- 26. Slama, C., Abubakirov, N. K., Gorovits, M. B., Baltaev, U. A. and Saatov, Z., Insect Biochem. Mol. Biol., 1993, 23, 181-185.
- 27. Dinan, L., Experientia, 1992, 48, 305-308.
- 28. Vokac, K., Budesinsky, M. and Harmatha, J., in Xth Ecdysone Workshop Abstracts, Liverpool, 1992.
- 29. Clement, C. Y., Bradbrook, D. A., Lafont, R. and Dinan, L., Insect Biochem. Mol. Biol., 1993, 23, 187-193.
- Raynor, M. W., Kithinji, J. P., Bartle, K. D., Gumes, D. E., Mylchreest, I. C., Lafont, R., Morgan, E. D. and Wilson I. D., J. Chromatogr., 1989, 467, 290-298.
- 31. Bathori, M., Szenderei, K., Kalasz, H., Lafont, R. and Girault, J. L., Chromatographia, 1988, 25, 627-630.
- 32. Reum, L. and Koolman, J., in *Ecdysone: From Chemistry to Mode of Action* (ed. Koolman, J.), Thieme, Stuttgart, 1989, pp. 131-143.
- 33. Porcheron, P., Moriniere, M., Grassi, J. and Pradelles, P., Insect Biochem, Mol. Biol., 1989, 19, 117-122.
- 34. Tanaka, Y. and Takeda, S., Naturwissenschaften, 1993, 80, 131-132.
- 35. Gu, S. H. and Chow, Y. S., J. Insect Physiol., 1996, 42, 625-632.
- 36. Sehnal, F. and Akai, H., Int. J. Insect. Morphol Embryol., 1990, 19, 79-132.

- 37. Takemoto, T., Ogawa, S., Nishimoto, N., Hirayama, H. and Taniguchi, S., Yakugaku Zasshi., 1967, 87, 748.
- 38. Shigematsu, H. and Moriyama, H., J. Insect Physiol., 1970, 16, 2015-2022.
- 39. Shigematsu, H., Moriyama, H. and Arai, N., J. Insect Physiol., 1974, 20, 867-875.
- 40. Takemoto, T., Akihara, S., Hikino, Y. and Hikino, H., Chem. Pharm. Bull., 1968, 16, 672.
- 41. Ito, T., Koizumi, J., Yanagawa, H., Harada, M. and Muroga, A., Tech. Bull. Seric. Exp. Stn., 1968, 92, 21-40.
- 42. Ito, T., Horie, Y. and Watanabe, K., Annot. Zool. Jpn., 1970, 40, 175-181.
- 43. Anonymous, Acta Entomol. Sin., 1977, 20, 147-154.
- 44. Ninagi, O., Maruyama, C., Mizusawa, H., Kosakai, Y., Wakabayashi, M. and Maruyama, M., Bull. Natl. Inst. Entomol. Sci., 1993, 9, 7-17.
- 45. Maribashetty, V. G., Chandrakala, M. V., Jyothi, H. K. and Aftab Ahamed, C. A., J. Seric., 1997, in press.
- 46. Kajiura, Z. and Yamashita, O., Comp. Biochem. Physiol., 1992, 101A-2, 277-280.

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RESEARCH ARTICLE

Calcutta's industrial pollution: Groundwater arsenic contamination in a residential area and sufferings of people due to industrial effluent discharge – An eight-year study report

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An industry was producing 20-30 tons of Parin Green [Copper acetoarsenite (Cu(CH₃COO)₂3Cu(AsO₂)] per year and was discharging most of the effluent without proper treatment in an open land just outside the boundary of the factory. Due to the high porosity of the soil, arsenic percolated and contaminated the underground aquifer. More than 7000 people living around the discharge point, were exposed to arsenic contaminated water. Primary inves-

tigations and follow-up studies in the area, carried out for the last 8 years, have revealed that some of the distant tubewells which were earlier free from arsenic, are getting contaminated now. In May 1997, a preliminary analysis of arsenic in the urine, hair and nails of some of the people drinking contaminated water from CMC deep tubewells indicated a higher arsenic concentration than in the normal population.

INSTANCES of arsenic contamination in the world are mainly of two categories: (a) natural groundwater contamination; and (b) the contamination of water, air and the environment caused by the use of arsenical pesticides, industrial activities, mining and smelting operations. In category (a), the major cases where a large number of people have been affected are to be found in Taiwan¹, Chile^{2,3}, Mexico^{4,5}, China⁶, West Bengal-India⁷⁻¹⁵, and Bangladesh¹⁶. In India, Bangladesh and China alone, millions are exposed to arsenic and fluoride¹⁷. The actual cause of the contamination is still not known but over-exploitation of underground water for agriculture is expected to be one¹⁸. A summary of groundwater contamination all over the world has been reported elsewhere¹⁹.

In category (b), a major incident took place in Germany (1946–1974) in an arsenical pesticide manufacturing company where 1393 workers were employed²⁰. Mortality was studied and 240 people were found to be affected. Likewise, in the village Toroku, Japan²¹, arsenopyrite in the period 1920–1962 was used to produce arsenic oxide and about 300 people in that small village were affected. Till December 1987, 144 cases of chronic arsenic poisoning (CAP) had been officially recognized.

The mortality experience had been assessed of 2802 workers who worked, during 1940–1964, at a copper smelter at $Tacoma^{22}$, Washington, USA. It was, at that time, one of the largest producers of refined copper in the US. Concentration of airborne arsenic around the plant was very high, $0.9-259 \,\mu g/m^3$. The arsenical content in urine, hair and nails of the workers was also very high and deaths due to cancer in the respiratory system were also significantly elevated.

A similar copper smelter in Srednogorie, Bulgaria²³ caused severe arsenic toxicity among the residents, mostly due to inhalation and partly by ingestion of locally-produced food products like vegetables. 32,000 people lived around the factory. This was the largest copper refinery in Bulgaria and had begun operations in 1959.

In Japan, typical cutaneous manifestations of chronic arsenic poisoning were detected in 7 out of 28 male workers who had been exposed to arsenic in the form of lead arsenate and calcium arsenate in the manufacturing of insecticides²⁴. The lesions were symmetric punctuated palmo-planter hyperkeratosis and bronze hyperpigmentation.

Two serious incidents of air pollution by arsenic from smelters in the USA have also been recorded. The first incident took place in Anaconda, Mont^{25,26} where smelters were processing 9070 tons copper per day and the rate of emission of arsenic trioxide was 26,884 kg/day. Although no atmospheric concentrations were in record, edible plants contained arsenic trioxide up to 482 µg/g, causing a serious health hazard in the surrounding area. The second incident occurred in a small Western town near a gold-smelter²⁷ manufacturing 36 tons of arsenic trioxide per day. A summary of the cases of man-made arsenic contamination episodes all over the world has been given elsewhere¹⁹.

Although all major cases of arsenic contamination due to industrial activities occurred in the past and were reported from developed countries, the manufacture and use of arsenical pesticides and smelting operations have now been restricted in those countries. However, in developing countries the use of arsenical pesticides has not been seriously restricted and smelting operations are flourishing to meet the demands of the developed countries. In many cases, waste products from developed countries are being used as raw materials for metal manufacturing (battery scrap is being used for making lead) in developing nations.

During July-September 1989, a number of local and national newspapers in Calcutta reported that the residents of P. N. Mitra Lane, in Behala, which is situated in the southern part of Calcutta under the Calcutta Municipal Corporation's Ward no. 116, were suffering from arsenic poisoning because of drinking arsenic contaminated groundwater. A few had died and some had been hospitalized, while skin lesions and other symptoms of arsenic poisoning were noticed among most people of the locality. But neither the source of the contamination nor the period for which the people had been drinking the contaminated water was known at that point of time.

To find out the source of arsenic in groundwater in P. N. Mitra Lane, a scientific study was undertaken by us. The study confirmed that a factory situated close to P. N. Mitra Lane and producing 20–25 tons of the insecticide Paris-Green (copper acetoarsenite) per year, for about 20 years, had contaminated the aquifers by discharging its arsenic-containing effluent in a nearby open area. We also prepared a clinical report 30.

In this paper we will describe

- (a) the detailed study done over the last 8 years and the present status of the arsenic-affected P. N. Mitra Lane and its surroundings;
- (b) the present dermatological features and arsenic in hair, nails and urine of some arsenic patients who were consuming arsenic contaminated water 8 years ago and are at present consuming safe water;
- (c) how arsenic in groundwater is spreading to the surrounding areas which were safe earlier, and the level of arsenic in the hair, nail and urine of some residents who are consuming arsenic contaminated water at present from deep tubewells (about 150 m);
- (d) an approximate amount of arsenic still present in the soil of the effluent-discharge area and its consequence if not removed.

Industries within Calcutta

Within the core city of Calcutta consisting of 100 wards (104 km² area) there are 11,516 different types of small and big registered industries³¹ and a large number of unregistered factories. There is not a single ward in Cal-

cutta which does not have a factory registered under the Factories Act. Some of these factories produce and use very toxic chemicals. For example, 2150 factories produce acids, chemicals, paints and varnish, many deal with highly toxic compounds, some of which are suspected carcinogens. In Tangra, Tiljala and Topsia there are about 538 tanneries within a very small area. They discharge waste at 36-54 l per kg of hide processed and their effluent is discharged into drains without proper treatment. As a result, the entire locality smells foul. Studies of the tanneries in Calcutta show that some of the water sources near the area have become contaminated with chromium compounds and some of them have chromium, more than 1,000 times the permissible level of $0.05 \,\mu\text{g/ml}$. The most important point to note in this context is that most of these factories are located at the centre of a thickly populated area. In many cases the factories form a part of houses people live in, and what is worse is that, in many cases, same rooms are used for both manufacturing and dwelling. As per the Gazette notification published in 28 November 1974, some trades like the manufacture of chemicals (nitroglycerine, saltpetre, etc.) have been listed as offensive (on pollution basis), and out of the 100 wards in the Calcutta municipal area, no less than 68 wards have been found to have such manufacturing units.

More than 10,000 residents of Ward nos 66 and 67 in the city's Tiljala area breathe the emissions of 27 factories producing lead ingot from battery scrap. The factories were earlier using 15-20 m high chimneys that did not meet the prescribed minimum stack height for pollutant dispersion. So the area surrounding the factories contains a high amount of lead and other toxic metals³². Although the factory owners are presently installing treatment plants, the crucial question remains: should such lead factories operate in densely-populated residential areas?

Again, not far from the city, in Kalipark, Dum Dum, there is a factory in a densely-populated area producing lead ingot from lead ore. The gaseous emission from the factory, which has a chimney 18 m high, has affected thousands of people living around the unit. Recent studies indicate that the whole area is contaminated with lead, nickel, cadmium, arsenic and mercury. The lead content in the soil of a resident's plot has been found to be close to the amount present in the lead ore³³.

About 250 acid chemical processing (HCl, HNO₃ and H₂SO₄) units are situated around CMC's Ward no. 14 or the Bagmari-Muraripukur area. The people of the locality have complained many times to the local authorities about the smell of acid. The problem becomes acute during winter when, due to inversion, the acid fumes are not easily dispersed. Howrah, situated opposite Calcutta on the west bank of the Ganges, is known as an industrial city. It is often called 'Sheffield of West Bengal'. Thousands of factories are located in Howrah.

The arsenic-affected area, its surroundings, and method of Paris-Green preparation by the factory Aceto Chemical Private Limited (ACPL)

Calcutta, the megacity, has 141 wards under the Calcutta Municipal Corporation (CMC) and its night and day time population figures are about 4.3 million and about 7.0 million respectively. The arsenic-affected area in Behala, in the southern part of the city, has 26 wards. Within these 26 wards, the most affected area is ward 116, having a population of about 27,000 and P. N. Mitra Lane is the worst-hit zone within that ward. Ward 116 is surrounded by wards 117, 118, 120 and 121 (Figure 1). The chemical factory ACPL had been producing the pesticide and P. N. Mitra Lane is situated behind the factory (Figure 1).

About 1,50,000 people live in wards 116, 117, 118, 120 and 121. P. N. Mitra Lane, Kalabagan, Tarapark, Chanditala, Bahadur Road are a few densely-populated areas surrounding the factory ACPL (Figure 1). The ACPL has an area of about 6500 m² and had 110 workers working in two shifts in the manufacturing, packaging, loading of their different chemical products including Paris-Green. Paris-Green is a mixture of cupric arsenite and the copper salt of acetic acid in the ratio of 3:1 (ref. 34). Paris-Green was manufactured by the APCL by the reaction as shown below

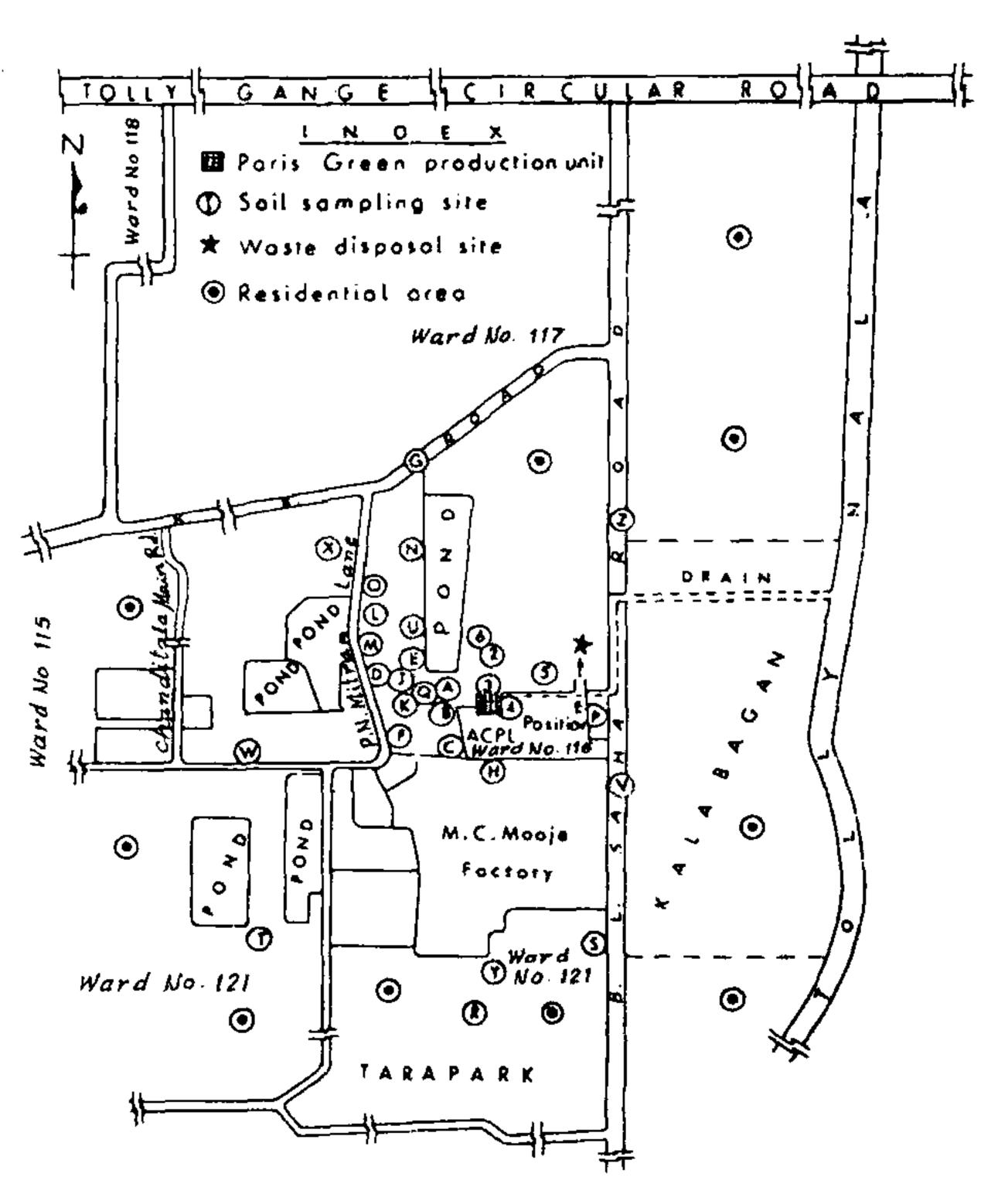


Figure 1. The map showing the position of Paris-Green production unit, waste disposal site, soil sampling locations and surrounding wards.

 $As_2O_3 + NaOH \rightarrow NaAsO_2 + excess NaOH$ $\downarrow Cu(CO_3)_2$ $Cu(AsO_2)_2 + Cu(OH)_2 \cdot Cu(CO_3)_2$ $\downarrow CH_3COOH$ $Cu(CH_3COO)_2 \cdot 3Cu(AsO_2)_2$.

The reaction is considered to be complete when a green product precipitates from the solution. The precipitate was then filtered. The effluent released contained some excess sodium arsenite, copper salt and some of the fine particles of precipitated Paris-Green due to an inefficient filtering system (done on cloth filter). The whole operation system (mixing of raw materials, dissolving, filtering, drying of solid Paris-Green, powdering and packaging in polyethylene bags and drums) of Paris-Green preparation was done manually and in one room only, containing two exhaust fans for ventilation. A survey of the factory area, both inside and outside, indicates that there were two small settling tanks used for the waste water of the factory. The excess waste water from the settling tanks used to be discharged into an open drain connected to Tally Nala (canal), which finally joins the river Ganges (Figure 1). However, the maximum amount of the waste water from the Paris-Green unit was directly discharged, without proper treatment, into an open land of pioneer pitch board packaging factory for 20 years, and the land turned barren (Figure 1).

The present Managing Director of West Bengal Chemical Industries Ltd., was the works manager in ACPL during 1980–82. He said that the effluent contained a high level of arsenic and suggested the installation of a treatment plant, but the factory owners ignored his suggestion³⁵.

Geological, geomorphological and groundwater regime of the study area

Geologically the area constitutes a part of the lower Gangetic alluvium of the Quaternary period. The panel diagram¹⁹ from an inventory of four bore-hole sediments in the area shows the area is blanketed by a clay layer of varying thickness (2.0–3.0 m). The clay bed is underlain by an extensive layer of sand of varying thickness with patches of silt rich fraction especially near its upper part. The sandy layer also contains some interfingering clay layers, especially in its eastern and western parts. The unconfined aquifers extend from a depth of around 4 m to about 190 m/bgl (below ground level) while the confined aquifers occur below a depth of around 210 m being separated from the unconfined aquifer by a 20 m thick clay layer.

Geomorphologically, two characteristic landforms, viz. the levees and abandoned distributary channels

could be recognized from interpretation of Landsat Imagery aided by field checks. Such landforms have been largely modified by human habitation and small remnants of such landforms are left here and there. The river Adi-Ganga (Tally Nala) flows sluggishly in a winding path along the eastern part of the study area. Along both the banks of the river, levees have been developed which form slightly raised land masses (3 m above the channel bottom) on both the banks. The levees, composed mostly of micaceous silt, slope away gently from the river banks. The other landforms, viz. the abandoned distributary channels occur in the form of isolated water bodies of various sizes and shapes in lowlands adjoining the levees.

Hydrogeological study of the region suggests that deeper aquifers in the Calcutta region are mainly recharged from Hooghly district in the west and Nadia district in the north. As the porous, permeable and spatially extensive alluvial sand occurs on and near the surface, the ultimate source of shallow groundwater is the rain water. The rainfall in and around the study area (194 cm/year) partly evaporates, partly moves off to the sea as surface run off and partly enters the ground to contribute to the subsurface water regime. From the configuration of sediments and inventory of tubewells, it has been observed that groundwater in the arsenic affected area occurs under unconfined, semiconfined and confined conditions but most of the tubewells of the area (depth 22-39 m/bgl) tap groundwater from the unconfined aquifer.

Materials and methods

Flow injection-hydride generation-atomic absorption spectrometry (FI-HG-AAS) was used for analysis of most of the water, urine and digested hair, nail samples. A detailed description of the instrumentation and FI-HG-AAS procedure has been given earlier^{8,9}. Total arsenic content in water was also analysed spectrophotometrically using our modified Ag-DDTC in CHCl₃ with hexamethylenetetramine³⁶. A Shimadzu (Japan) double beam spectrophotometer (Model UV-150-02) was used. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used. X-ray fluorescence and electron probe micro analysis (EPMA) have been described in our earlier publications^{29,37-39}. All reagents are of analar grade. Details of the reagents and glassware are given elsewhere^{8,9}. Water samples were collected from tubewells (bore-wells). The mode of collection and details of the bore-wells are as described earlier²⁹. Samples of hair, nail and urine were collected from affected persons and persons drinking arsenic-contaminated water. The procedure for cleaning and the mode of digestion have already been described^{9,12}.

Procedure for determination of inorganic arsenic and its metabolites in urine and total arsenic in water, hair and nail

A detailed procedure for determination of total arsenic in water, hair and nail has been described elsewhere. In this study we have determined total arsenic in water both by FI-HG-AAS and spectrophotometrically. Spectrophotometrically using our procedure is reliable for arsenic 0.04 mg/l and above, whereas by FI-HG-AAS we can determine arsenic up to 0.003 mg/l with 95% confidence. Dilution of sample is necessary for above 0.05 mg/l. Total arsenic in hair, nail and arsenic metabolites in urine is measured by FI-HG-AAS. Mode of collection and analytical procedure for digestion and analysis of bore-hole sediment has been described earlier²⁹.

Results and discussion

We came to know about the arsenic problem in P. N. Mitra Lane and sufferings of people from daily newspapers during July-September, 1989. The source due to which contamination occurred could not be identified immediately. However, from our scientific studies²⁸ in the affected area we could identify high concentrations of arsenic near the effluent discharge area of the factory ACPL, which was producing chemical compounds. However, the factory denied their involvement in this contamination. We collected soil samples from inside the factory and also identified a high level of arsenic in the soil. We published a scientific report²⁸ covering the arsenic in tubewell water of residents and the probable source of arsenic. Further, we published convincing evidence²⁹ proving factory ACPL was producing Paris-Green, an insecticide (copper acetoarsenite), and discharging the arsenic-rich effluent in the nearby area of P. N. Mitra Lane and was responsible for the arsenic contamination of the groundwater aquifer. The report was given to the factory management, the government, and to the local authority. Finally, the government ordered the closure of the factory in 1991.

Tubewell water analysis for arsenic

During September 1989 we first analysed 31 tubewells only from the residential areas of P. N. Mitra Lane close to the effluent-discharge area of the factory ACPL. In that area, there was only one CMC deep tubewell (100 m) and the rest were shallow household tubewells ranging between 20 and 40 m. All the tubewells except the CMC deep tubewell had an arsenic concentration above the WHO recommended value (0.01 mg/l). However, the majority of the residents were using their own tubewells for drinking and cooking purposes, and before our

analysis they were not aware that their tubewells are arsenic-contaminated. Most of the people suffering from arsenical skin lesions were from P. N. Mitra Lane area. Table 1 shows the arsenic concentration of the 30 shallow tubewells we had analysed for P. N. Mitra Lane during September 1989.

Immediately after our analytical report, the people of P.N. Mitra Lane stopped drinking the water from their contaminated tubewells and began using the deep CMC tubewell. A second CMC deep tubewell was also installed in the area. From the results of Table 1, it is evident that most of the tubewells were highly contaminated and their water was unsuitable for drinking.

From 1990 January to 1996 March, we further analysed 230 available tubewell waters, both shallow and those of deeper depth (up to 125 m), from P. N. Mitra Lane and its surrounding area, covering a radius of about 0.5 km. These areas are: R. B. Road (Ward no. 116), B. L. Saha Road (Ward no. 116,117), Canal Road (Ward no. 117), Kalabagan (Ward no. 116), Tarapark (Ward no. 121), Chanditala Main Road (Ward no. 116).

Table 1. Arsenic concentration (mg/l) in 30 shallow tubewells* in P. N. Mitra Lane measured during September 1989 and quantity of arsenic withdrawn in one year due to domestic use**

Tubewell no.	Concentration of arsenic (mg/l)	Quantity of arsenic with- drawn (kg) in one year
1	1.08	0.142
2	0.18	0.023
3	5.08	0.667
4	11.86	1.558
5	15.50	2.036
6	2.58	0.339
7	0.26	0.034
8	2.66	0.349
9	7.08	0.930
10	6.70	0.880
11	8.50	1.117
12	1.48	0.194
13	5.08	0.667
14	0.03	0.004
15	0.21	0.027
16	10.11	1.328
17	0.18	0.023
18	0.06	0.007
19	0.05	0.006
20	0.06	0.007
21	23.08	3.033
22	0.11	0.014
23	0.12	0.016
24	0.09	0.012
25	0.05	0.006
26	0.10	0.013
27	0.18	0.023
28	0.25	0.033
29	0.83	0.109
30	0.41	0.054

^{*}Now, most of these tubewells have been sealed or dismantled.

^{**}Total amount withdrawn in one year is 13.7 kg.

We found that in many areas the groundwater, which we had measured earlier and found safe, was getting contaminated with time. However, the concentration of arsenic in all these distant tubewells was not as high as we found in P. N. Mitra Lane (Table 1). 35% shallow tubewells were found to have arsenic contents above the maximum permissible limit (0.05 mg/l to 0.3 mg/l). We had also found that some deep tubewells, which had been found to be safe earlier, were getting contaminated. During 1991–1996, many of the tubewells that we had found to be contaminated, were sealed either by the Calcutta Municipal Corporation (CMC) or by the local people. At present people of the P.N. Mitra Lane and surrounding area are not using shallow tubewells for drinking and cooking. Instead, they are now using the CMC's deep (up to 125 m) tubewells.

During March-April 1997, we analysed the available tubewells from P.N. Mitra Lane and its surrounding areas. We have found out of 75 CMC tubewells (depth > 100 m), 43 tubewells contain arsenic below WHO recommended value, 26 tubewells contain 0.01-0.049 mg/l and 6 tubewells contain between 0.05 and 0.299 mg/l. Again, out of 35 private tubewells (depth 20-40) m), 16 tubewells contain arsenic less than 0.01 mg/l, 10 contain 0.01-0.049 mg/l and 8 tubewells contain 0.05-0.099 mg/l. Only one old private tubewell of P. N. Mitra Lane is most contaminated and the local people use it for washing purposes. Its present arsenic concentration is 7.5 mg/l and 8 years back it was 15.5 mg/l. The results show that even after 8 years its concentration becomes almost half but is still very high (about 750 times higher than WHO's recommended value). Even the distant tubewells are getting contaminated with time.

Study report of arsenic in soil

In our earlier publications²⁹ we had reported arsenic in soil along with copper in 8 soil samples collected in 1989, and confirmed the presence of Paris-Green in soil. We further reported that arsenic and copper were the highest near the effluent discharge point. The instrumental techniques we used 19,29,37,39 to quantify and identify the species are XRF (X-ray Fluorescence), EPMA (Electron Probe Micro Analyser), LAMMA (Laser Microprobe Mass Analyser) and ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy). Our XRD study¹⁹ of the arsenic-rich soil samples and the Paris-Green product of the company revealed a great deal of similarity, i.e. the presence of Trippketite (CuAs₂O₄), Cupric Aceto Arsenite (Paris Green). Thus it was proved that company ACPL was responsible for this contamination. We carried out this study from 1989 to 1995. We could not collect soil sample after 1995, as we could not get access to the area any more. Figure 1 shows the locations of the soil samples we collected and Figure 2

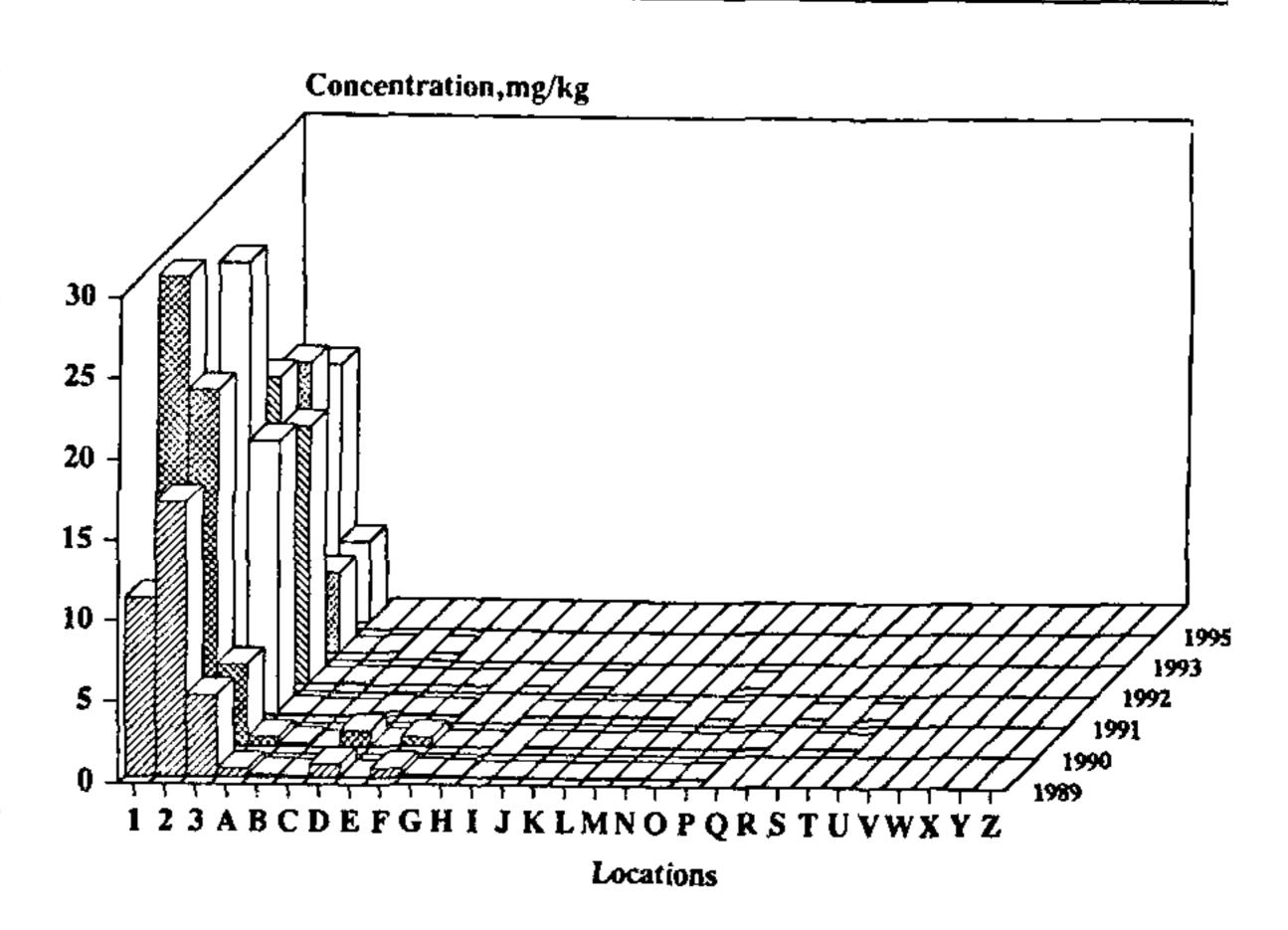


Figure 2. The variation of arsenic concentration (mg/kg) in different locations with time.

shows the distribution with time, and location and concentration. It seems that till 1995, the concentration of arsenic had not been reduced substantially. From Figure 2 it is apparent that arsenic in the discharge area increased from 1989 to 1990 and further in 1991, and after that it started decreasing. The reason is that the factory owners, knowing that they would have to close down the factory, began producing as much Paris Green as they could before shutting it down. In fact, from 1992 the factory stopped the production of Paris-Green. Although we have not been able to analyse arsenic from the disposal area after 1995, we suspect that plenty of arsenic is still present in the dumping area. Those living around the discharge point still complain that from time to time, depending on the direction of the wind, they get a garlic odour. We suspect that biomethylation and formation of methylated arsenic compounds may be responsible for the garlic odour. It is expected that the dumped area of effluent discharge containing high arsenic is suitable for such microbial transformation 40-42.

Families suffering from arsenicosis

Our tubewell water analysis from September 1989 to May, 1991 revealed that about 7000 people of Ward 116 living around the factory were exposed to arsenic contamination. The highest concentration recorded in tubewell water in the area was 23.08 mg/l. From June 1991, the people of P. N. Mitra Lane got safe pipe-line water supply through Calcutta Municipal Corporation from a distant source. From 1989 till March 1997 we have identified, from P. N. Mitra Lane, 47 families suffering from arsenicosis, and the total number of people we have identified from these families as having arsenical skin lesions are 149. During the last 8 years, 5 out of these 149 people have died, 3 of internal cancer. The

remaining 144 people are now drinking safe water. However, the affected people have these common complaints regarding their health: (i) feeling of weakness, (ii) acute bronchial problem, (iii) their lesions have remained more or less unaltered and (iv) liver disorders. Those who had diffuse melanosis, i.e. colour of the body turned bronze to black almost regained their colour after drinking safe water. Those who had only light spotted melanosis now apparently have no such pigment. But those who had heavy spotted melanosis still show the symptom with leucomelanosis (spotted pigmentation and depigmentation). Patients with keratosis on palms and soles complained that their lesions are more or less unaltered. In some cases it is less but still persisting.

During the last 8 years, we had analysed, from time to time, the urine, hair, nails and examined the dermatological features of the victims. The fact that has emerged from our 8 year-long study is that skin lesions, particularly keratosis and leucomelanosis, continue to persist even when urine, hair and nails show almost normal value of arsenic. Table 2 shows the analytical result of urine, hair, nails and dermatological features of 15 arsenic victims measured during May 1997. Even

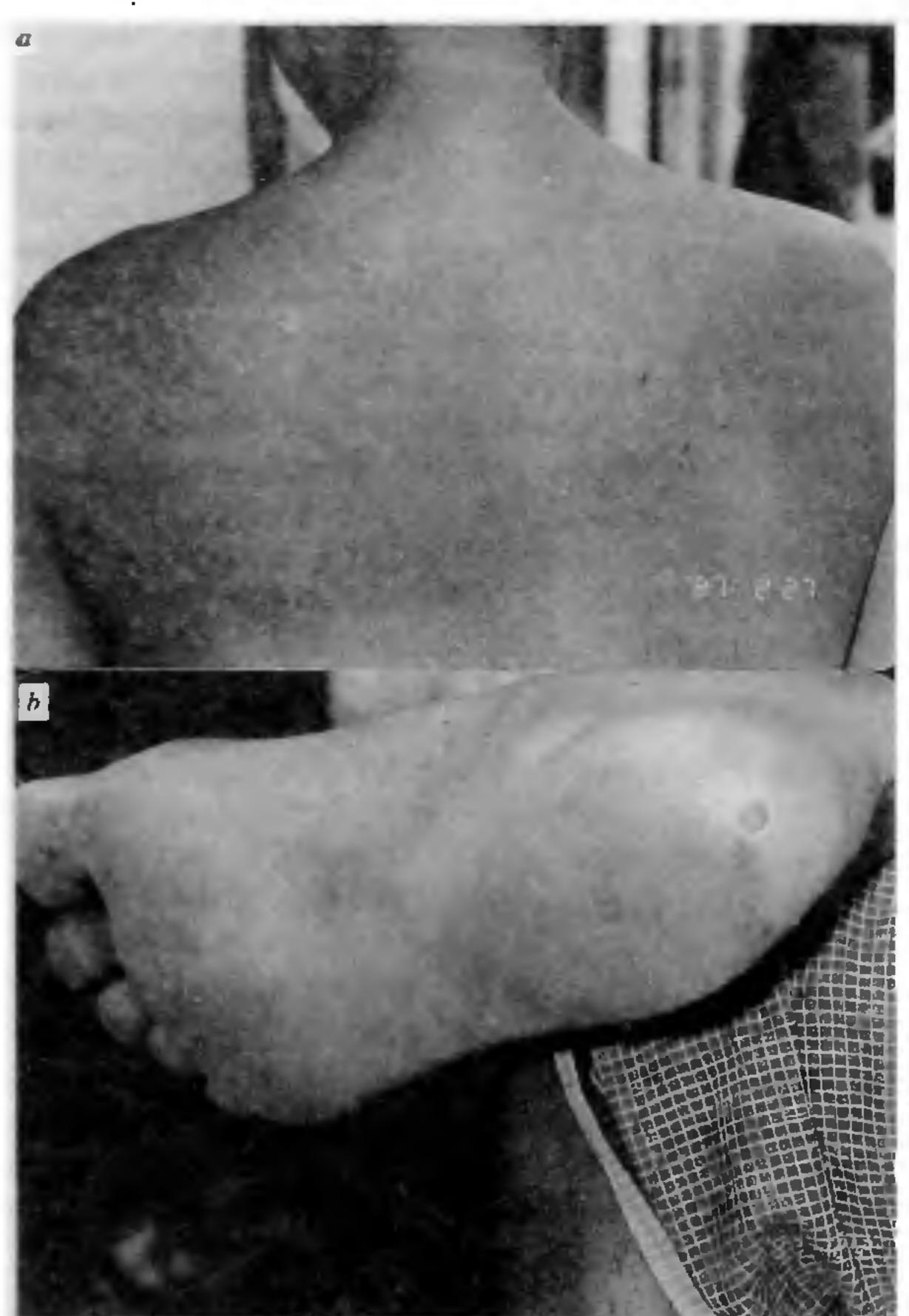


Figure 3. a, Spotted melanosis (rain drop pigmentation) of Patient no. 1 in Table 2. b, Keratosis on sole. Patient no. 2 in Table 2.

			Others	Ulcer and biopsy is	advised	Biopsy is advised										Neurological problem	Severe lung problem	•	
ne, Behala, Calcutta measured in March 1997	Chronic	bronchitis	(years)	10		13	15	10-15	12	10	v	ſ	15	15	10	12		15	.
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s of P. N. M		Pa	Spotted	++		+	+	+	+	‡	+	+	++	+	+	++	+	1	+
Table 2. Arsenic in urine, hair, nail and dermatological features of patients of P. N. Mitra Lau			Leuco	+	÷	+	ı	+	+	‡	+	+	+	I	į	+	++	+	++
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d dermatolo	Melanosis	ık	Diffuse	1		ī	1	ı	ı	I	i	ſ	I	ı	I	1	ì	ſ	
hair, nail as		Trunk	Spotted	+		+	ı	+	ı	1	‡	ı	1	++	‡	+	+	‡	ſ
nic in urine,	Arsenic in	nail	(mg/kg)	~ 1.11	•	0.42	0.99	Ϋ́	Ϋ́	Ϋ́	Ϋ́	1.12	0,89	0.55	1	0.85	0.58	68'0	0.41
able 2. Arse	Arsenic in	hair	(mg/kg)	0.54		ď Z	Ϋ́	Ν	Ν	AN	Ϋ́	0.94	0.83	0.49	0.76	0.42	0.42	Ϋ́	0.32
I	Arsenic in	urine	(µg/l)	11.0	•		38.0	9.0		21.0		•	13.0	38.0	16.0	9.0	Ϋ́	0.6	٧X
		Age/	sex	38/M	7000	39/M	35/M	36/F	40/M	32/M	63/M	22/F	45/F	43/M	50/F	30/M	50/F	46/M	32/F
		Patien	no.		•	7	m	4	S	9	7	00	6	10	11	12.	13	4	15

Mild;

available;

Not

after safe drinking water for eight years, much of their skin lesions refused to disappear. Figures 3 a, b show the rain drop pigmentation (spotted melanosis), keratosis on sole of two patients (patient no. 1 & 2). The symptom did not disappear even after using safe water for 8 years.

Approximate arsenic burden to the effluent discharge area

From the official information we had gathered, ACPL was producing 20-25 tons of Paris-Green per year, and they were doing so for 20 years. Unofficial reports say the amount manufactured was much higher. After June 1992, when the factory was closed down, we could go inside the factory, and a survey of the factory area, both inside and outside, indicated that effluent was regularly discharged in a corner of the factory after the production of Paris-Green (Figure 1). Although there was a connection between the factory and Tally Nala (as in Figure 1) through an open drain, and from the Tally Nala, the waste could reach river Ganges, the factory authority did not normally use this drain for their total waste disposal. Instead, they were releasing the arsenic waste water through point P (Figure 1) to an open space (315 m²) which is 1.8-2 m below the surface level.

It is expected that arsenic from the effluent discharge point passed through the soil barrier and contaminated the aquifer. A bore-hole was made up to 24.3 m deep to know the lithological log of Paris-Green waste disposal site (Figure 4). Figure 4 shows that only 0.65 m clay barrier exists at 16.15 m. From the soil chemistry it is found that at the Paris-Green disposal site soil is mainly silty clay loam (nearly 40%) which has high infiltration

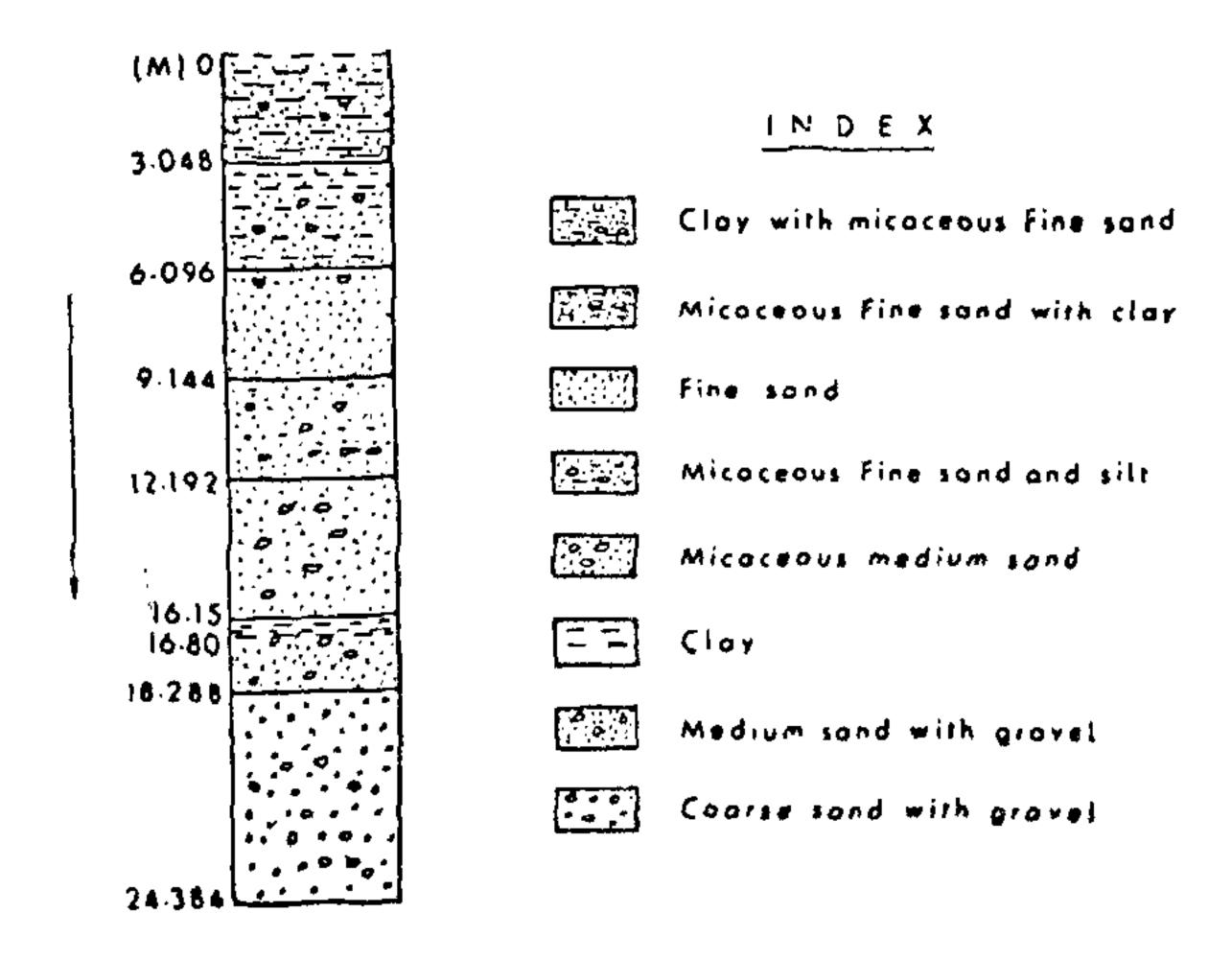


Figure 4. Detailed lithological log of Paris-Green waste disposal site, P. N. Mitra Lane, Behala.

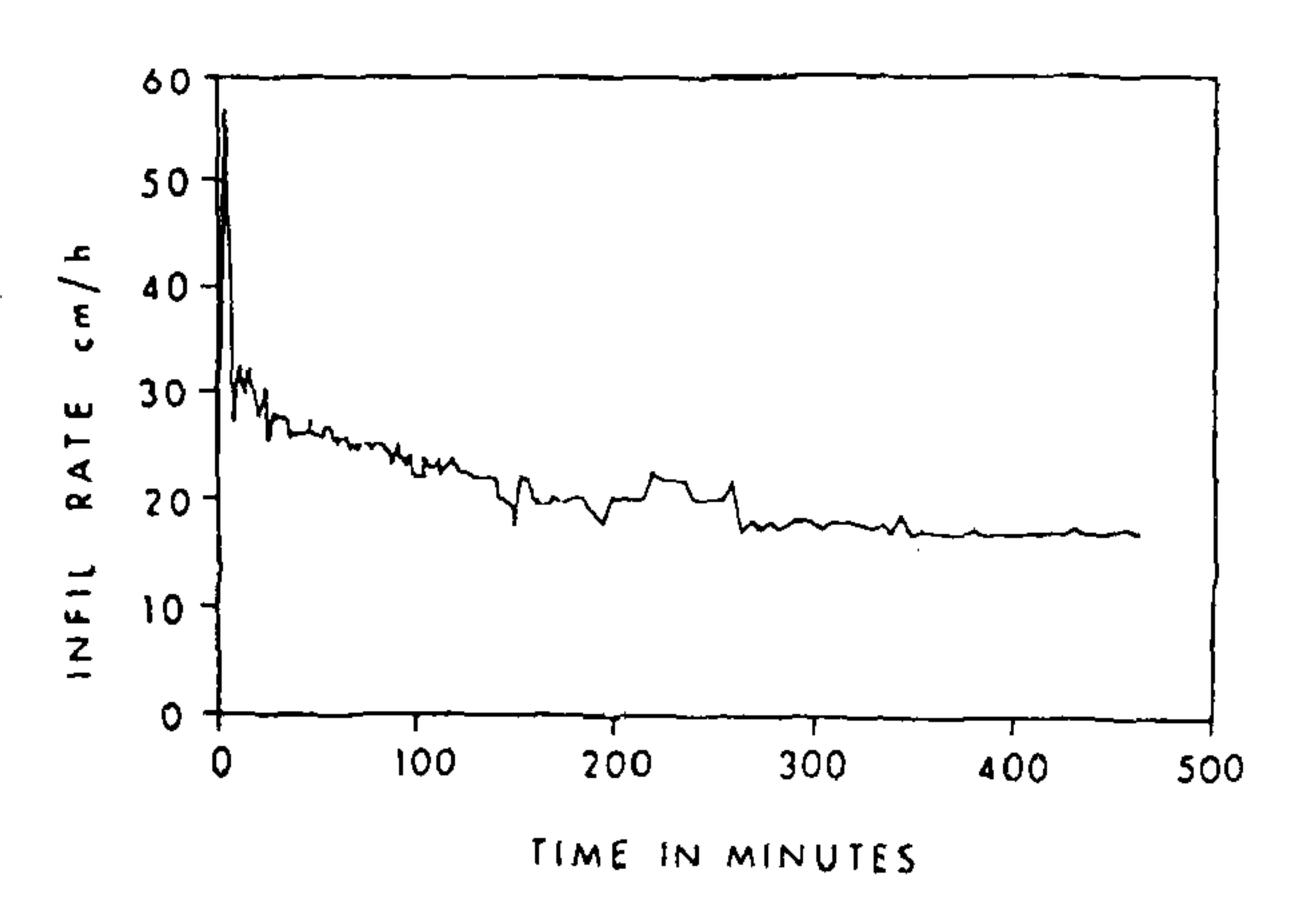


Figure 5. Changes of infiltration rate (cm/h) with time (min).

rate. The infiltration tests was also done near the disposal site (post-monsoon period) and rate of infiltration is given in Figure 5, i.e. rate of infiltration with time, indicating very high rate of infiltration, which agrees with silty loam characteristic of soil. As the Paris-Green effluent disposal area is below 1.8-2.0 m from surface level and the soil is silty loam in nature, during rainfall the rain water leached more water soluble arsenic from soil and infiltrated into underground water, thus contaminating the shallow aquifers and building up the groundwater table. The XRD study confirmed 19 the presence of Paris-Green, in soils near the effluent discharge. Thus it is expected that the effluent was not treated to remove arsenic before disposal. Paris-Green is slightly soluble in water but in presence of water and carbon dioxide it may decompose to give water-soluble phytotoxic arsenic compound 19,43. Paris-Green when spread over soil may undergo degradation due to microbial action with formation of water-soluble arsenic compounds. It has been known for almost 100 years that inorganic arsenic compounds such as cupric arsenite, copper acetoarsenite, arsenic trioxide can liberate a poisonous gas, trimethylarsine by action of mold in soil under damp conditions^{44,45}. The residents of P. N. Mitra Lane living close to the effluent discharge point used to complain (and still complain) of garlic odour. Our result of DMAA and MMAA compounds from water-soluble soil near the discharge further confirmed that methylated forms of arsenic compounds are produced in effluent disposal area.

We mentioned earlier that the factory was officially producing 22-25 tones of Paris-Green per year for 20 years and stopped production after June 1991. So, we wanted to know how much arsenic was present in the effluent discharge area. The total area of effluent discharge is 315 m² (15 m × 21 m). We analysed the arsenic with depth and Table 3 shows the results. To know the amount of arsenic in each layer hence in total depth

Table 3. Determination of acid digested (total) Cu, Cr, Ni and As of hore-hole soil samples near effluent discharge area of P. N. Mitra Lane, Behala, Calcutta

Depth (m)	As (µg/g)	Cu (µg/g)	Cr (µg/g)	Ni (μg/g)		
0 (topsoil)	16795.90	9927.40	3286.08	41.23		
0.038	30952.40	11315.20	5007.93	29.95		
0.457	4246.20	4720.30	19.97	07.20		
0.762	3035.86	2065.90	28.24	24.00		
1.067	2089.50	549.54	69.07	12.29		
1.372	1238.90	138.45	13.63	_		
1.829	981.89	133.12	42.34	38.36		
3.050	521.26	168.07	7.40	15.64		
6.096	98.96	29.32	6.62	15.76		
9.150	396.61	510.27	59.20	9.77		
12.200	126.80	166.50	30.16	16.01		
15.240	98.70	154.30	26.70	5.86		
18.290	93.40	200.16	23.93	10.60		
21.340	64.30	39.91	5.98	7.32		
24.400	43.89	29.80	4.74	8.77		

Table 4. Arsenic in urine, hair, nails of some people drinking contaminated water from deep tubewell in Aryapally, Behala

Age/ sex	Arsenic in urine* (µg/l)	Arsenic in hair** (mg/kg)	Arsenic in nail*** (mg/kg)	Concentration of arsenic in drinking water (mg/l)
9/M	200.00	1.46	1.53	0.086
9/F	79.10	0.21	0.77	0.068
12/M	255.17	NA	NA	0.068
15/M	55.17	0.32	0.63	0.068
25/F	124.14	0.66	1.28	0.068
38/M	55.17	0.49	0.99	0.068
2/F	120.69	NA	1.15	0.068
62/M	151.72	0.61	0.87	0.068
18/M	165.52	0.36	0.83	0.068

NA: Not available.

up to 24 m, we need to make a large number of boreholes. Since we could not do that, we made a very approximate calculation considering a single bore-hole. Considering weight of the soil of 315 m² from each depth and arsenic concentrations, a few tons of arsenic are present in the disposal area. The factory ACPL was also using chromium and nickel as catalyst in their preparation of other products, thus the soil was contaminated from chromium and nickel (Table 3). Further, a simple calculation shows that from 30 shallow tubewells of P. N. Mitra Lane area where we had analysed arsenic in tubewell in 1989 (Table 1), in one year about 13 kg of arsenic came out with pour water (considering six members in a family and 360 l of water

coming out from each tubewell per day). We do not know how many years before 1989 the residents were using their tubewells.

Potential danger

It is evident from our water analysis during April-May, 1997 that some distant deep tubewells which were earlier contamination free are now getting contaminated. Although concentrations are low, even deep tubewells show arsenic concentrations above the maximum permissible limit (0.05 mg/l). We have analysed the arsenic in urine, hair and nails of some members who drink this water. Table 4 shows the results. The results indicate that arsenic is on the higher side compared to the people who are drinking safe water (Table 2). True, none of them have arsenical skin lesions but consumption of such water for a long time may cause adverse effects⁴⁶. Moreover, epidemiological studies carried out⁴⁷ in the arsenic-affected area of South 24-Parganas show that even by drinking water in the range 0.01-0.049 mg/l, 13 cases of pigmentation and 4 cases of thickness of palm and sole out of 3235 persons are found.

Conclusion

It is clear from the study that a substantial amount of arsenic is present in the effluent discharge area and it is urgently needed to remove that soil in order to prevent more arsenic from being added to the aquifer. This is more important because most of the people of the surrounding areas use groundwater for drinking and there is always the risk of arsenic contamination.

- 1. Lu, F. J., Lancet, 1990, 336, 115-116
- 2. Borgono, J. M. and Greiber, R., in *Trace Substance in Environmental Health-V* (ed. Hemphil, D. D.), Proceedings of University of Missouri's 5th Annual Conference on Trace Substances in Environmental Analytical Health, Columbia, 1997, pp. 13-24.
- 3. Borgono, J. M., Xicent, P., Venturine, H. and Infants, A., Environ. Health Perspect., 1997, 9, 103-105.
- 4. Cebrian, M. E., Albores, A., Aguilar, M. and Blakely, E., Human Toxicol., 1983, 2, 121-133.
- 5. Chaverz, A., Perez, H. C., Tovar, E. and Garmilla, M., Salud Publ. Mex., 1964, 6, 432-435.
- 6. Lianfang, W. and Jianzhong, H., in Arsenic in the Environment (ed. Nriagu, J. O.), John Wiley & Sons, New York, 1994, pp. 159-172.
- 7. Das, D., Chatterjee, A., Samanta, G., Mandal, B. K., Roy Chowdhury, T., Chowdhury, P. P., Chanda, C. R., Basu, G., Lodh, D., Nandi, S., Chakraborty, T., Mandal, S., Bhattacharjee, S. M. and Chakraborti, D., Analyst, 1994, 119, N168-N170.
- 8. Chatterjee, A., Das, D., Mandal, B. K., Roy Chowdhury, T., Samanta, G. and Chakraborti, D., Analyst, 1995, 120, 643-650.
- 9. Das, D., Chatterjee, A., Mandal, B. K., Samanta, G., Chanda, B. and Chakraborti, D., Analyst, 1995, 120, 917-924.

^{* =} Normal excretion levels of arsenic in urine range from 0.005 to 0.040 mg per day (1.5 l). (ref. 12)

^{** =} Normal amount of arsenic in hair is about 0.08 to 0.25 mg/kg with 1.0 mg/kg being indication of the presence of excess arsenic.

^{*** =} Normal arsenic content of nails 0.43-1.08 mg/kg (ref. 12).

- 10. Das. D., Samanta, G., Mandal, B. K., Roy Chowdhury, T., Chanda, C. R., Chowdhury, P. P., Bose, G. K. and Chakraborti, D., Environ. Geochem. Health, 1996, 18/1, 5-15.
- 11. Roy Chowdhury, T., Mandal, B. K., Samanta, G., Basu, G. K., Chowdhury, P. P., Chanda, C. R., Karan, N. K., Dhar, R. K., Lodh, D., Das, D., Saha, K. C. and Chakraborti, D., in Arsenic: Exposure and Health Effects, Chapman & Hall, New York, 1997, pp. 91-111.
- 12. Mandal, B. K., Roy Chowdhury, T., Samanta, G., Basu, G. K., Chowdhury, P. P., Chanda, C. R., Lodh, D., Karan, N. K., Dhar, R. K., Tamili, D. K., Das, D., Saha, K. C. and Chakraborti, D., Curr. Sci., 1996, 70, 976-986.
- 13. Mandal, B. K., Roy Chowdhury, T., Samanta, G., Basu, G. K., Chowdhury, P. P., Chanda, C. R., Lodh, D., Karan, N. K., Dhar, R. K., Tamili, D. K., Das, D., Saha, K. C. and Chakraborti, D., Curr. Sci., 1997, 72, 114-117.
- 14. Guha Mazumder, D. N., Das Gupta, J., Santra, A., Pal, A., Ghose, A., Sarkar, S., Chattopadhaya, N. and Chakraborti, D., in Arsenic: Exposure and Health Effects, Chapman & Hall, New York, 1997, pp. 112-123.
- 15. Mandal, B. K., Roy Chowdhury, T., Samanta, G., Mukherjee, D. P., Chanda, C. R., Saha, K. C. and Chakraborti, D., Sci. Total Environ., in press.
- 16. Dhar, R. K., Biswas, B. K., Samanta, G., Mandal, B. K., Chakraborti, D., Roy, S., Jafar, A., Islam A, Ara, G., Kabir, S., Khan, A. W., Ahmed, S. A. and Hadi, S. A., Curr. Sci., 1997, 73, 48-59.
- 17. Susheela, A. K. (ed.), Fluoride Toxicity, Proceedings of the 13th Conference of the International Society for Fluoride Research (ISFR), New Delhi, 13-17 November, 1983.
- 18. Welch, A. H., Lico, M. S. and Hughes, J. L., Groundwater, 1988, 26, 333-347.
- 19. Chatterjee, A., Ph D thesis, Jadavpur University, Calcutta, India, 1995.
- 20. Mabuchi, K., Lilienfeld, A. M. and Snell, L. M., Arch. Environ. Health, 1979, 34, 312-319
- 21. Hotta, N. and Japanasesa, J., Constitutional Medicine Ku-mamoto, 1989, 53, 1-2.
- 22. Enterline, P. H. and Marsh, G. M., in Arsenic, Industrial, Bio-medical, Environmental Perspectives (eds Leader, W. H. and Fensterheim, R. L.), Van Nostrand Reinhold, New York, 1983, pp. 226-244.
- 23. Nilsson, R., Jha, A. N., Zaprianov, Z. and Natarajan, A. T., Frenius. Environ. Bull., 1993, 2, 59-64.
- 24. Hamada, T. and Horiguchi, S., Jpn. J. Int. Hlth, 1976, 18, 103-105.
- 25. Hawkins, W. D. and Swain, R. E., J. Am. Chem. Soc., 1907, 29, 970-998.
- 26. Hayword, J. K., J. Am. Chem. Soc., 1907, 29, 998-1009.
- 27. Birmingham, D. J., Key, M. M., Itolandays, D. A. and Perone, V. B., *Arch. Drm.*, 1965, 91, 457-464.

- 28. A preliminary report of arsenic poisoning: An episode of contamination in Behala, Calcutta, School of Environmental Studies, Calcutta, India, 1989.
- 29. Chatterjee, A., Das, D. and Chakraborti, D., Environ. Pollution, 1993, 80, 57-65.
- 30. Guha Mazumder, D. N., Das Gupta, J., Chakraborty, A. K., Chatterjee, A., Das, D. and Chakraborti, D., Bull. WHO, 1992, 70, 481-485.
- 31. Classified inventory of licensed sources of non-domestic contamination to Calcutta's drainage channels, Department of Fisheries, Government of West Bengal, 1984.
- 32. Samanta, G. and Chakraborti, D., Environ. Technol., 1996, 17, 1327-1337.
- 33. Samanta, G., Chatterjee, A., Das, D., Samanta, G., Chowdhury, P. P. Chanda, C. R. and Chakraborti, D., Environ. Technol., 1995, 16, 223-231.
- 34. Ottinger, R. S., Blumenthal, J. L., Dalporto, D. F., Gruber, G. I., Santy, M. J. and Shih, C. C., EPA-670/2-73-053-f, TRW Systems Group, redondo Beach, CA., 1973, vol. 6, pp. 67-141.
- 35. Chakraborti, D., The Sunday Statesman, 18 February 1996, pp. 1-2.
- Chakraborti, D., Valentova, M. and Sucha, L., Anal. Chem., 1982, 17, 31-42.
- 37. Chakraborti, D. and Raeymaekers, B., Int. J. Environ. Anal. Chem., 1988, 32, 121-133.
- 38. Chakraborti, D., Van Vaeck, L. and Van Espen, P., Int. J. Environ. Anal. Chem., 1988, 32, 109-120.
- 39. Chakraborti, D., Ghosh, D. and Niyogi, S., Int. J. Environ. Anal. Chem., 1987, 30, 240-253.
- 40. Mc Bride, B. C., Meriles, H., Cullen, W. R. and Pickett, W., in Organometals and Organometalloids Occurrence and Fate in the Environment (eds Brickman, F. E. and Bellana, J. M.), Am. Chem. Soc. Sysp. Ser., 1978, pp. 82-95.
- 41. Chattenger, F., Chem. Rev., 1945, 36, 315-361.
- 42. Cox, D. P. and Alexander, M., Bull. Environ. Contam. Toxicol, 1973, 9, 84-88.
- 43. Pesticides Manual (eds Martin and Wathing), Fifth edition, 1984, p. 401.
- 44. Whorton, J. C., Bull. Hist. Med., 1971, 45, 219-241.
- 45. Challenger, F., Adv. Enzymol., 1951, 12, 429-491.
- 46. Smith, A. H., Hopenhayn-Rich, C., Bates, M. N., Goeden, H. M., Hertz-Ppicciotto, I., Duggan, H., Wood, R., Kosnett, M. J. and Smith, M. T., Environ. Health Perspect., 1992, 97, 259-267.
- 47. Guha Mazumder, D. N., Curr. Sci., 1997, 72, 114.

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