contained penta- and hexachlorobenzene, dibenzothiophene derivative and linear aliphatic hydrocarbons.

| Groups of compounds reliably identified | Number of samples | Sample Codes |
|---|---|---|
| **ORGANOHALOGEN COMPOUNDS** | | |
| Dichlorobenzenes | 3 | IT9058, IT9059, IT9060 |
| Trichlorobenzenes | 3 | IT9058, IT9059, IT9060 |
| Tetrachlorobenzenes | 3 | IT9058, IT9059, IT9060 |
| Pentachlorobenzene | 2 | IT9059, IT9060 |
| Hexachlorobenzene | 2 | IT9059, IT9060 |
| Chlorinated benzenamines | 3 | IT9058, IT9059, IT9060 |
| Chlorinated diazobenzenes | 1 | IT9060 |
| Chlorinated pyridine derivatives | 1 | IT9058 |
| PCBs | 1 | IT9060 |
| **POLYCYCLIC AROMATIC HYDROCARBONS** | | |
| Naphthalene and its derviatives | 1 | IT9058 |
| **PHENOLIC COMPOUNDS** | | |
| Cresols | 1 | IT9060 |
| **PHTHALATES** | | |
| DEHP | 1 | IT9060 |
| **OTHER AROMATICS** | | |
| Dibenzothiophene and its derivatives | 1 | IT9059 |
| Benzaldehyde | 1 | IT9060 |
| Benzothiazole derivatives | 1 | IT9060 |
| Benzenamine and its derivatives | 1 | IT9060 |
| Carbazole derivatives | 1 | IT9060 |
| Organophosphorus compounds | 1 | IT9060 |
| Diphenyl ether | 3 | IT9058, IT9059, IT9059 |
| **ALIPHATICS** | | |
| Linear alkanes and alkenes | 2 | IT9059, IT9060 |

***Table 3.2a. Groups of organic compounds reliably identified in sediment and industrial wastewater samples collected in the vicinity of the Vapi Industrial Estate, Gujarat, INDIA***

| Sample Code | Compounds isolated | Number reliably identified (%) | Halogenated Compounds | PAHs | Phenolic compounds | Phthalates | Organosulphur compounds | Organonitrogen compounds | Organophosphorus compounds | Other aromatics | Aliphatics |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **IT9058** | 18 | 12(67%) | 10 | 1 | 0 | 0 | 0 | 0 | 0 | 1 | 0 |
| **IT9059** | 35 | 22(63%) | 11 | 1 | 0 | 0 | 1 | 0 | 0 | 1 | 11 |
| **IT9060** | 79 | 37(47%) | 17 | 1 | 2 | 1 | 1 | 2 | 1 | 2 | 10 |

***Table 3.2b . Results of organoscreen analysis of sediment and industrial wastewater samples collected in the vicinity of the Vapi Industrial Estate, Gujarat, INDIA***

| Sample Number | Cd (mg/kg) | Cr (mg/kg) | Co (mg/kg) | Cu (mg/kg) | Pb (mg/kg) | Mn (mg/kg) | Hg (mg/kg) | Ni (mg/kg) | Zn (mg/kg) |
|---|---|---|---|---|---|---|---|---|---|
| IT9060 | 66.4 | 339.1 | 17.3 | 329.1 | 245.5 | 222.7 | 2.6 | 55.5 | 659.1 |

***Table 3.3a Results of heavy metal analysis (expressed as mg/kg dry weight) Vapi, Gujarat, India 1999***

| Sample Number | Cd (ug/l) | Cr (ug/l) | Co (ug/l) | Cu (ug/l) | Pb (ug/l) | Mn (ug/l) | Hg (ug/l) | Ni (ug/l) | Zn (ug/l) |
|---|---|---|---|---|---|---|---|---|---|
| IT9058 | 50 | 90 | <10 | 180 | 70 | 990 | 2 | 70 | 390 |
| IT9059 | 4820 | 16500 | 170 | 17410 | 13190 | 3680 | 61 | 1090 | 53230 |

***Table 3.3b Results of heavy metal analysis (expressed as ug/l) Vapi, Gujarat, India***

Sediment sample IT9060 collected from the black stream of apparently untreated effluent contained more organic compounds which could be isolated and reliably identified than liquid sample IT9059 from this channel. Nonetheless, these included the compounds isolated from the liquid sample. 17 organohalogen compounds were reliably identified in the sediment sample including di-, tri-, tetra-, penta- and hexachlorobenzenes, chlorinated benzenamines, chlorinated diazobenzenes and PCBs. Other organic compounds found in this sample included cresols, a phthalate ester (DEHP), benzaldehyde, a benzothiazole derivative, N-alkylated benzenamines, a carbazole derivative, the pesticide chlorpyrifos and linear aliphatic hydrocarbons.

The range of organic compounds found in the sample IT9058 indicates that that CETP is ineffective in removing a wide range of toxic, persistent and bioaccumulative compounds. These, along with similar contaminants from the channel which appears to bypass the CETP (IT9059 and IT9060), are introduced into the Damanganga River. More information on toxicity, uses, production and environmental behaviour of key organic compounds is presented in Appendix 3.

Heavy metals analysis results show that both the effluent (IT9059) and the sediment (IT9060) collected are heavily contaminated with cadmium, chromium, copper, lead, mercury, nickel and zinc.

Levels of these metals in unpolluted rivers are extremely low; as described above, cadmium, chromium and mercury concentrations are usually less than 1 ug/l, whereas concentrations of copper, lead, nickel and zinc generally range from 20-50 ug/l (ATSDR 1997). This effluent contained mg/l levels of cadmium, chromium, copper, lead, nickel and zinc, along with concentrations of mercury usually only associated with discharges from the chlor-alkali and gold mining industries. These levels are thousands of times greater than those that would occur naturally. Therefore the continued discharge of this effluent is of very great concern, as is the disposal of the contaminated sludge that remains in the channel.

In addition, even the effluent that has been through the CETP (IT9058) contains high

levels of cadmium, and detectable levels of chromium, copper, lead, manganese, mercury, nickel and zinc. It is also probable that, were it to be sampled, the sludge at the bottom of the settling tank would be very heavily contaminated, as many of the metals will simply partition out of the water phase and into the sludges. No information is available on the fate of the contaminated CETP sludges.

Of all the samples collected and analysed for heavy metals in the current study, these were by far the most contaminated. Possible sources have been described above, and details on the environmental behaviour of these metals, and their toxicological properties can be found in the appendices at the end of this report.

# 4. Sarigam

## 4.1 Introduction

The town of Sarigam is situated approximately 15 kilometres south of Vapi. A separate industrial estate has been expanding in the area over recent years, and there have been reports by the local community of contamination of the ground water in the area. It has likewise been reported that some industries in the area pump untreated wastewater into the ground via bore-holes. The introduction of a CETP to handle the treatment of combined wastewaters from industries in the area has been proposed.

## 4.2 Description of sampling site

In order to determine the current levels of contamination of the ground water, a sample (IT9062) was taken from a bore-hole in the village of Sarigam, close to the Okarkhadi. The landowner reported that the bore-hole had been introduced to replace an open well, the water from which had become too contaminated for use. The same owner also reported that the quality of the water from the bore-hole had progressively decreased over a number of years.

| Sample Number | Sample Description |
|---|---|
| IT9062 | Groundwater collected from a 30-45 metre deep bore-hole in the town of Sarigam. |

***Table 4.1 Description of the sample collected from Sarigam, Gujarat, India 1999.***

## 4.3 Results and discussion

Groundwater sample IT9062 collected from the village of Sarigam was analysed for volatile organic compounds (VOC) only. Organoscreen analysis of this sample showed the presence of five compounds: benzene, chlorobenzene, 1,3- and 1,4-dichlorobenzenes, and trichloroethene. Chlorinated compounds found in this sample have been quantified. The results of quantitative analysis are presented in Table 4.2.

| Compound | MDL, ug/l* | Concentration, ug/l |
|---|---|---|
| **Trichloroethene** | **5** | **20** |
| **Chlorobenzene** | **5** | **85** |
| **1,3-Dichlorobenzene** | **5** | **10** |
| **1,4-Dichlorobenzene** | **5** | **5** |

***Table 4.2 Concentration of volatile organochlorine compounds found in groundwater sample IT9062, Sarigam, Gujarat, India. * MDL – minimum detectable level***

As was mentioned in the description of the sampling in Sarigam, some industries in this area reportedly pump untreated wastewater into the ground via bore-holes. Thus, the appearance of the chemical contaminants found in the sample IT9062 may be of little surprise.

Industrial wastewater discharges, solid chemical wastes and dump leachates have been reported to be the major source of environment pollution by chlorinated benzenes (Howard 1989). Dichlorobenzenes can be moderately to tightly absorbed to particles when released to soil. Nevertheless, they have also been detected in various groundwaters around hazardous waste disposal areas indicating that these contaminants are able to leach (Howard 1989). Environmental release of chlorobenzene may also be expected to derive from its use as a solvent, either through fugitive emissions or volatilisation from pesticides for which it used as a carrier. Indeed, the results obtained from analysis of waste waters and sediments in this study indicate the high mobility, and ubiquitous distribution, of dichlorinated benzenes.

Trichloroethene, widely used as organochlorine solvent, may be introduced to the environment from direct manufacture discharges or it could be formed in groundwater which is contaminated with various other chlorinated solvents under anaerobic conditions i.e. through partial degradation (Hashsham *et al*. 1995, Loran & Olsen 1999, Butler & Hayes 1998, Miller *et al*. 1998). Chlorinated solvents have a density greater than water (CRC 1969) and groundwater plumes of these contaminants may form pools of residual solvent below the water table (Rivett *et al.* 1994). Chlorinated solvents could dissolve into groundwater from the existing immiscible phase and move with the general flow of groundwater. Modelling studies suggest that individual plumes may extend for several kilometres from their source (Burston *et al.* 1993). Chlorinated solvents may undergo reductive dechlorination under anaerobic conditions, though it has been reported that final transformation into methane and ethane is significantly retarded if several of these compounds are present together (Hughes & Parkin 1996a & b).

Contamination of the groundwater by chlorinated solvents is a world-wide problem and occurs in most cases in the vicinity of the industrial sites where these compounds are involved in the technological processes. Trichloroethene was the most ubiquitous pollutant in the investigation of groundwater pollution in the Coventry region (UK) (Lerner *et al.* 1993).

Quantitatively, only trichloroethene has exceeded the permissible levels set for drinking water in the sample of groundwater from Sarigram. According to the US Environmental Protection Agency (US EPA 1999) the levels of trichloroethene in drinking water should not be more than 5ug/l, which is four times lower that levels of this solvent found in the sample IT9062. Levels of 1,4-dichlorobenzene in the sample were lower than US EPA

limits. Nevertheless, the presence of these chemicals in unchlorinated groundwater is of concern. There are no limit values for chlorobenzene and 1,3-dichlorobenzene in drinking water, despite the fact that these chemicals are also hazardous. Animal studies have reported liver necrosis, renal toxicity and effects on the pancreas, blood and lymph and adrenal glands (Ware 1988a, Meek *et al.* 1994a) following exposure to chlorobenzene.

Benzene was the most abundant contaminant in this sample. Various industries use benzene to make other chemicals, such as styrene, cumene (for various resins), and cyclohexane (for nylon and synthetic fibres). Benzene is a component of crude oil and gasoline (ATSDR 1997) and is used for the manufacturing of some types of rubbers, lubricants, dyes, detergents, drugs, and pesticides. Benzene in water and soil breaks down quite slowly. It is slightly soluble in water and can pass through the soil into underground water (ATSDR). Eating or drinking foods containing high levels of benzene can cause vomiting, irritation of the stomach, dizziness, sleepiness, convulsions, rapid heart rate, coma, and death. It is also found that benzene can cause cancer of the blood-forming organs. The US Department of Health and Human Services (DHHS) has determined that benzene is a known human carcinogen (DHHS 1998).

Further information on toxicity, common sources and environmental behaviour of organic compounds found in this study is given in Appendix 3.

## Conclusions

Common effluent treatment plants (CETPs), which operate in Ankleshwar, Nandesari and Vapi Industrial Estates, have been promoted as the long-term solution to the problem of contaminated wastewater disposal in India. While such CETPs may well address part of the problem relating to high loading of surface waters with degradable organic material, BOD, solids and nutrients, these plants are fundamentally incapable of degrading or detoxifying the wide range of heavy metal and persistent organic contaminants which are also present. At best they can achieve a redistribution of these contaminants from the liquid to the solid sludge phase, reducing the immediate loading to surface waters but creating an additional contaminated waste stream which must be disposed of. In addition, many of the more volatile organic compounds (VOCs) may be released to the atmosphere before they can be degraded. For example, Haas and Herrmann (1996) estimate typical VOC losses from settlement ponds receiving effluents containing organic compounds in the mg or g per litre range, to be of the order of 10-100g per m per day.

Some of the less persistent organic compounds (e.g. 2,4-dichlorophenol or halogenated benzenamines) can be degraded by microbiological processes. However, to achieve acceptable and reproducible degradation of such compounds, specific process designs are generally required, including an inoculum of micro-organisms acclimated to survive with, and metabolise, the waste compounds in question (Fulthorpe & Allen 1995, Gonzalez *et al.* 1996). Many organisms appear to be capable of degrading chlorinated long-chain aliphatic compounds, but fewer strains can metabolise chlorinated aromatics (Mohn & Tiedje 1992). Complex and expensive plant, and long effluent residence times, are often required in order to achieve removal to an acceptable standard (Tunay *et al*. 1994). The upflow anaerobic sludge blanket plant is one such system (Duff *et al.* 1995).

Treatment systems are frequently subject to stimulation or inhibition as a result of changes in the flow rate and composition of wastewaters (Limbert & Betts 1995, Jin &

Battacharya 1996), or of changes in environmental variables such as process temperature and temperature of the inflowing effluent (Liss & Allen 1992). Activated sludge digestion appears to be particularly sensitive to changes in flow rate resulting from batch production processes (McAllister *et al*. 1993, Rebhun & Galil 1994). Shock loading with higher concentrations of particular compounds can perturb biodegradation processes in a manner which may be highly complex and difficult to predict (Lu & Tsai 1993, Torslov & Lindgaardjorgensen 1994, Strotmann *et al.* 1995). In addition, it should be noted that systems designed specifically to treat chemical wastes are frequently less efficient at achieving conventional biological treatment to reduce BOD, suspended solids and related variables.

In contrast to the specific bioreactor systems described above, a typical common effluent treatment plant, as in this study, would receive wastewaters from a wider range of industrial processes. This, by definition, would result in more complex and variable effluent composition and supply rates, rendering specific process design practically impossible (Eckenfelder & Musterman 1994). The mixing of highly complex waste streams, some of which may be hot and contain chemically active compounds, can result in the synthesis of new compounds in a largely unpredictable manner (see: Johnston *et al.* 1996). In addition, a large proportion of higher chlorinated organic compounds are highly resistant to biodegradation (Gruttner *et al.* 1994a, Middeldorp *et al.* 1996), while metal contamination can never be addressed through such processes, other than to scavenge them from the dissolved to the particulate fraction (Gruttner *et al.* 1994b). As a result, many of the most toxic and persistent components of chemical waste streams may simply pass through the CETP unmodified.

For example, the chlorinated benzenes are among the most persistent organochlorine compounds, being highly resistant to microbial degradation. Indeed, mono-, di- and tri-chlorobenzenes may be formed as persistent end-products from the biodegradation of other organochlorines (Middeldorp *et al.* 1996). In the study of the composition of domestic sewage sludge from the 1950s, which had been treated through anaerobic digestion, stored on site for five years and subsequently applied to farmland, di- and tri-chlorobenzenes were identified as the principle anthropogenic organic contaminants (Wang *et al.* 1992). Their presence is thought to have resulted initially from the use of dichlorobenzene in lavatory sanitizers.

In conventional biological sewage treatment systems, and simple industrial effluent treatment plants, chlorinated benzenes tend to bind tightly to the particulate fraction (Liljestrand & Lee 1991) on account of their poor water solubility. This results in their accumulation in sewage sludges or in sediments of receiving waters (e.g. Chapman *et al.* 1996). The presence of other organic solvents in suspension may, however, lead to higher solubility in the liquid phase. Under such conditions, typical of the mixed industrial effluents likely to enter a common treatment plant, dichlorobenzenes may inhibit the degradation of other compounds (Robertson & Alexander 1996), or increase the susceptibility of the bacterial consortium to toxic shock e.g. fluctuating concentrations of phenolics (Limbert & Betts 1995).

Biodegradation of chlorobenzenes, particularly higher chlorinated forms, is generally a slow process and one which requires careful selection of bacterial strains which are both resistant to, and capable of metabolising, these compounds (Limbert & Betts 1994). Other processes, such as high temperature hydrogenation (Gioia *et al.* 1994), are effective

in destroying di- and tri-chlorobenzenes but are expensive to install and run, and require considerable expertise to operate.

Englande (1994) emphasised the fact that there are no simple "off the shelf" solutions available for dealing with complex waste streams arising from diverse chemical manufacturing processes. Waste reduction strategies must form a central part of any waste management program, be it on the scale of a single process or plant, or of an industrial development region as a whole. Biological treatment plants may be effective in addressing certain limited physical, chemical and biological parameters, but can form only part of an overall waste management strategy. Brenner *et al.* (1994) and Belkin *et al.* (1994), discussing the strategy for the Ramat Hovav industrial complex in Israel, recognised the need to trace recalcitrant waste streams back to their origins and begin to address them at source. This necessarily involves detailed chemical characterisation of all the waste streams produced, leading to a re-evaluation of the raw materials and processes employed, in order to identify mechanisms for the reduction of use and release of persistent, toxic pollutants (Unden 1994). Ultimately it may be necessary to reformulate products in order to meet the long-term goal of elimination of priority pollutants at source.

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