Contamination of soil and water inside and outside the Union Carbide India Limited, Bhopal

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POLLUTION MONITORING LABORATORY

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1. POLLUTION MONITORING LABORATORY OF CSE

The Centre for Science and Environment (CSE), a non-governmental organization based in New Delhi, has set up the Pollution Monitoring Laboratory (PML) to monitor environmental pollution. PML is an ISO 9001:2000 certified laboratory accredited by SWISO, CH-5610, Wohlen, Switzerland, conducting Pollution Monitoring and Scientific Studies on Environmental Samples. The Lab has highly qualified and experienced staff that exercise Analytical Quality Control (AQC) and meticulously follow what is called Good Laboratory Practices (GLP). It is equipped with most sophisticated state-of-the-art equipments for monitoring and analysis of air, water and food contamination, including Gas Chromatograph with Mass Detector (GC-MS), Gas Chromatograph (GC) with ECD, NPD, FID and other detectors, High Performance Liquid Chromatograph (HPLC), Atomic Absorption Spectrometer (AAS), UV-VIS Spectrophotometer, Mercury Analyzer, Respirable Dust Sampler etc. Its main aim is to undertake scientific studies to generate public awareness about food, water and air contamination. It provides scientific services at nominal cost to communities that cannot obtain scientific evidence against polluters in their area. This is an effort to use science to achieve ecological security.

2. INTRODUCTION

The city of Bhopal in Madhya Pradesh suffered the world's worst ever industrial disaster in December 1984, when around 5,00,000 inhabitants were exposed to toxic gas (Methyl Isocyanate) from the Union Carbide India Ltd (UCIL) pesticides factory. Thousands of people died immediately, with estimates ranging from 3,000 to 20,000. Whereas the components of the toxic gas release remained in the environment for a comparatively short time, the factory, now abandoned, remains heavily contaminated with a range of persistent pollutants, both organic and inorganic in nature.

UCIL used to manufacture three different kinds of pesticides: Carbaryl (trade name Sevin), Aldicarb (trade name Temik), and a formulation of Carbaryl and gamma-hexachlorocyclohexane (γ-HCH) sold under the trade name Sevidol. Carbaryl and Aldicarb fall under carbamate group of insecticides; both are moderately persistent, highly toxic; highly water soluble and mobile in soils.

For manufacturing Sevidol, γ-HCH was extracted from the technical grade HCH which is a mix of several chemical forms (isomers) of HCH (mainly α, β, γ and δ–HCH). UCIL used to buy technical grade HCH, extract γ-HCH and throw the remaining isomers as wastes.

5HCH and its isomers are highly persistent and toxic organochlorine pesticides and presence of different isomers of HCH is likely because of the processing of HCH in the plant, use of γ-HCH for Sevidol formulation and dumping of other isomers within the factory and outside in the waste dump site (also called by UCIL as solar evaporation pond).

Hexachlorobenzene (HCB) is an impurity in the technical grade HCH and was also produced as a by product of various chemical processes in the UCIL factory.

Chlorinated benzene compounds are highly persistent and were either used by UCIL as solvents or are degradation products of HCH or HCB. For instance, 1,2 dichlorobenzene or ortho-dichlorobenzene was used as solvent for producing alpha-naphthol – a chemical used in the production of Sevin, the main product of UCIL. Chlorinated benzene compounds are also used as insecticides and fungicides.

Heavy metal like mercury was used as a sealant in the Sevin plant and Chromium was used as a coolant in the cooling plant of the UCIL factory.

PML studied the chemistry of the processes used for producing various pesticides in UCIL and based on it, selected four groups of chemicals for testing soil and water samples. In Chlorinated benzene compounds it tested 1,2 dichlorobenzene (1,2 DCB), 1,3 dichlorobenzene (1,3 DCB), 1,4 dichlorobenzene (1,4 DCB) and 1,2,3 trichlorobenzene (1,2,3 TCB). In organochlorine pesticides it tested hexachlorobenzene (HCB) and α, β, γ and δ isomers of HCH. In carbamates, it tested Carbaryl and Aldicarb – the two main products of UCIL. And, in heavy metals it tested five heavy metals – lead, cadmium, chromium, mercury and arsenic.

3. REVIEW OF LITERATURE

The National Environmental Engineering Research Institute (NEERI), Nagpur has conducted number of environmental surveys in and around the UCIL premises. In 1997, Eveready Industries India Ltd, which bought Union Carbide's share in Union Carbide India Ltd., commissioned NEERI to find out the extent of contamination at the Bhopal plant site. NEERI found high levels of toxins and identified hot spots. Presence of Carbaryl, Lindane, Alpha-napthol etc. was reported in their findings.

Another study found residues of 1- naphthol which is the degradation product of carbamates in sixty two samples of soil, surface and ground waters (Ponds, well and hand pumps) that were obtained from different locations in and around Bhopal, India (Dikshith et.al., 1990).

A study by NEERI in Oct. 2003 collected the ground water samples around UCIL premises. 1,2,3, TCB was detected in some of the groundwater samples. Pesticides like lindane, α-Endosulfan, heptachlor, aldrin, dieldrin, BHC, endrin and 4,4 DDT were also detected in some of the samples (Chakrabarti et.al., 2003).

Heavy metals, chlorinated hydrocarbons and pesticides were detected in all samples of soil, ground water, vegetables and breast milk around residential areas adjoining UCIL factory premises. In all the samples four heavy metals viz. Cr, Ni, Pb, Hg were found in very high concentrations. The total HCH pesticide concentration was very prominent in all four samples particularly it was up to 9 mg/kg in soil sample (Aggarwal and Nair, 2002).

The State Research Laboratory of the Public Health Engineering Department reported serious chemical contamination in samples taken from 11 tube-wells in the area surrounding the Union Carbide factory. This laboratory repeated its exercise in 1996 and reported similar results. Municipal authorities declared water from over 100 tube wells to be unfit for drinking (Union Carbide Report, The International campaign for justice in Bhopal, 1996).

In 1999, Greenpeace International carried out surveys in order to gain an insight in to the nature and severity of chemical contamination (Greenpeace, 1999). Greenpeace analysed samples of solid wastes, soils and groundwater within UCIL and its surrounding areas. Greenpeace found samples to be contaminated with volatile organic compounds and heavy metals. Later in 2002 Greenpeace Laboratory collected twelve “stockpile” samples from six locations inside the site and four soil samples were collected from the Solar Evaporation Ponds. Eleven of the twelve stockpile samples were found to contain carbaryl at concentrations in the parts per billion range. Ten contained hexachlorocyclohexanes, with total concentrations varying between tens of parts per million and almost 10%. HCB was detected in many samples and the concentration up to about 100 ppm (Greenpeace Report, 2002).

4. HEALTH EFFECTS

HCH

Hexachlorocyclohexane (HCH), commonly known as benzene hexachloride (BHC), is a synthetic chemical that exists in eight chemical forms called isomers. The technical grade comprises of five isomers - α, β, γ, δ and ε. The γ HCH referred to as Lindane has the insecticidal properties.

A variety of toxicological effects, such as reproductive and neurotoxic impairments, have been recorded for lindane and other isomers of HCH in test animals. The alpha and beta isomers are associated with liver and kidney effects in laboratory animal studies. Alpha HCH exhibits most carcinogenic activity and is classified as a probable human carcinogen along with technical grade HCH . Beta HCH metabolically the most stable isomer is the predominant isomer accumulating in tissues and classified as a possible human carcinogen.

Chronic effects of exposure to lindane are nervous disorders, increased liver weight and liver tumours in mammals. Lindane is an endocrine disruptor which is capable of imitating certain hormones in humans and thereby disrupting the physiological functions which these hormones control. There is a significant body of evidence which suggests that in areas where lindane is used extensively, and particularly where cattle are exposed to it, the incidence of breast cancer is higher. The international Agency for Research on Cancer (IARC) has concluded that lindane is a possible human carcinogen (class 2B), and the US EPA has classified it similarly as a class B2/C possible human carcinogen.

Chlorinated Benzenes

All these compounds have relatively low acute toxicity, but show chronic toxicity because of their relatively low water solubility and high lipid solubility that favor their penetration of most membranes by diffusion, including pulmonary and gastrointestinal epithelia, the brain, hepatic parenchyma, renal tubules, and the placenta. In addition there are the phenomena of bioaccumulation and biomagnifications which lead to higher concentrations and subsequent adverse effects.

Dichlorobenzenes cause depression of central nervous system, respiratory tract and eye irritation, anemia, skin lesions, vomiting, headaches, anorexia, weight loss, atrophy of the liver, blood dyscrasias, porphyria and chromosomal disorders in blood samples. The adverse effects include increases in liver and kidney weights and hepatotoxicity.

1,3-dichlorobenzene has the ability to damage the thyroid, liver and kidney. It causes irritation in eyes, respiratory system and skin.

The primary exposure to 1,4-dichlorobenzene is from breathing contaminated indoor air. It affects the liver, skin, and central nervous system. It is irritating to the eyes and the respiratory tract effects blood cells, resulting in hemolytic anemia and on the central nervous system. It is also terratogenic, and carcinogenic.

Hexachlorobenzene

Hexachlorobenzene (HCB) is an organochlorine fungicide, has been classified by the International Agency for Research on Cancer (IARC) as a Group 2B carcinogen (possibly carcinogenic to humans). Animal carcinogenicity data for hexachlorobenzene show increased incidences of liver, kidney (renal tubular tumours) and thyroid cancers. Chronic oral exposure in humans has been shown to give rise to a liver disease (porphyria cutanea tarda), skin lesions with discoloration, ulceration, photosensitivity, thyroid effects, bone effects and loss of hair. It may cause embryo lethality and teratogenic effects. Human and animal studies have demonstrated that hexachlorobenzene crosses the placenta to accumulate in foetal tissues and is transferred to breast milk. Hexachlorobenzene has a half life in the soil of between 3 to 6 years.

Carbaryl

Carbaryl (Trade Name - Sevin, Chemical Name – 1-naphthol N-methylcarbamate.) a wide - spectrum carbamate insecticide is used to control a wide variety of pests, including moths, beetles, cockroaches, ants, ticks, and mosquitoes. In the environment, carbaryl breaks down primarily through hydrolysis and microbial degradation to 1-naphthol and carbon dioxide. Early toxicity symptoms of acute carbaryl exposure may include headache, malaise, muscle weakness, nausea, gastrointestinal cramps, sweating, and restlessness. Signs of acute carbaryl intoxication may include pin-point pupils, tearing, excessive salivation, nasal discharge, vomiting, diarrhea, muscle twitching, slurred speech, and ataxia. Severe poisoning can result in convulsions, central nervous system depression, coma, and death.

Chronic exposure to carbaryl results in cholinesterase inhibition, which is reversible upon discontinuation of exposure. Symptoms include -Headaches, memory loss, muscle weakness and cramps, and anorexia are caused by prolonged low-level exposure of humans to carbaryl resulting from cholinesterase inhibition. Kidney and liver effects have been observed in rats chronically exposed to carbaryl by ingestion.

Aldicarb

Aldicarb is a systemic insecticide. It is one of the most acutely toxic pesticides, less than one thousandth of an ounce is a lethal dose for a human. The oral LD50 is between 0.3 and 0.9 mg/kg of body weight. It causes chronic damage to the nervous system, suppresses the immune system, and adversely affects fetuses. Epidemiologists found that low level consumption of aldicarb-contaminated water was associated with one immune system abnormality (an increase in the number of T8 cells). Aldicarb’s primary metabolite is almost as toxic as aldicarb itself.

Lead

Lead can cause several unwanted effects, such as disruption of the biosynthesis of hemoglobin and anemia, rise in blood pressure, kidney damage, miscarriages and subtle abortions, disruption of nervous systems, brain damage, declined fertility of men through sperm damage, diminished learning abilities of children, behavioral disruptions of children, such as aggression, impulsive behavior and hyperactivity. Lead can enter a fetus through the placenta of the mother. Because of this it can cause serious damage to the nervous system and the brain of unborn children. Chronic exposure of lead includes loss of short-term memory or concentration, depression, nausea, abdominal pain, loss of coordination, and numbness and tingling in the extremities. Fatigue, problems with sleep, headaches, stupor, slurred speech, and anemia are also found in chronic lead poisoning. In acute poisoning, typical neurological signs are pain, muscle weakness, paraesthesia and rarely symptoms associated with encephalitis. Abdominal pain, nausea, vomiting, diarrhea, and constipation are other acute symptoms

Chromium

It is present in two chemical states. Chromium (III) is an essential trace micronutrient required for carbohydrate, protein and fat metabolism. The other Chromium (IV) is the non-essential and the toxic form. These are corrosive and allergic to the skin. Long-term exposure, particularly air-borne chromium is associated with lung cancers. Chromium (IV) compounds are enlisted as carcinogens by the International Agency for Research on Cancer (IARC). Adverse effects of the hexavalent form on the skin may include ulcerations, dermatitis, and allergic skin reactions. Inhalation of hexavalent chromium compounds can result in ulceration and perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis, bronchospasms and edema. Respiratory symptoms may include coughing and wheezing, shortness of breath, and nasal itch.

Mercury

It is the only metal that can exist as both liquid and vapor from at ambient temperatures. Mercury is extremely toxic with no biological functions. There are no mechanisms in the body to remove mercury once it enters the living system. Hence, the metal gets bio-concentrated and biomagnified within the food chain. Chronic exposure of mercury affects the nervous system, causing tremors, spasms and loss of memory, severe depression, and increased excitability, delirium, hallucination and personality changes. Renal damages have been observed in chronically exposed workers.

Arsenic

Arsenic is one of the most toxic elements that can be found. Exposure to inorganic arsenic can cause various health effects, such as irritation of the stomach and intestines, decreased production of red and white blood cells, skin changes and lung irritation. It is suggested that the uptake of significant amounts of inorganic arsenic can intensify the chances of cancer development, especially the chances of development of skin cancer, lung cancer, liver cancer and lymphatic cancer. A very high exposure to inorganic arsenic can cause infertility and miscarriages in women, and it can cause skin disturbances, declined resistance to infections, heart disruptions and brain damage in both men and women.

Finally, inorganic arsenic can damage DNA. A lethal dose of arsenic oxide is generally regarded as 100 mg.

Cadmium

Human uptake of cadmium takes place mainly through food. Cadmium is first transported to the liver through the blood. There, it binds with proteins to form complexes that are transported to the kidneys. Cadmium accumulates in kidneys, where it damages filtering mechanisms. This causes the excretion of essential proteins and sugars from the body and further kidney damage. It takes a very long time before cadmium that has accumulated in kidneys is excreted from a human body. Other health effects that can be caused by cadmium are diarrhea, stomach pains and severe vomiting, bone fracture, reproductive failure and possibly even infertility, damage to the central nervous system, damage to the immune system, psychological disorders, possibly DNA damage or cancer development.

5. OBJECTIVES OF THE STUDY

The main objective of this study was to assess the extent of chemical contamination of soil and water samples from Union Carbide India Limited Factory and residential areas adjoining the factory. PML tested water and soil samples from in and around the UCIL factory for the presence of chlorinated benzene compounds, organochlorine and carbamate pesticides and heavy metals – toxic chemicals that were either used as ingredients or were the wastes generated or were the products of the plant.

6. SAMPLING

Scientists from PML visited Bhopal on October 28-29, 2009 to collect soil and water samples from inside and outside the UCIL factory.

PML collected 8 soil samples: One sample from the waste stored in the waste storage shade in UCIL; six soil samples from various places inside the UCIL factory and one soil sample from the solar evaporation pond (which is outside the UCIL premises) and where UCIL used to dump its wastes. UCIL also used to dump wastes within the factory premises.

PML collected 12 water samples: One water sample from inside the factory – which is rain water collected in a ditch within the plant premises and other eleven water samples were collected from handpump, borewell and dugwell from residential areas around the UCIL factory. The samples were collected from colony adjacent to the factory boundary wall to colony 3.5 km away from the factory. **Sample details are given in Annexure 1A and 1B**.

All soil samples were taken at a depth of 20-30 cm below the surface in transparent polythene bags labeled and sealed. All water samples were collected in Polypet bottles and stored at 6^0C, and out of direct sunlight, from the time of collection through analysis.

As carbamates are sensitive to alkaline hydrolysis and heat, due to the extreme instability of carbamates in alkaline media, samples of water were preserved immediately after collection by acidifying to pH 4-5 with 0.1 N chloroacetic acid. Samples for heavy metal analysis were preserved by acidifying to pH <2 with HNO_3.

7. MATERIALS AND METHODS

A total of 12 water and 8 soil samples were analyzed for 5 Chlorinated benzenes, 4 organochlorines, 2 carbamate pesticides and 5 heavy metals with a widely and internationally used methodology based on United States Environment Protection Agency (USEPA) protocols for Organochlorines with GC-ECD (Method 8081) and Carbamates by HPLC with post-column fluorescence method (EPA method 8318A). Heavy Metal were analysed by AAS - flame and vapour technique. The identity of pesticides detected in the samples by GC-ECD was confirmed by GC-MS, Model Finnigan Polaris Q Ion trap GC-MS with EI ionization (70eV), in Full Scan mode.

7.1 Equipments

- Thermoquest-Trace GC with the ^{63}Ni selective Electron-Capture Detector
- GC column: DB-5, J&W make (30m X 0.25mm X 0.25µm)
- GC-MS Model Finnigan Polaris Q Ion trap
- HPLC Agilent technologies (1100 series) equipped with Fluorescence detector and Post Column Derivatization unit
- HPLC Column: Zorbax ODS column - 5µm, 4.6mm x 250mm
- 10-µl & 50-µl syringe from Hamilton Co.
- Atomic Absorption Spectrometer (Thermo) Solar M-6 Series
- Hot plate, Ultracentrifuge, Rotary evaporator (Buchi type) etc.

7.2 Chemicals

All the solvents and reagents - acetone, methylene chloride, methanol, hexane were HPLC grade, Nitric acid, Hydrogen peroxide (30%), Ethylene Glycol, $KMnO_4$, Hydroxyl Ammonium Chloride, Sodium Borohydride, Sodium Hydroxide, Potassium persulfate etc. used for the analysis were purchased from Merck.

7.3 Glassware

Beaker, volumetric flask, conical flask, funnel, pipettes, glass slides, watch glass, glass rod. All the glassware were cleaned with detergent and 10% nitric acid and rinsed thoroughly with distilled water before use.

7.4 Standards

Organochlorine and carbamate pesticides and Chlorinated benzenes reference standards were obtained from Sigma chemicals USA. Heavy metal standards were purchased from Merck

7.5 Sample extraction, Clean up and Analysis

7.5.1 Chlorinated Benzene compounds and Organochlorines

Water samples were extracted at neutral pH with methylene chloride using EPA Method 3510 (separatory funnel), and soil samples were extracted with methylene chloride-acetone (1:1) using EPA Method 3540 (Soxhlet), and Cleanup was done by Florisil (Method 3620). Chlorinated benzene compounds and Organochlorine Pesticides were analysed by GC-ECD (EPA Method 8081B).

Analysis

Chlorinated benzene compounds and organochlorine were analysed by Gas Chromatograph (Thermoquest-Trace GC) with the ^{63}Ni selective electron-capture detector (ECD). After cleanup, the extract was analyzed by injecting 2μl of aliquot into GC equipped with a narrow-bore fused-silica capillary column (DB-5; 30m X 0.25mm X 0.25μm).

- Detector temperature: 300^{o}C.
- Injector Temperature: 250^{o}C,
- Oven Temperature: 50^{o}C (hold 4 minutes) to 120^{o}C at 6^{o}C /min; then 120^{o}C to 275^{o}C (hold 3 minute) at 25^{o}C /min.
- Carrier gas: Nitrogen @ 1mL/min
- Run time: 25.9 minute

Peak identification was performed by the GC software (Chromcard-32 bit Ver 1.06 October 98) with calibration table set up with a relative retention time window of 0.65%. The samples were calibrated (retention time, area count) against standard mixture of known concentration of 9 standards. Identification of compounds was performed by comparing the retention time (Rt) of the samples GC-peaks with the Rt of the pesticide standards (See Table 1). The compounds present in high concentrations were analyzed after appropriate dilution of the sample extracts with hexane.

Table 1: Chlorinated benzenes and Organochlorine compounds investigated in the soil and water samples by GC-ECD

S. No	Compound	Acronym	CAS	Molecular Weight	Retention Time (minutes)
1	1, 2 Dichlorobenzene	1,2-DCB	95-50-1	147	12.48
2	1, 3 dichlorobenzene	1,3- DCB	541-73-1	147	11.68
3	1, 4 Dichlorobenzene	1,4 DCB	106-46-7	147	11.86
4	1, 2, 3 Trichlorobenzene	1,2,3-TCB	87-61-6	181.45	17.1
5	Hexachlorobenzene	HCB	118-74-1	284.78	21.77
6	α-Hexachlorocyclohexane	α-HCH	319-84-6	290.83	21.68
7	β-Hexachlorocyclohexane	β-HCH	319-85-7	290.83	21.93
8	γ-Hexachlorocyclohexane	γ-HCH	58-89-9	290.83	22.00
9.	δ -Hexachlorocyclohexane	δ-HCH	319-86-8	290.83	22.21

The calibration curves for all of the pesticides were linear (R2 ≥0.999) in the investigated concentration range. Each sample was analysed in triplicate and reproducibility of the results was more than 90% by the method. The recovery of all the investigated chlorinated benzenes and organochlorine compounds under the experimental conditions was more than 80%. The relative standard deviation (RSD) for the determination of most of the compounds was within 10%.

The reliability of the method (stability of the GC-retention time, calibration range, recovery, repeatability of determination, etc.) was checked for the present investigation, and was found to be satisfactory for the analysis. The GC retention times (RT) of the investigated compounds were stable throughout the study, with a maximum variation <1%.

7.5.2 Carbamates

Carbaryl and Aldicarb were analysed by HPLC using the post-column fluorescence (EPA method 8318A). Carbamates were extracted from water samples using methylene chloride in a separatory funnel (EPA Method 3510) and soil samples were extracted with acetonitrile on a platform shaker and clean up was done with C18 reverse phase cartridges and final sample was filtered with disposable 0.45 µm filters and 20 µl of the extract was injected into HPLC.

After elution from the column, the analytes were hydrolyzed in a post column reaction with sodium hydroxide at 95^{O}C to form methyl amine. Methyl amine was reacted with o-phthalaldehyde (OPA) and 2-mercaptoethanol (or N,N-dimethyl-2-mercaptoethylamine) to form a highly fluorescent isoindole which is detected by a fluorescence detector.

Analytes were quantified using the external standard technique under following HPLC conditions:

Solvents and flow rate

Solvent A: Reagent water, acidified with 0.4 mL of phosphoric acid per liter of water

Solvent B: Methanol/acetonitrile (30:70, v/v)

Flow rate: 0.5 mL/min

Injection volume: 20 μL

Gradient elution program

Time (min)	Solvent A (%)	Solvent B (%)
0.00	90	10
0.02	80	20
15.02	0	100
20.02	90	10

Post-column hydrolysis parameters

Solution: 0.05 N aqueous sodium hydroxide

Flow rate: 0.3 mL/min

Temperature: 95 ^{0}C

Post-column derivatization parameters

Solution: *o*-phthalaldehyde/2-mercaptoethanol

Flow rate: 0.3 mL/min

Temperature: 37 ^{0} C

Fluorometer parameters

Excitation wavelength: 340 nm

Emission wavelength: 418 nm cut off filter

Calibration curves for Carbaryl and Aldicarb were prepared at the concentrations of 0.1–5 μg/ml. The samples were calibrated (retention time, area count) against standard mixture of known concentration and analytes were quantitated using the external standard technique (See Table 2).

Table 2: Carbamates investigated in the soil and water samples by HPLC post Column Florescence Method

Sl.No.	Carbamate	Trade Name	CAS	Molecular Weight	Retention Time (minutes)
1	Carbaryl	Sevin	63-25-2	201.22	9.45
2	Aldicarb	Temik	116.06-3	190.26	9.70

7.5.3 Confirmation by GC-MS (Method 8270C)

The identity of pesticides detected in the samples by GC-ECD was confirmed by GC-MS, Model Finnigan Polaris Q Ion trap GC/MS with EI ionization (70eV), in Full Scan mode. The analytes were identified by their: (a) characteristic retention time; (b) primary ion; and, (c) secondary ions to increase specificity. The samples were injected using a programmable temperature injector (PTV) in a capillary column DB-5 MS (30m x 0.25 mm x 0.25 μm).

- Injector Temperature: 250°C,
- Oven Temperature: 50°C (hold 4 minutes) to 120°C at 6°C /min; then 120°C to 275°C (hold 3 minute) at 25°C /min.
- Carrier gas: Helium @ 1mL/min
- Run time: 25.9 minute

2.0μl of the final extract was injected at a temperature of 250°C keeping the ion source at 200°C; Multiplier: 1100 Volts; AGC: 50, 3 microscan; Default: Tune parameters: Autotune Tune File. Mass Range: 50 -650 m/z, solvent delay 4 minutes.

7.5.4 Digestion & Analysis of Heavy Metals by AAS

7.5.4.1 Water

For the determination of Lead (Pb), Cadmium (Cd) and Chromium (Cr) in water, samples were digested according to the EPA method 3010A and then analysed in Atomic Absorption Spectrometer (AAS). Air-acetylene flame was used for the determination of Pb and Cd while nitrous oxide-acetylene flame was used for the determination of Cr. For Arsenic, samples were digested according to EPA method 7062 and analysed in AAS by borohydride reduction using the vapour technique.

For mercury, samples were digested according to EPA method 7470A. These digested samples were then analysed in AAS using vapour technique by borohydride reduction as described in the Thermo Electron Corporation's methods manual.

7.5.4.2 Soil

For the determination of Lead (Pb), Cadmium (Cd) and Chromium (Cr) in soil, samples were digested according to the EPA method 3050B and then analysed in Atomic Absorption Spectrometer (AAS). Air-acetylene flame was used for the determination of Pb and Cd while nitrous oxide-acetylene flame was used for the determination of Cr. For Arsenic, samples were digested according to EPA method 7062 and analysed in AAS by borohydride reduction using the vapour technique.

For mercury, samples were digested according to EPA method 7471B. These digested samples were then analysed in AAS using vapour technique by borohydride reduction as described in the Thermo Electron Corporation's methods manual.

8. RESULTS AND DISCUSSION

Pollution Monitoring Lab (PML) tested water and soil samples from in and around the UCIL factory for the presence of chlorinated benzene compounds, organochlorine and carbamate pesticides and heavy metals – toxic chemicals that were either used as ingredients or were the wastes generated or were the products of the plant. The results prove that the plant site is highly contaminated and has contaminated the groundwater of the surrounding areas.

8.1. The Contamination within the factory premises

The results of the testing of one stored waste sample, six soil samples and one surface water sample within the factory premises and one soil sample from the waste disposal site (solar evaporation pond) clearly shows that the land within the UCIL factory and the waste disposal site is highly contaminated with pesticides, chlorinated benzenes and heavy metals.

- **Waste sample from Waste storage Shed (S1)**

The waste stored within the UCIL premises had all chlorinated benzene compounds and all organochlorine pesticides tested by the PML. The Carbaryl content in this sample was as high as 9859 ppm. Among chlorinated benzenes, 1,2 dichlorobenzene was detected at a concentration of 2.4 ppm. Among HCH isomers γ-HCH was detected at a concentration of 0.19 ppm. β-HCH the most persistent isomer was detected at a concentration of 1 ppm (Annexure 2B).

This sample also had 4 out of the 5 heavy metals tested. The mercury content was as high as 1065 ppm. Chromium arsenic and lead were detected at a concentration of 86.18, 0.73 and 23.22 ppm respectively (Annexure 3B).

- **Soil samples from within the factory premises (S2-S7)**

HCH and its isomers, HCB, 1,3 dichlorobenzene and 1,4 dichlorobenzene were detected in all soil samples. In five soil samples 1,2 dichlorobenzene and 1,2,3 trichlorobenzene were found. Aldicarb was found in three soil samples and Carbaryl in one.

The total pesticide and chlorinated benzene compounds content in the soil sample within the premises ranged from 105 ppm (S3; Outside the pond in the dump site within UCIL's premises) to 5874 ppm (S5; Sevidol formulation plant). The Lindane content in the soil sample from the Sevidol formulation plant was 2782 ppm.

Among the carbamates highest concentration was detected in the soil sample collected from sevidol formulation plant. Carbaryl was detected at a concentration of 7.47 ppm and Aldicarb at 190.69 ppm (Annexure 2B).

Arsenic and Chromium were found in all soil samples. Mercury was found in two samples and Lead in five out of the six samples. Cadmium was not detected in any sample. Chromium was found in the range of 18 ppm - 298 ppm. The highest concentration of Chromium was found in the pilot plant pit near Temik plant (S6) (Annexure 3B).

Though mercury was found in only two samples, their concentrations were quite high. In the soil sample collected from the floor of the Sevin plant (S7), the concentration of mercury was 8188 ppm. Even now the elemental mercury can be seen in the sevin plant structure.

- **Soil Sample from Solar Evaporation Pond (S8)**

The soil sample contained all chlorinated benzene compounds and organochlorine pesticides. It also had four out of five heavy metal tested by PML. The chromium content in this sample was 1065 ppm. UCIL was using the chromium as coolant and was throwing cooling water in the solar evaporation pond (Annexure 3B).

- **Surface Water sample from within the factory premises (W1)**

The surface water sample collected within the factory premises had the highest level of contamination of the entire water sample tested by the PML. Three Chlorinated benzenes and all Organochlorines and both carbamate pesticides were detected in this sample. HCH and its isomers were detected at a concentration of 0.0154 ppm. α and β isomer were detected at a concentration of 0.0064 ppm and 0.0057 ppm respectively. Carbaryl was detected at a concentration of 0.26 ppm (Annexure 2A).

8.2. The Contamination outside (W2-W12)

Groundwater samples collected from colonies around the UCIL factory were contaminated with chlorinated benzene compounds and organochlorine pesticides.

Carbaryl pesticides were found in four ground water samples. Carbaryl was detected in the range of 0.0002-0.028 ppm (2-280 times the individual pesticide limit of IS:14543). Aldicarb was detected in one hand pump sample in front of Safiq Kirana store, New Arif Nagar (400 m behind UCIL's wall) (W3) at a concentration of 0.0005 ppm (5 times the individual pesticide limit of IS:14543).

The concentration of total pesticides found in all water samples were 1.1 to 59.3 times the only mandatory water standard in India fixed by the Bureau of Indian Standard (IS:14543). The average concentration in all groundwater samples was 0.006 ppm which is 12 times the standard (Annexure 2A).

The water sample collected from the hand pump near Chaurasia Samaj Mandir in Shiv Nagar (W11) was the most contaminated. It has highest concentration of carbaryl (0.011 ppm or 110 times the standard), lindane (0.004 ppm; 40 times the standard) and mercury (0.024 ppm; 24 times the standard). This place is more than 3 km away from the UCIL factory (Annexures 2A and 3A).

8.3. GC-MS confirmation

The chlorinated benzenes and organochlorines detected in water and soil samples were confirmed by GC-MS. Characteristic ions – primary and secondary ions and the retention time for chlorinated benzenes and organochlorines detected in samples from Bhopal are given in Table 3 below.

Table 3. Characteristic ions for Chlorinated Benzenes and Organochlorines Pesticides

S. No	Compound	Acronym	CAS	Molecular Weight	Primary ion	Secondary ion	Retention Time (minute)
1	1, 2 Dichlorobenzene	1,2-DCB	95-50-1	147	180	182,145	10.09
2	1, 3 dichlorobenzene	1,3- DCB	541-72-1	147	146	148,111	9.33
3	1, 4 Dichlorobenzene	1,4 DCB	106-46-7	147	146	148,111	9.61
4	1, 2, 3 Trichlorobenzene	1,2,3-TCB	87-61-6	181.45	180	182,145	14.8
5	Hexachlorobenzene	HCB	118-74-1	284.78	284	142,249	20.90
6	α-Hexachlorocyclohexane	α-HCH	319-84-6	290.83	183	181,109	20.88
7	β-Hexachlorocyclohexane	β-HCH	319-85-7	290.83	181	183,109	21.15
8	γ-Hexachlorocyclohexane	γ-HCH	58-89-9	290.83	183	181,109	21.24
9.	δ -Hexachlorocyclohexane	δ-HCH	319-86-8	290.83	183	181,109	21.52

9. CONCLUSIONS

The results of the testing of one stored waste sample, six soil samples and one surface water sample within the factory premises and one soil sample from the waste disposal site (solar evaporation pond) clearly shows that the land within the UCIL factory and the waste disposal site is highly contaminated with pesticides, chlorinated benzenes and heavy metals.

- The waste stored within the UCIL premises had all chlorinated benzene compounds and all organochlorine pesticides tested by the PML. The total pesticide concentration in the waste sample was as high as 9867ppm.
- The surface water sample collected within the factory premises had the highest level of contamination of the entire water sample tested by the PML. The total pesticide content in the sample was 0.28 ppm.
- The soil samples contained all chlorinated benzene compounds and organochlorine pesticides. It also had four out of five heavy metal tested by PML.
- The concentration of pesticides found in all water samples were 1.1 to 59.3 times the only mandatory water standard in India fixed by the Bureau of Indian Standard (IS:14543). The average concentration in all groundwater samples was 0.006 ppm which is 12 times the standard.
- The profile of chemicals found within the UCIL factory and in the waste disposal site of UCIL matches the chemicals found in the groundwater sample in the colonies outside the factory premises. There is no other source of these chlorinated benzene compounds and pesticides then UCIL. The topography of the area also points towards contamination of the groundwater due to the UCIL. The plant is located at a slightly higher altitude than the residential colonies with a gently sloping terrain.
- Carbamate pesticides, as a general group, are considered to be moderately-persistent in the environment. But finding carbamates in groundwater, 25 years since the plant shut down, clearly means that the UCIL plant is acting as a continuous source of groundwater contamination.
- For more than 25 years (even before the accident took place and just a few years after manufacturing began) the residents of the area have been exposed to chemical-laced groundwater. And, they will continue to be exposed till the site remains contaminated.
- The waste stored within the factory premises is just but small part of the total contamination present in the site. The focus of the government to just dispose off the stored waste and ignore the site contamination problem is not going to solve the environment problems emanating from the UCIL factory.

10. References

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Annexure 1A: Sample Details – Water

S. No.	Sample Code	Site of Collection	Date of Collection	Time of Collection
1	W1	From the pond in the dump site within UCIL's premises	28-Oct-09	4.00 pm
2	W2	Hand pump in front of the Leelabai's shop, Atal Ayub Nagar (10 m behind the UCIL's wall)	29-Oct-09	10.00 am
3	W3	Hand pump in front of Safiq Kirana store, New Arif Nagar (400 m behind UCIL's wall)	29-Oct-09	10.45 am
4	W4	Tube well adjacent to the Masjid (in front of Sharif Khan Bardanewale's house), Nawab Nagar	29-Oct-09	11.15 am
5	W5	Sample taken from the pipeline connected to the Tube well near Kirana Store of Guddu Bhai, Annu Nagar	29-Oct-09	11.45 am
6	W6	Tube well inside the house of Dildar Khan, Blue Moon Colony	29-Oct-09	12.20 pm
7	W7	Hand Pump near the house of Jagdish Prasad Mishra, Annu Nagar	29-Oct-09	12.55 pm
8	W8	Hand pump near temple, Dayanand Sundar Nagar	29-Oct-09	1.20 pm
9	W9	Tube well in front of Durga Mandir, Garib Nagar (Chand Bari)	29-Oct-09	1.40 pm
10	W10	Hand pump inside the house of Mr. Lila Kishan Rathore (H. No. 1437), Gali No. 7 (Ram Bai Gali), Prem Nagar	29-Oct-09	2.10 pm
11	W11	Hand pump near Chaurasia Samaj Mandir, Shiv Nagar	29-Oct-09	2.35 pm
12	W12	Dug Well in Gali No. 2, J. P. Nagar (Near Hazra Bi house)	29-Oct-09	2.55 pm

Note:

- Samples were collected in separate bottles for Organochlorines, Carbamates & Heavy Metals
- For Carbamate analysis water samples were preserved by acidifying to pH 4 - 5 with 0.1 N Chloroacetic Acid
- For Heavy metal analysis water samples were preserved by acidifying with Nitric Acid to pH<2
- All samples were stored at $6^{O}C$, and out of direct sunlight, from the time of collection till analysis.

Annexure 1B: Sample Details – Soil

S. No.	Sample Code	Site of Collection	Date of Collection	Time of Collection
1	S1	Waste storage shed of UCIL – taken from the sack adjacent to the wall marked D/A 24	28-Oct-09	3.20 pm
2	S2	Outside the pond in the dump site within UCIL's premises.	28-Oct-09	3.40 pm
3	S3	Inside the pond in the dump site within UCIL's premises.	28-Oct-09	3.50 pm
4	S4	From the corner plot of the dump site (now being used as playground) within UCIL's premises.	28-Oct-09	4.10 pm
5	S5	From the Sevidol formulation plant	28-Oct-09	4.30 pm
6	S6	From the pilot plant pit (adjacent to the boundary wall) near Temik Plant	28-Oct-09	5.00 pm
7	S7	From the ground floor of the Sevin Plant	28-Oct-09	6.00 pm
8	S8	From Solar Evaporation Pond of UCIL, parallel to the under-construction flyover	29-Oct-09	4.30 pm

Note:

- All samples were collected in transparent polythene bags labeled and sealed
- All samples were stored at $6^{O}C$, and out of direct sunlight, from the time of collection till analysis.

Annexure 2A: Chlorinated benzenes, Organochlorine and Carbamate Pesticides in Water Samples (All values in ppm)

S. No.	Class	Compound	IS:14543 Limit mg/L	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W11	W12
1	Chlorinated Benzene	1,3 DCB	0.0001	0.0004	0.0002	0.0002	0.0001	ND	0.0002	0.0002	0.0002	0.0002	0.0002	0.0008	0.0002
2	Chlorinated Benzene	1,4 DCB	0.0001	0.0004	0.0003	ND	0.0002	ND	0.0003	0.0002	0.0002	0.0003	0.0002	0.0025	0.0004
3	Chlorinated Benzene	1,2 DCB	0.0001	ND	ND	ND	ND	ND	0.0002	ND	ND	0.0004	0.0001	0.0002	0.0002
4	Chlorinated Benzene	1, 2, 3 TCB	0.0001	ND	ND	ND	ND	ND	ND	ND	ND	0.0002	0.0001	0.0002	0.0002
5	Chlorinated Benzene	HCB	0.0001	0.0013	ND	0.0001	ND	ND	ND	ND	ND	ND	ND	0.0001	ND
6	Organochlorine	α HCH	0.0001	0.0064	0.0002	0.0001	ND	0.0001	ND	ND	0.0001	0.0001	0.0001	0.0002	0.0006
7	Organochlorine	β HCH	0.0001	0.0057	0.0003	0.0002	ND	ND	ND	0.0010	0.0001	0.0001	0.0004	0.0001	0.0004
8	Organochlorine	γ HCH	0.0001	0.0003	0.0004	0.0001	0.0003	0.0003	0.0005	0.0003	0.0005	0.0011	0.0010	0.0038	0.0019
9	Organochlorine	δ HCH	0.0001	0.0030	0.0002	0.0008	0.0001	0.0001	0.0001	0.0004	0.0001	0.0001	0.0002	0.0001	0.0002
10	Carbamate	Carbaryl	0.0001	0.2600	0.0008	0.0276	ND	ND	0.0002	ND	ND	ND	ND	0.0113	ND
11	Carbamate	Aldicarb	0.0001	0.0030	ND	0.0005	ND	ND	ND	ND	ND	ND	ND	ND	ND
		Total Pesticides	**0.0005**	**0.2805**	**0.0025**	**0.0297**	**0.0008**	**0.0005**	**0.0016**	**0.0023**	**0.0012**	**0.0024**	**0.0023**	**0.0193**	**0.0042**
		No of times the limit of total pesticides (0.0005mg/L)		**561.0**	**5.1**	**59.3**	**1.6**	**1.1**	**3.2**	**4.6**	**2.4**	**4.8**	**4.6**	**38.6**	**8.5**

Notes:

- Organochlorine Pesticides were analysed by Gas Chromatograph - ECD (EPA Method 8081B)
- Carbamates were analysed by High Performance Liquid Chromatograph (HPLC) using Post Column with Fluoroscence Detector (EPA method 8318A)
- ND: Not Detected

Annexure 2B: Chlorinated benzenes, Organochlorine and Carbamate Pesticides in Soil Samples (All values in ppm)

S. No.	Class	Compound	S1	S2	S3	S4	S5	S6	S7	S8
1	Chlorinated Benzene	1,3 DCB	0.65	113.41	1.78	112.29	489.75	29.17	8.01	0.49
2	Chlorinated Benzene	1,4 DCB	0.95	63.69	0.57	108.72	541.70	83.12	7.90	0.62
3	Chlorinated Benzene	1,2 DCB	2.37	20.92	ND	16.54	1017.08	20.75	11.02	0.14
4	Chlorinated Benzene	1, 2, 3 TCB	1.34	6.47	ND	104.68	507.05	4.94	23.72	0.09
5	Chlorinated Benzene	HCB	0.41	50.57	4.56	5.16	1.12	1.70	12.37	1.34
6	Organochlorine	a HCH	0.43	129.80	8.65	116.12	114.08	76.71	71.63	3.38
7	Organochlorine	b HCH	1.08	171.06	29.69	238.81	111.36	47.83	63.36	4.32
8	Organochlorine	g HCH	0.19	555.93	45.23	702.32	2782.14	264.22	198.01	10.39
9	Organochlorine	d HCH	0.73	206.09	14.94	104.94	111.79	101.64	79.83	1.74
10	Carbamate	Carbaryl	9858.61	ND	ND	ND	7.47	ND	ND	ND
11	Carbamate	Aldicarb	ND	116.51	ND	56.17	190.69	ND	ND	ND
		Total Pesticides	**9866.77**	**1434.45**	**105.42**	**1565.75**	**5874.23**	**630.08**	**475.85**	**22.52**

Notes:

- Organochlorine Pesticides were analysed by Gas Chromatograph - ECD (EPA Method 8081B)
- Carbamates were analysed by High Performance Liquid Chromatograph (HPLC) using Post Column with Fluoroscence Detector (EPA method 8318A)
- ND: Not Detected

Annexure 3A: Heavy Metals in Water Samples (All values in ppm)

S. No.	Sample Code	Arsenic	Mercury	Lead	Cadmium	Chromium
WHO drinking water standard		**0.01**	**0.001**	**0.01**	**0.003**	**0.05**
EU drinking water standard		**0.01**	**0.001**	**0.01**	**0.005**	**0.05**
Indian Packaged drinking water standard (IS 10500)		**0.05**	**0.001**	**0.01**	**0.01**	**0.05**
Indian Drinking water standard (IS 10500)		**0.05**	**0.001**	**0.05**	**0.01**	**0.05***
1	W1	ND	ND	ND	ND	ND
2	W2	ND	ND	ND	ND	ND
3	W3	ND	ND	**1.22**	**0.09**	ND
4	W4	ND	ND	ND	ND	ND
5	W5	ND	ND	ND	ND	ND
6	W6	ND	ND	ND	ND	ND
7	W7	ND	ND	ND	ND	ND
8	W8	ND	ND	ND	ND	ND
9	W9	ND	ND	ND	ND	ND
10	W10	ND	ND	ND	ND	ND
11	W11	ND	**0.024**	ND	ND	ND
12	W12	ND	ND	ND	ND	ND

Notes:

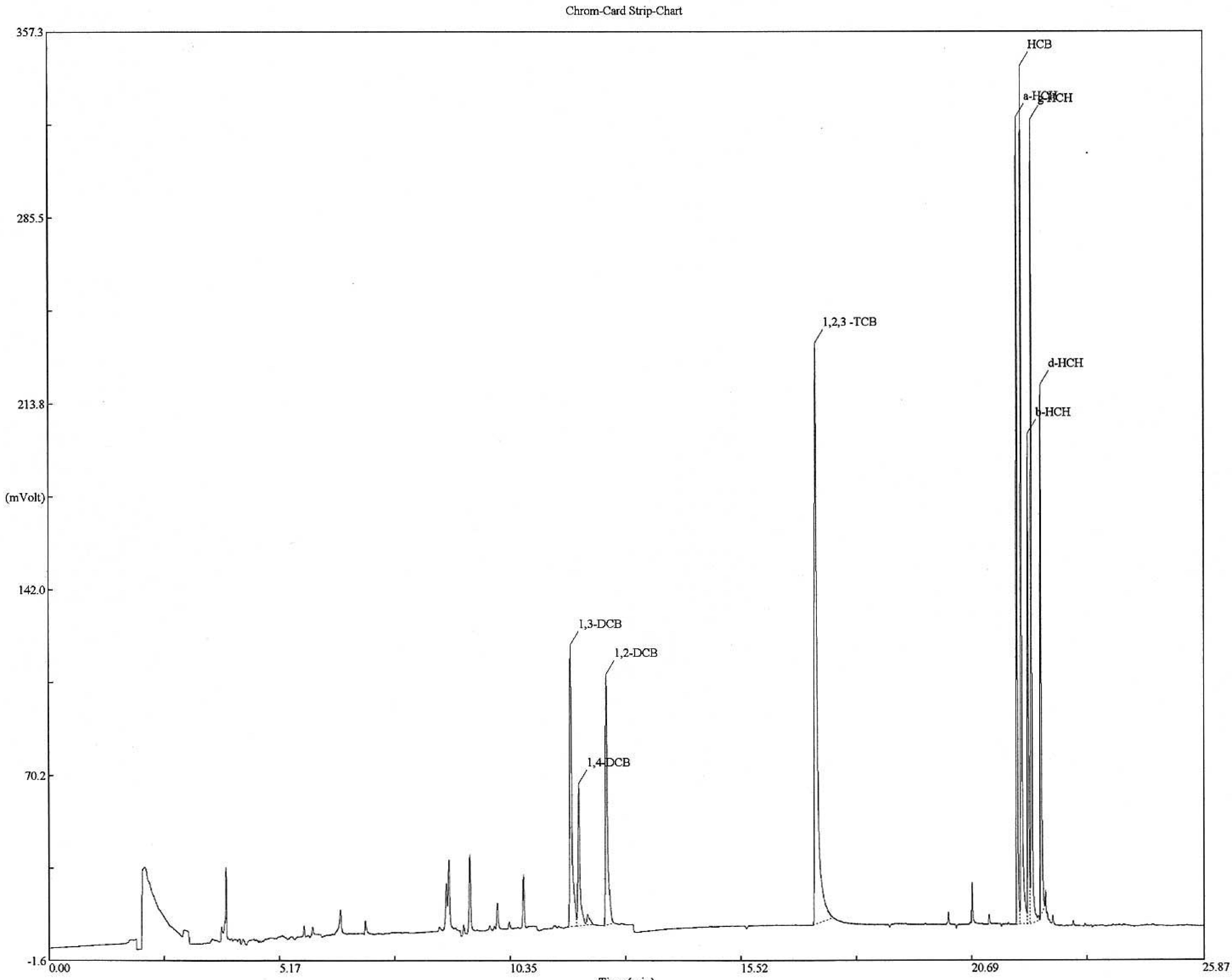
- *Standard for hexavalent chromium
- ND: Not detected

Annexure 3B: Heavy Metals in Soil Samples (All values in ppm)

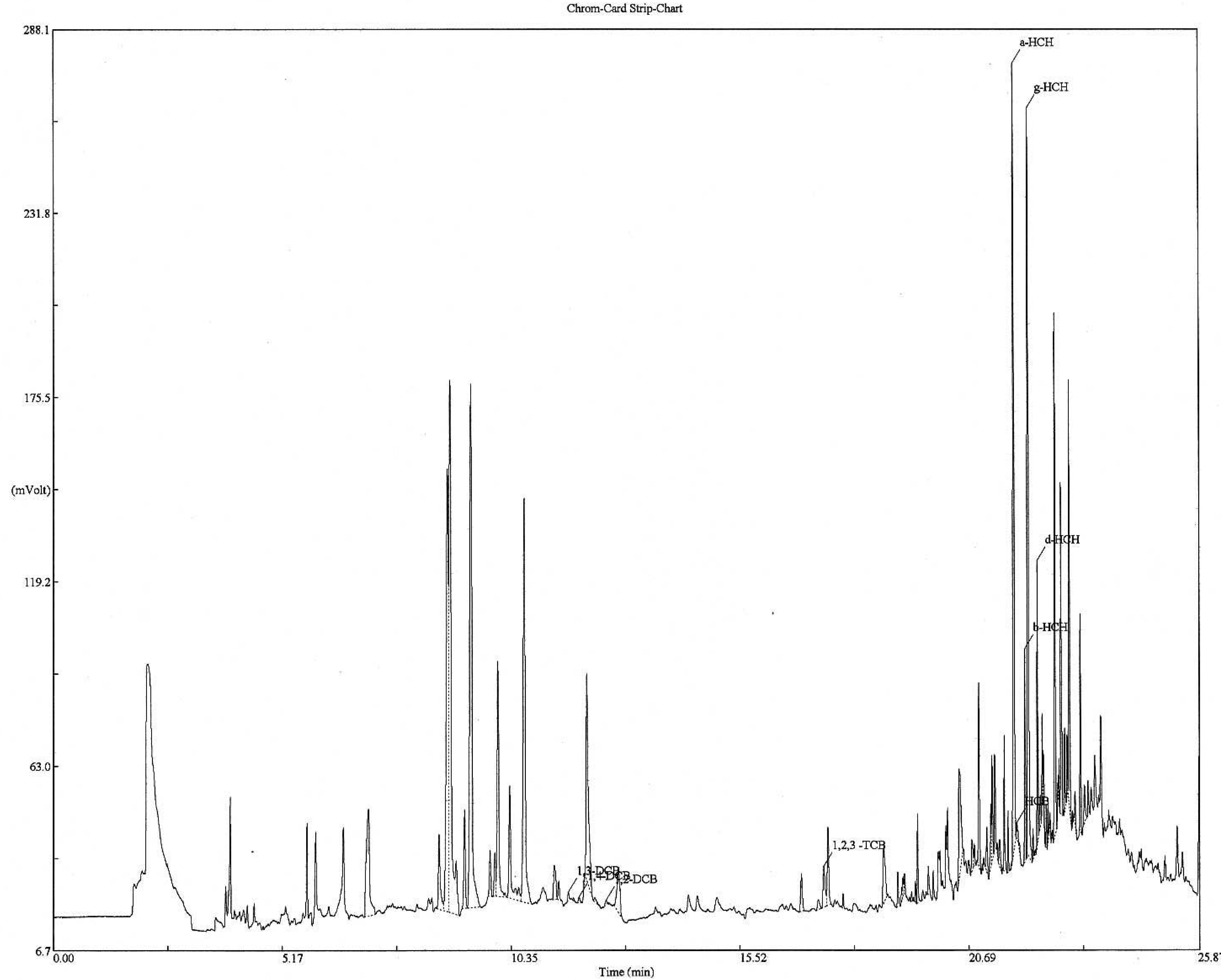
S. No.	Sample Code	Arsenic	Mercury	Lead	Cadmium	Chromium
1	S1	0.73	1064.61	23.22	ND	86.18
2	S2	1.97	ND	46.39	ND	70.84
3	S3	1.17	ND	17.13	ND	74.05
4	S4	0.48	ND	4.85	ND	18.18
5	S5	3.14	ND	ND	ND	108.40
6	S6	0.53	74.14	111.78	ND	297.70
7	S7	2.84	8188.33	84.05	ND	192.13
8	S8	1.13	18.00	22.34	ND	1064.57

Notes:

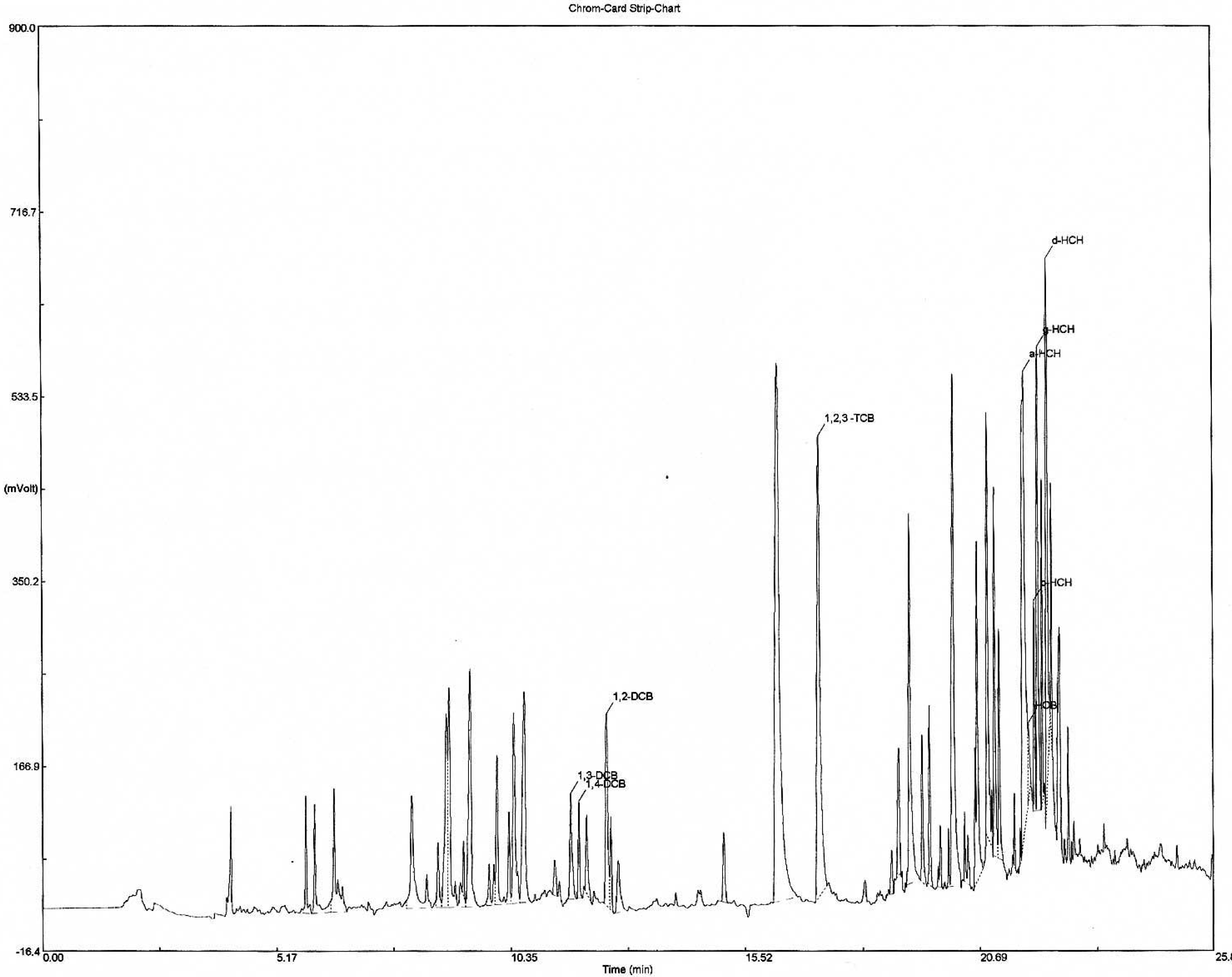
- ND: Not detected



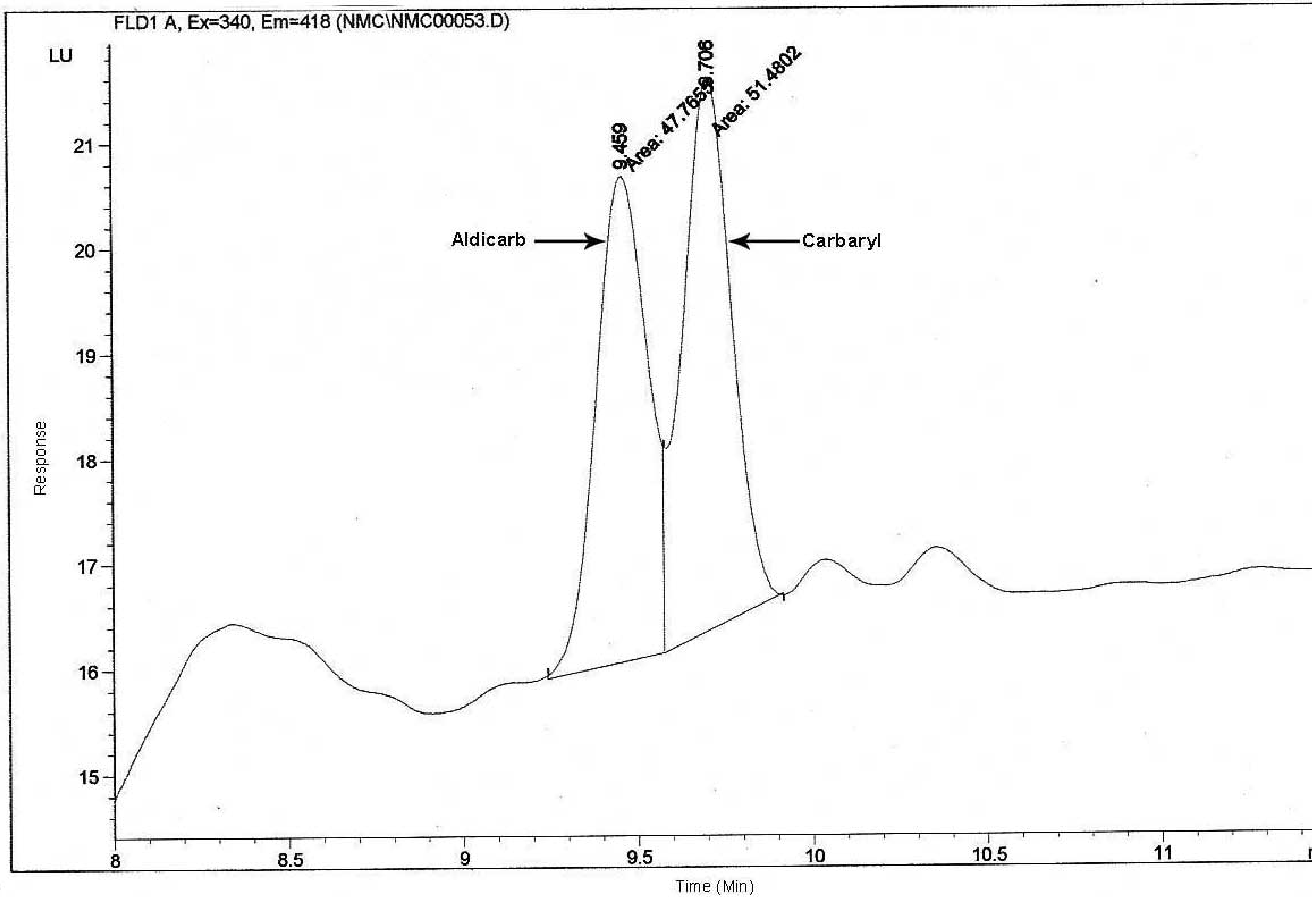
Chromatogram 1: GC Chromatogram of the standard mixture of Chlorinated Benzenes and Organochlorines



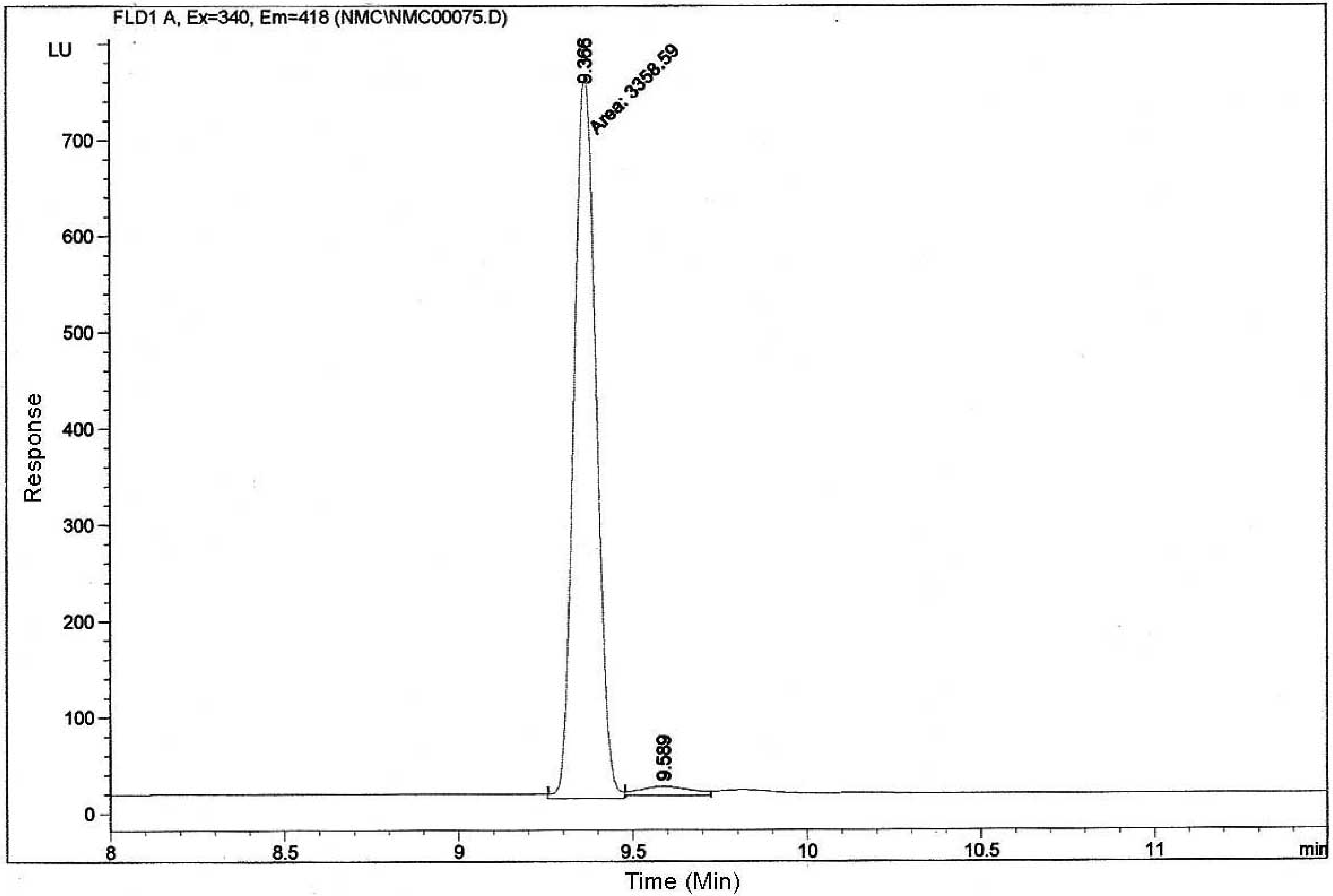
Chromatogram 2: GC Chromatogram of sample extract – Water (W012)



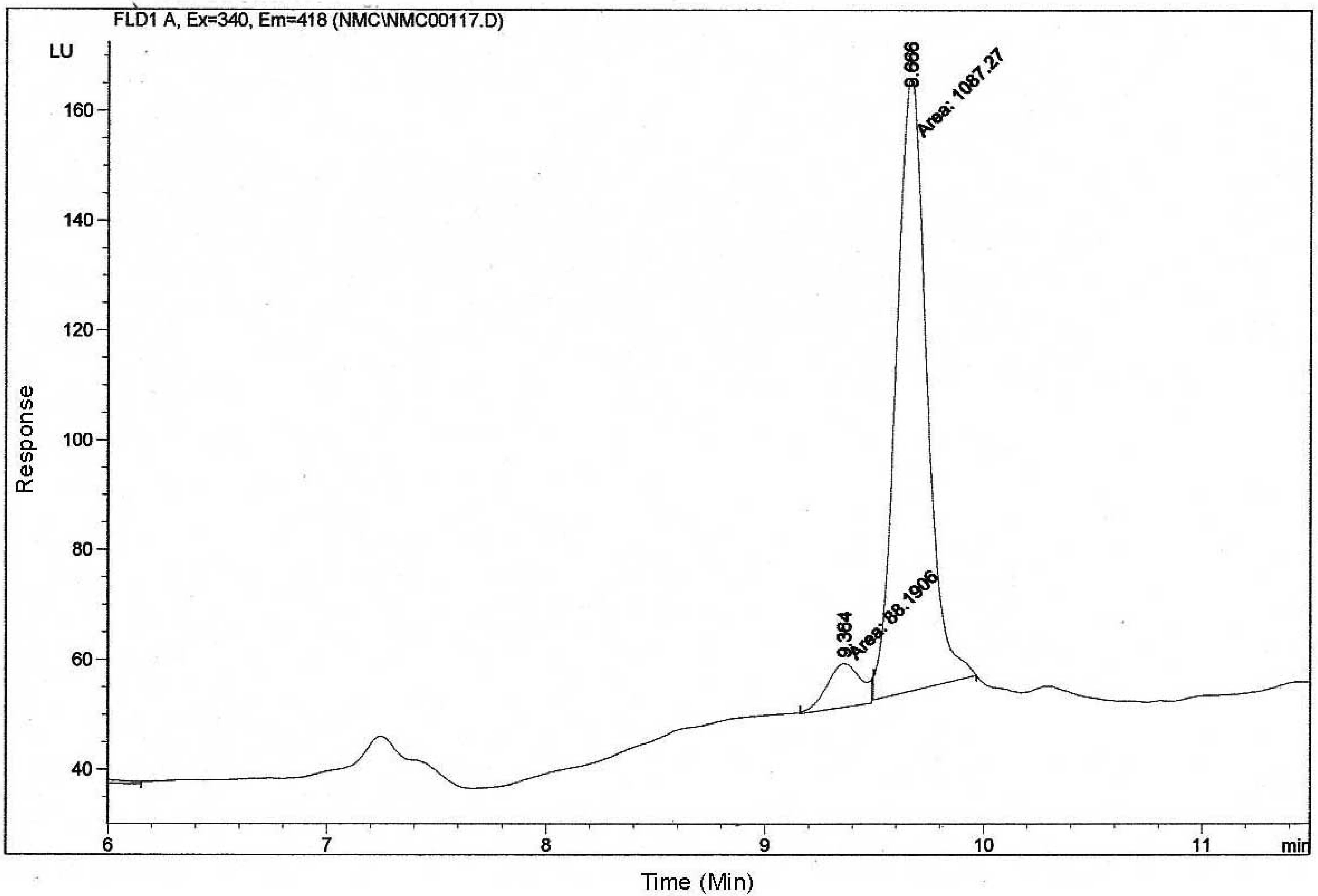
Chromatogram 3: GC Chromatogram of sample extract – Soil (S05)



Chromatogram 4: HPLC Chromatogram of the standard mixture of carbamates



Chromatogram 5: HPLC Chromatogram of sample extract – Water (W01)



Chromatogram 6: HPLC Chromatogram of sample extract – Soil (S05)