

**TOXIC HOTSPOTS:
A Greenpeace Investigation of
HINDUSTAN INSECTICIDES LTD
UDYOGMANDAL INDUSTRIAL ESTATE, KERALA**

Persistent organic pollutants and other contaminants
in samples taken in the vicinity of the Hindustan Insecticide Ltd plant,
Udyogmandal industrial estate, Kerala, India.

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1. Executive summary

Hindustan Insecticides Ltd has been manufacturing pesticides at its Udyogmandal site (Kochi, Kerala) since 1956 and, according to the Ministry of Chemicals and Fertilizers, continues to produce DDT and endosulfan. The plant, located adjacent to a wetland, apparently discharges its effluent to an open channel (the Kuzhikundam Creek).

Greenpeace International visited the Udyogmandal Industrial Estate on 22nd May 1999 and collected samples of water and sediment from the creek, and of soil/sediment from the adjacent wetlands, for analysis of organic contaminants and heavy metals. The results of these analyses demonstrate that:-

- sediment from the creek sampled 10m downstream from HIL contained more than 100 organic compounds, 39 of which were organochlorines, including DDT and its metabolites, endosulfan and several isomers of hexachlorocyclohexane (HCH).
- in contrast, sediment collected immediately upstream from HIL contained none of these compounds at detectable levels (and no identifiable organochlorines), strongly suggesting that discharges and/or run-off from the HIL plant have resulted in heavy contamination of the creek sediments with a range of pesticide residues and other hazardous organochlorine chemicals.
- DDT and HCH were also detectable in the water/effluent sampled downstream from HIL, indicating that production of these insecticides, and their release to the creek, is continuing.
- DDT and its metabolites were also detectable in the wetlands surrounding the Udyogmandal estate. Although it cannot be ruled out that the presence of these residues might result from direct application of DDT for malaria vector control, the presence in these samples of other chlorinated chemicals also identified in the creek (particularly chlorinated benzophenones) suggests that overspill of the creek and/or other uncontrolled discharges from the estate might be leading to more widespread contamination of the wetland.

In summary, the results of this investigation strongly support the conclusion that the manufacture of DDT and other pesticides at the Hindustan Insecticides Ltd plant is ongoing, and is resulting in the continued release of these and a diverse mixture of other organochlorine chemicals to the environment. Determination of the sources of contaminants in the surrounding wetlands demands further investigation.

2. Introduction

Hindustan Insecticides Ltd (India), located on the Udyogmandal Industrial Estate in Kochi, Kerala, has been manufacturing pesticides since 1956. According to the official web-site of the Ministry of Chemicals and Fertilizers (Government of India 1999), the Udyogmandal plant continues to produce a range of pesticides, its principal products being the insecticides DDT and endosulfan. The plant is situated close to an area of wetlands and appears to discharge its effluent directly to the Kuzhikundam Thodu creek, a tributary to the Periyar River, in common with many of the other industrial units on the estate.

The current study was conducted in order to characterise the chemical nature of any effluents being discharged from the HIL plant to the Kuzhikundam Thodu creek, and the impact of such discharges on overall levels of contamination in the sediments of the creek. Samples of soil/sediment were also collected from several locations in the wetlands adjacent to the plant, in order to determine whether the operations at this or neighbouring plants were resulting in more widespread contamination of the surrounding environment.

3. Methods and Sampling Sites

A total of six samples were collected in the vicinity of the Hindustan Insecticides Ltd (HIL) site on 22nd May 1999, including one sample of water/effluent from the creek, two sediment samples from the same creek (one upstream from HIL and another downstream) and three samples of soil/sediment from the surrounding wetland area. All soil samples were collected at a depth of approximately 20-30 cm.

All samples were collected and stored in pre-cleaned glass bottles (rinsed thoroughly with nitric acid and analytical grade pentane in order to remove all heavy metal and organic residues). Soil/sediment samples were collected in 100ml bottles. The single aqueous sample was collected in a 1-litre bottle, ensuring that no air bubbles were present. All samples were immediately sealed and cooled upon collection, and returned to the Greenpeace Research Laboratories for analysis.

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

3.1 The Kuzhikundam Thodu effluent creek

The Kuzhikundam Thodu creek flows through a number of different industrial units on the Udyogmandal estate. According to local sources, many plants discharge untreated or partially treated wastewaters into this creek.

Immediately upstream from the HIL site, this creek flows through the Fertilisers and Chemicals Travancore (FACT) site. Immediately downstream from HIL, the creek flows through the edge of the Merchem site (see Fig. 1). According to local sources, there are no regular discharges to the creek from the Merchem plant.

Two samples of sediment were collected from this effluent creek. One sample (IT9011) was collected at the point at which the creek enters the HIL site, in order to determine the nature of contaminant inputs from plants situated upstream from HIL. At this location, the air above the creek was choking, making it impossible to breath close to the level of the water.

The second sample (IT9010) was collected from the creek at its point of exit from the Merchem site, approximately 10 metres downstream from its exit from the HIL site, as it was not possible to gain access to the creek closer to the HIL boundary. This sample consisted of a black and oily sludge. A sample of the water/effluent flowing in the creek (IT9009) was also collected at this point. These two samples were collected in order to give an indication of the type of effluent being discharged into the creek by HIL.

These sediment and water samples were collected at 7am, coinciding with the time at which, according to local information, effluent was routinely discharged by HIL. At the time of sampling, however, there was no clear indication that effluent was being discharged. Moreover, as a result of the preceding monsoon rains, any effluent discharged to the creek would have been considerably diluted with rainwater flow at the time of sampling.

3.2 Wetlands in the vicinity of the Hindustan Insecticides Ltd.

Three samples of soil/sediment (IT9006-8) were collected from different locations close to the HIL site, in order to determine whether any contaminant signature relating to the HIL plant could be detected in the adjacent wetlands. All three areas from which the samples were collected were waterlogged.

One sample (IT9008) was collected approximately 8 metres north of the Kuzhikundam Thodu creek, at a location approximately 10 m northwest of the HIL site boundary. This sample consisted mainly of clay-like material, which locals believe may have been gypsum from the FACT plant, carried into the area during periods of flood. We were unable to verify this assumption.

A second sample (IT9006) was collected from the wetlands southwest of the "Amanthuruthu" (reclaimed wetland) area, approximately 150 metres west of the HIL site, and approximately 80 metres south of the Kuzhikundam Thodu creek.

The third sample (IT9007) was collected from the wetlands east of the "Amanthuruthu" area, approximately 150 metres north of the Merchem site wall, and approximately 170 metres from the Kuzhikundam Thodu creek. This area is extremely waterlogged, and is reported by locals to be used as a wastewater 'overflow' area by HIL and other companies. Local residents also reported that people who regularly wade through this area to reach their homes develop bad skin irritations and patches of skin colouration.

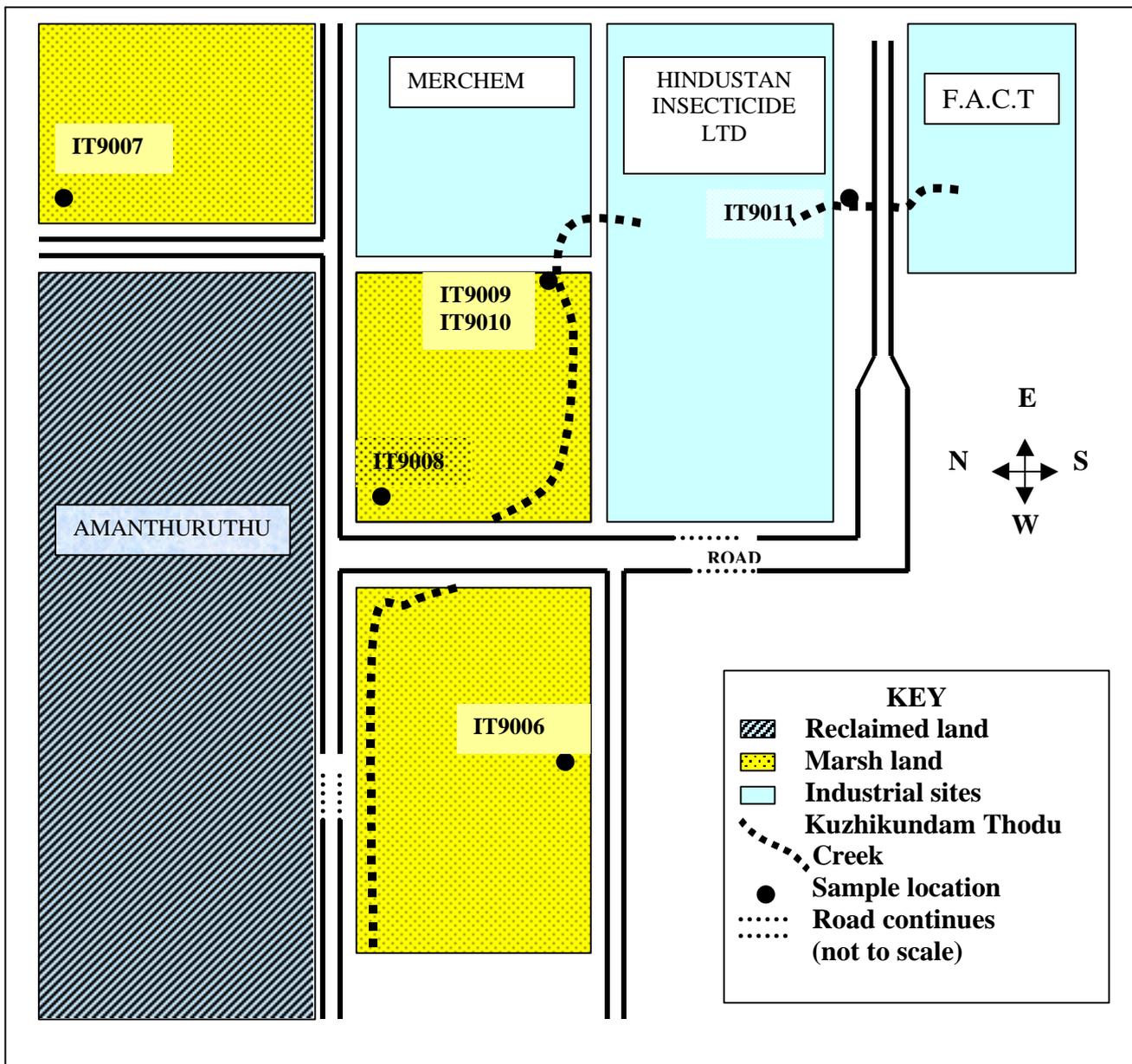


Figure 1. Sketch of the HIL site and vicinity, Udyogmandal industrial estate, Kochi, Kerala, India 1999 (F.A.C.T., Fertilisers and Chemicals Travancore).

Sample Number	Sample locations	Sample Description
IT9011	Kuzhikundam Thodu creek	Sediment collected from Kuzhikundam Thodu creek as it enters the HIL site from the FACT site (upstream from HIL).
IT9010		Sediment collected from Kuzhikundam Thodu creek as it leaves the Merchem site (downstream from HIL).
IT9009		Water/wastewater collected from Kuzhikundam Thodu creek as it leaves the Merchem site (d/s from HIL, see IT9010).
IT9006	Marshlands in the vicinity of Hindustan Insecticides Ltd.	Soil sample collected from marshland southwest of Amanthuruthu, approximately 150 metres west of the HIL site wall, and approximately 80 metres from the Kuzhikundam Thodu creek.
IT9007		Soil sample collected from marshland east of Amanthuruthu, approximately 150 metres north of the Merchem site wall, and approximately 170 metres from the Kuzhikundam Thodu creek.
IT9008		Clay/soil sample collected from marshland south of Amanthuruthu, approximately 10 metres north of the HIL site wall, and approximately 8 metres from the Kuzhikundam Thodu creek.

Table 1. Descriptions of samples collected from the Udyogmandal industrial estate, Kochi, Kerala, India 1999.

4. Results and discussion

The results of organic screen analysis are presented in Table 2 and Table 3. The results of heavy metal analysis are presented in Table 4. A list of all the organic compounds which were reliably identified (greater than 90% spectral match quality) and groups of compounds tentatively identified is presented in Appendix 2 (Table 5).

Sample Code	Compounds isolated	Reliably identified	DDT & its metabolites	HCHs, chlorinated cyclohexenes & cyclopentenes	Other organohalogen compounds	PAHs	Sulphur & Organosulphur compounds	Other aromatics	Aliphatics
IT9011	16	5(32%)	0	0	0	0	0	2	3
IT9010	111	56(51%)	9	5	25	6	2	1	7
IT9009	62	27(44%)	7	3	6	4	0	0	7
IT9006	18	10(56%)	4	0	1	0	0	0	5
IT9007	29	12(42%)	3	0	0	0	0	8	1
IT9008	20	10(50%)	8	0	0	0	0	0	1

Table 2. Results of organic screen analysis of sediment, soil and wastewater samples collected in the vicinity of the Hindustan Insecticides Ltd., Udyogmandal Industrial Estate, Kochi, Kerala, India 1999

Groups of compounds reliably identified	Number of samples	Sample Codes
ORGANOHALOGEN COMPOUNDS		
DDT and its metabolites:		
DDT	3	IT9008, IT9009, IT9010
DDD	5	IT9006, IT9007, IT9008, IT9009, IT9010
DDE	5	IT9006, IT9007, IT9008, IT9009, IT9010
DDM	1	IT9010
DDMU	3	IT9008, IT9009, IT9010
Endosulfan and its derivatives	1	IT9010
Hexachlorocyclohexanes:		
alpha-HCH	2	IT9009, IT9010
beta-HCH	1	IT9010
gamma-HCH	2	IT9009, IT9010
delta-HCH	1	IT9010
Chlorinated cyclohexene	1	IT9010
Chlorinated cyclopentene	1	IT9009
Chlorinated benzophenones	2	IT9008, IT9010
Chlorinated butadienes	2	IT9009, IT9010
PCB (monochlorinated)	1	IT9010
Dichlorobenzenes	3	IT9006, IT9009, IT9010
Trichlorobenzenes	2	IT9009, IT9010
Tetrachlorobenzenes	2	IT9009, IT9010
Pentachlorobenzenes	1	IT9010
Chlorinated diphenylsulfone	1	IT9010
Chlorinated diphenylsulfide	1	IT9010
Chlorinated styrenes and ethylbenzene	1	IT9010
POLYCYCLIC AROMATIC HYDROCARBONS		
Naphthalene and its derivatives	2	IT9009, IT9010
PHENOLIC COMPOUNDS		
Phenol and its derivatives	1	IT9011
PHTHALATES		
DEHP	1	IT9010
ORGANOSULPHUR COMPOUNDS		
Sulfur, mol. (S8)	1	IT9010
Benzothiazole, 2-(methylthio)-	1	IT9010
OTHER AROMATICS		
Benzaldehyde	1	IT9010
Alkylated benzenes	1	IT9007
ALIPHATICS		
Cyclic	3	IT9008, IT9010
Linear alkanes and alkenes	5	IT9006, IT9007, IT9009, IT9010, IT9011

Table 3. Groups of organic compounds reliably identified in sediment, soil and wastewater samples collected in the vicinity of the Hindustan Insecticides Ltd., Udyogmandal Industrial Estate, Kochi, Kerala, India 1999

4.1 Organic contaminants

4.1.1 Kuzhikundam Thodu creek (IT9009-11)

Analysis of sample IT9011, collected immediately upstream from the HIL plant, contained relatively few organic contaminants, and was characterized principally by the presence of non-chlorinated aliphatic and phenolic compounds. Aliphatic hydrocarbons are key

components of crude or refined oil-based chemicals and appear as common contaminants in the sediments of channels receiving discharges or run off from industrial operations. Of the two phenolic chemicals identified, 2,6-bis(1,1-dimethylethyl)-4-methylphenol, also known as butylated hydroxytoluene (BHT), is used as an antioxidant in food products, rubbers, soaps and in the production of plastics and other petrochemical products (Jobling et al. 1995). It is also manufactured for use as an antiskinning agent in paints, varnishes and other surface finishes. BHT is also one of the main degradation products of the herbicide Terbutol (2,6-di-tert-butyl-4-methylphenyl N-methylcarbamate) (Suzuki et al. 1995 & 1996). However, given the diversity of industries located on the Udyogmandal estate, it is not possible to determine the origin of these chemicals in the sediment sampled in the current study.

In contrast, sediment IT9010, collected immediately downstream from the HIL and Merchem plants, showed very heavy contamination with a wide range of organic compounds, including a predominance of chlorinated chemicals. Of 111 compounds resolved in the analysis, only 56 could be identified to a high degree of reliability. Of these, however, 39 compounds (approximately 70%) were organochlorines.

Among the organochlorines identified in this sample were two isomers of DDT, several DDT metabolites (DDD, DDE, DDM and DDMU), four isomers of hexachlorocyclohexane (HCH), including the gamma-isomer lindane, two isomers of endosulfan and its metabolite endosulfan ether. This sample would appear to contain, therefore, a very clear signature of pesticide residue contamination arising from pesticide formulation at the HIL plant immediately upstream. Given that the sample was necessarily collected downstream of the Merchem plant, the possibility that some of the contaminants found had been introduced from that site cannot be discounted. Nevertheless, considering the nature of the contaminants found (with a predominance of chlorinated pesticides), the documented activities of Hindustan Insecticides Ltd and the apparent absence of any discharge from the Merchem site, operational discharges or run-off from the HIL site would appear to be the most likely source.

Many of the pesticide residues found in the downstream sediment were also isolated from the sample of water/effluent (IT9009) collected at the same location, suggesting that the contamination is not simply historic and that inputs of DDT, HCH and related compounds are still continuing. Such continued inputs might well be expected if the plant is still operating.

Box 1: DDT - DDT and its metabolites (particularly p,p'-DDE) are both acutely and chronically toxic to a wide range of organisms. Some members of the DDT group are endocrine disruptors, exhibiting varying modes of action, and several are weakly oestrogenic (e.g. Colborn *et al.* 1993, Guillette *et al.* 1994). Of these, o,p'-DDT is the most active. p,p'-DDE, the compound likely to be present at highest concentrations in humans, is a potent inhibitor of the androgen (male sex hormone) receptor (Longnecker 1997, Kelce *et al.* 1995). Although DDT is listed as "severely restricted" in India, it is still manufactured and used extensively, particularly as a malaria control agent. In fact, India is one of three countries world-wide to have used more than 100 000 tonnes of DDT since its initial formulation (Voldner & Li 1995). Because of its toxicity and persistence in the environment, DDT is included as one of the 12 UNEP POPs (UNEP 1995) which are targeted for elimination on a global basis.

Box 2: Hexachlorocyclohexane – HCH introduced to the environment from industrial discharges, insecticide applications or spills may cause significant damage. Acute toxic effects may include the death of animals, birds, or fish, and death or low growth rate in plants (Bunton 1996, Smith 1991). The insecticide load in surface waters does not ordinarily reach concentrations acutely toxic to aquatic fauna. However, lindane, a gamma-isomer of hexachlorocyclohexane, has high chronic toxicity to aquatic life. The effects of low insecticide concentrations often appear only after relatively long exposure times. Chronic exposure to lindane can be hazardous to freshwater macroinvertebrates even at unexpectedly low concentrations (Schulz *et al.* 1995). Such low-concentration effects may depend on both species and substance and therefore cannot be predicted from toxicity data at higher concentrations. Manufacture and usage of lindane continues in numerous countries, and production of technical HCH is suspected to be continuing in some parts of the world. Li (1999) concluded that India was probably still the most heavily contaminated country with respect to environmental levels of technical HCH.

In addition to these pesticide residues, numerous other organochlorine compounds were identified in the sediment sample collected downstream, including di-, tri- and tetrachlorinated benzenes, chlorinated benzophenones, chlorinated butadienes, a monochlorinated PCB and a number of chlorinated organosulphur compounds. The chlorinated benzenes and butadienes were also detected in the aqueous sample collected at the same location. Such a diversity of chlorinated chemicals is typical of the complex nature of contaminated effluent streams arising from the chlorine chemical sector. Although many of the individual compounds identified are widely recognised to be extremely hazardous, predicting the overall impact of the release to the environment of such complex and heavily contaminated waste streams is practically impossible.

4.1.2 Wetlands in the vicinity of Hindustan Insecticides Ltd. (IT9006-8)

Of the three soil/sediment samples (IT9006/78) collected from the wetland area (see Fig. 1), sample IT9008 contained the greatest range of organochlorine compounds, as may be expected given its close proximity to the HIL site. Moreover, whereas DDD and DDE were identified in the two more distant samples, only sample IT9008 was found to contain detectable levels of DDT itself, suggesting more recent introduction of the insecticide into this sample.

DDT and its metabolites accounted for the majority of the organic compounds identified in sample IT9008, although dichlorinated benzophenone and cyclohexadecane, an aliphatic hydrocarbon, were also found. In this regard it should be noted that a similar range of DDT metabolites and chlorinated benzophenones were identified in this sample as in the sediment sample IT9010, collected from the Kuzhikundam Thodu creek downstream from the HIL plant. While it cannot be ruled out that DDT might have been present in the wetland samples as a result of its application for malaria vector control, the presence also of dichlorobenzophenones in both samples implies that contamination of the wetlands with these chlorinated chemicals has resulted primarily from overspill of the effluent creek during times of heavy rain or perhaps from other deliberate releases of effluents or other wastes to the wetland area.

Box 3: Endosulfan – The pesticide Endosulfan is persistent in the environment, with a half life in soil of several years. It may accumulate in the bodies of fish and other organisms exposed to endosulfan-contaminated water. The main source of human exposure to endosulfan is via ingestion of food that contains this pesticide as a result of direct pesticide application or bio-concentration (ATSDR 1997). Endosulfan may be lethal to humans and animals by inhalation, oral or dermal exposure. The main target is the central nervous system. In studies on experimental animals, damage to the liver, kidney, gastrointestinal, haematopoietic and dermal systems and developing foetuses have also been demonstrated following exposure to endosulfan (ATSDR 1997, Nowak 1991). Endosulfan has also been found to exhibit some oestrogenic properties in freshwater invertebrates (Zou & Fingerman 1997).

As discussed above, both soil samples IT9006 and IT9007 also contained DDT metabolites. A total of 18 and 29 organic compounds were isolated from the samples IT9006 and IT9007 respectively. Ten organic compounds (56%) were reliably identified in the sample IT9006 including four DDT metabolites, 1,4-dichlorobenzene and four aliphatic hydrocarbons. The sample IT9007, in which twelve compounds (42%) were identified to a high degree of reliability, also contained alkylbenzenes additionally to three DDT metabolites and one aliphatic hydrocarbon. The presence of alkylbenzenes in the soil may indicate contamination by crude oil or refined oil-derived products, as alkylbenzenes are key components of such products (Overton 1994). It is not possible to speculate further about the possible sources of these contaminants in the wetland samples, although the possibility exists that they arise from additional controlled or uncontrolled releases of effluents or other wastes directly to the wetlands. Their presence in the wetland is clearly cause for some concern, however, and further research is required in order to identify sources.

Brief background information concerning the pesticides DDT, HCH and endosulfan is give in the text boxes 1-3 above. Further information on toxicity, uses, production and environmental behaviour of these and other key organic compounds identified in these samples is presented in Appendix 3.

4.2 Heavy Metals

4.2.1 Kuzhikundam Thodu creek (IT9009-11)

Analysis of nine metals was undertaken for all the samples in this study. Sample IT9011, sediment collected upstream from the HIL site, contained the highest levels of heavy metals recorded in the samples collected in this study. The sample contained concentrations of cadmium, chromium, copper, mercury and zinc which might be considered to be elevated above background i.e. above concentrations reported for sediments and soils from typical uncontaminated regions (USPHS 1997, Salomons & Forstner 1984). Of the metals considered in this study, cadmium was the most consistently

Solid Samples	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
IT9006	1.8	80.4	4.5	33.9	49.1	86.6	3.5	41.1	433.9
IT9007	2.0	57.8	3.9	24.5	26.5	85.9	3.8	27.5	413.7
IT9008	2.0	8.0	n/d	7.0	12.0	14.0	0.4	3.0	59.0
IT9010	n /d	57.6	5.7	22.6	30.2	142.5	0.7	6.6	67.9
IT9011	1.7	570.7	9.5	212.1	81.0	237.1	2.0	75.9	622.4
Aqueous sample	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
IT9009	<10	120	<10	70	<30	<10	<2	20	510

Table 4. Results of heavy metal analysis of sediment, soil and wastewater samples collected in the vicinity of the Hindustan Insecticides Ltd., Udyogmandal Industrial Estate, Kochi, Kerala, India 1999

elevated above background. There was, however, no evidence of severe contamination of the creek with heavy metals.

The relatively low levels of metals found in the one water/effluent sample (IT9009) collected from the Kuzhikundam Thodu creek as it left the Merchem site may have been

influenced by the onset of the monsoon and consequent high rainfall which had occurred shortly before sample collection took place.

4.2.2 Wetlands in the vicinity of Hindustan Insecticides Ltd. (IT9006-8)

Again, heavy metal concentrations showed some evidence of elevation above what might be expected for uncontaminated sediments although, with the exception of mercury (present at 3.5 and 3.8 mg/kg in samples IT9006 and 9007 respectively, approximately one order of magnitude higher than might be expected as background concentrations), such elevation was not great. Moreover, patterns of metal distributions showed no consistent relationship with vicinity of sampling site to the HIL or neighbouring plants. While it is possible that heavy metal concentrations in the sediments sampled are slightly elevated as a result of industrial activity in the region, the possibility that levels of these metals are naturally slightly higher than in uncontaminated sediments in other regions cannot be ruled out.

5. Conclusions

The results of this brief investigation give a strong indication that activities at the Hindustan Insecticides Ltd plant in Kochi, Kerala, have resulted in substantial contamination of the Kuzhikundam Thodu creek with DDT, endosulfan, HCH (BHC) and a wide range of other hazardous organochlorine chemicals and are resulting in the ongoing release of many of these chemicals to the environment. DDT and other organochlorines were also detectable in the wetlands surrounding the plant, although the verification of sources for these contaminants would require further research.

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