

CHAPTER V

APPLICATION OF NEW FUNCTIONALISED CHELATING RESIN COMPOUNDS FOR PRE-CONCENTRATION AND SEPARATION OF Cu(II), Pb(II), Zn(II), Cd (II), Cr(III) AND Fe(II) METAL IONS FROM
(I) RIVER WATER, (II) INDUSTRIAL WASTE WATER AND
(III) AGRICULTURAL SOIL SAMPLES.

(i) Pre-concentration and separation of heavy metals of Mahananda river water (Siliguri, Dt. Darjeeling, WB, India) during the period of immersion of Durga idols : Studies on the sorptions on solid supports synthesized by functionalizing polystyrene divinylbenzene resins with 2-mercapto isothiocyanate and 2 - amino 1, 3, 4 - thiadiazole.

Abstract

In this chapter two functionalised chelating resin compounds (4 and 9) have been used to pre-concentrate and separate heavy metal ions like Pb(II) and Cr(III). River water contaminated by paints, colours and dyes from the immersed Durga idols are examined for the extent of pollution level.

5.1 Introduction

Balasan (its source is Lepchajagat having the altitude 7672 m) and Mahananda (its source is Mahaldiram having altitude 7312m) have joined together at their confluence on the new border of ward No. 31 of Siliguri Municipal Corporation (SMC), Figure 5.1.1. From this point it flows assuming the name as Mahananda river. As per the view of survey of India, it originates from Mahaldiram ($26^{\circ}56'0''$ N – $88^{\circ}20'0''$ E) at an altitude of 7312m.

The catchment area of the Mahananda river looks like a leaf of the tree. Its small veins may be compared with the tributaries that come from the interfluves and join

with main artery or stream (the Mahananda). At the latitude $24^{\circ} 49' 30''$ N it seems to be the beginning of the stem or base of single channel and from there it flows south-east and south over the plains in an anastomosing way. Sometimes it creates havoc in the life of the people by means of natural or artificial obstructions. From the southern border of Darjeeling district, (Northern part of West Bengal, India) (Figure 5.1.2) it flows south-west and then south-east in a circular way over Bihar (India) covering about 92km and enters in Malda District (West Bengal, India). The length of the river from source to mouth is about 275km. It flows about 55km over the Darjeeling district, 72km over Malda, 20km along the border between Bihar and North Dinajpur (West Bengal, India) and 56 km over Bangladesh till it joins the Ganga river ($24^{\circ}28'0''$ N - $88^{\circ}19'30''$ E).

Every year during the months of September and October Durga Puja Festival is celebrated. More than 300 Durga idols (made of clay- average frontal surface area of 12m^2 for each idol) are used to be immersed in the Mahananda River near Lal Mohan Ghat, Siliguri, West Bengal, India. The river during winter season becomes almost a narrow stream when the depth of the river water is maximum 1m. Chemical paints which are used for idols generally are red, blue, orange and green in colours and are known to contain particularly chromium and lead in addition to some other heavy metals. During the period of immersion, the water gets contaminated by increased acidity, solid matters and compounds of heavy metals which are leached in the river water and the soil. Heavy metals like lead

and chromium are easily assimilated in an aquatic environment and can lead to the massive damage of flora and fauna of river ecosystem [1]. Lead is very persistent and bio accumulates in the aquatic system and it has strong adhesion potential to soil particles [2- 4].

Under the circumstances we undertook the studies on the estimations of the levels of contaminations of the water and soil samples collected during the idol immersion period to investigate the concentrations of these heavy toxic metal ions present. The estimation is very important because the whole population (about six lakhs) depends on the Mahananda river water supplied by the Municipal corporation for domestic consumptions and drinking purposes. For this purpose we have used efficiently the functionalized resin compounds synthesized by us in the laboratory. We like to report herein the results of the investigation both for water and the soils.

5.2 Methodology:

All the required chemicals used were procured from commercial sources as mentioned earlier. The names of the instruments and their manufactures are mentioned in Chapter III.

5.2.1 Sampling :

For sampling the procedure described in literature [5] was followed.

2.5 litre water was collected from the river near Lal Mohan Ghat in a clean polythene bottle (sample - 1) on 17th October, 2010 at 1pm before the immersion of the idols. On the same evening after the immersion of about 240 (80%) Durga idols at 10 pm, 2.5 litre water sample was collected in a polythene bottle (sample - 2). The day after, on the 18th October at 9am in the morning (ie, after 12 hours of the immersions) - again 2.5 litre water was collected in a polythene bottle (sample - 3). The soil sample of 500gm was collected (in an open mouth polythene bottle) from the river bed where the idols were immersed and left. The spots for the sample collections are shown in the Figures 5.1.3.

All the analyses were carried out with these collected samples.

5.2.2 Digestion of the Sample:

500ml each of samples 1- 3 were filtered separately by using Whatman filter paper (No. 42). Three samples (1, 2 and 3) were then placed in three different 1 liter round bottomed flasks separately and distilled on heating mantles till the volume of the samples reduced to about 50ml. Then 50 ml of these filtered (and volume reduced) water samples were placed in three separating funnels.

An aqueous solution of 1ml ammonium pyrrolidine dithiocarbamate (APDC) was added in each of the sample solution and was shaken for 30 seconds. Then 5ml

methyl isobutyl ketone (MIBK) was added in each solution and was shaken vigorously for 1 minute and left standing till the two phases separate. After separation of organic layer from the aqueous layer, the organic phase was transferred to three 50ml conical flasks respectively. All the 3 conical flasks were left standing in open air for 48h for the slow evaporation of the solvent so as to obtain the solid organic materials containing metal ions as the residues.

The solid residues of the 3 samples thus obtained were digested on oil bath with 5ml acid mixture ($\text{HNO}_3 : \text{HClO}_4 = 10 : 1$). The digestions were carried out for 30 minutes. The temperature of the oil bath was maintained at $100\text{-}120^\circ\text{C}$. After digestion the mixtures were cooled down to room temperature and diluted with distilled water. Then all the mixtures were transferred separately to three 50ml volumetric flasks and the volume of the contents were made up by adding distilled water.

5.2.3 Column Operation:

With compound 9

The column of the compound 9 was adjusted to pH - 6. Now 10ml digested sample (sample 1) was passed through the column for 20 minutes. The column was washed by distilled water several times after the sorption. The sorbed metal ions were then desorbed by 20ml 2M HNO_3 for 20 minutes. The desorbed metal ion

solution was collected in a 50ml volumetric flask and the volume made up. The concentration of metal ion present in it was estimated by AAS.

Other digested samples (sample 2 and sample 3) were sorbed similarly in the column of the compound **9** (pH - 6) and then desorbed by 2M HNO₃. The eluted metal ion solutions were collected in 50ml volumetric flasks and their concentrations were determined by AAS as before. The data are presented in Table 5.1.1

Table 5.1.1 water analysis (digested)

Sample	Compound	Metal ion μgL^{-1} of water	
		Pb(II)	Cr(III)
S1	9	2.25	BDL
S2	9	15.2	BDL
S3	9	38.4	10

BDL = Below Detection Limit

The experiments were further extended with water samples without concentrating the samples. The water samples for these experiments were also not digested. This procedure allowed us straightforwardly the determination of the amount of free metal ions present in the water samples collected from the river.

5.2.4 Experiments without digestion:

With compound 4

250ml water sample (sample 2 *as described above*) was filtered through Whatman filter paper (No. 42) and the filtrate collected. 200ml of the filtrate was passed through the column through 3 hour 20 minutes period. The column was made up of compound 4, and was adjusted to pH - 6. After complete sorption, the column was washed thoroughly with distilled water. The sorbed metal ion was then desorbed by 20ml 2M HCl and was transferred to a 50ml volumetric flask and the volume made up.

With compound 9

250ml water sample (sample 3 *as described above*) was filtered through filter paper (Whatman No. 42). 200ml of the filtrate was passed through the column of compound 9 adjusted to pH - 6 for 3 hour 20 minutes. The sorbed metal ions were washed by distilled water and then desorbed with 20ml 2M HNO₃ and transferred into a 50ml volumetric flask for subsequent determination of the concentration of the metal ions. All the results of estimations are presented in the Table 5.1.2

Table 5.1.2 water analysis (undigested)

Sample	Compound	Metal ion μgL^{-1} of water	
		Pb(II)	Cr(III)
S2	4	11.95	BDL
S3	9	15.2	16.25

BDL = Below Detection Limit

5.2.5 Soil digestion :

The literatures followed for the purpose were [6- 8].

5.2.5.1 With HNO_3 : HClO_4 = 10 : 1 mixture

The air dried and sieved 1.0g soil sample (soil was collected on 18th October, 2010, at 9.00 AM) in the morning from the bed of the river Mahananda at Siliguri after the immersions of the idols in the afternoon of the day before, was mixed with 10ml acid mixture (HNO_3 : HClO_4 = 10 : 1). The mixture was placed in a 50ml conical flask. Then the mixture was digested slowly on silicone oil bath at 200-220^oC for 30 minutes. It was cooled down to room temperature and diluted by distilled water (20ml) and filtered and washed. The filtrate and the washings were collected in a 50ml volumetric flask and the volume made up.

5.2.5.2 *With aqua regia*

In another experiment, 1.0g of soil sample was mixed with 30ml aqua regia and was placed in a 100ml round bottomed flask and heated. The mixture was refluxed for 2 hours. Then the mixture was allowed to evaporate slowly under a hood to dryness. The solid residue thus obtained was treated with 30ml water and was filtered. The filtrate was collected in a 50ml volumetric flask and the volume made up.

5.2.5.3 *Microwave assisted digestion :*

A mixture of 1.0g soil sample (dried and sieved) was treated with a mixture of 6ml conc. HCl and 2ml conc. HNO₃ was placed in a 100ml polytetrafluoro ethylene reactor (PTFE) inside a microwave oven. The mixture was irradiated for different power and time period. However, the total time period of irradiation never exceed 10 minutes. The mixture was then cooled down to room temperature, diluted and filtered. The filtrate was collected in a 50ml volumetric flask and the volume made up.

Column operation:

(a) 30ml of the sample solution as prepared via the procedure 5.2.5.1 was passed through the column of compound **4** (pH-6).The metal ions thus sorbed were desorbed by 20ml 2M HNO₃ and collected in a 50ml volumetric flask.

(b) 30ml each of the sample solutions as prepared via the procedures 5.2.5.2 and 5.2.5.3 respectively were passed through the column of compound **9** (pH-4).The

metal ions thus sorbed were desorbed by 20ml 3M HNO₃ respectively for both the samples and collected them separately in two 50ml volumetric flasks. The data of the analyses are presented in Table 5.1.3.

Table 5.1.3 soil analysis (collected on 18th October, 2010)

Digestion medium	Compound	Metal ion $\mu\text{g g}^{-1}$ soil	
		Pb	Cr
HClO ₄ , HNO ₃ (oil bath)	4	1.43	5.00
Aqua regia (Reflux)	9	13.90	3.43
Aqua regia (microwave oven)	9	46.20	BDL

BDL = Below Detection Limit

Figure 5.1.1 Map of the Siliguri Municipal Corporation

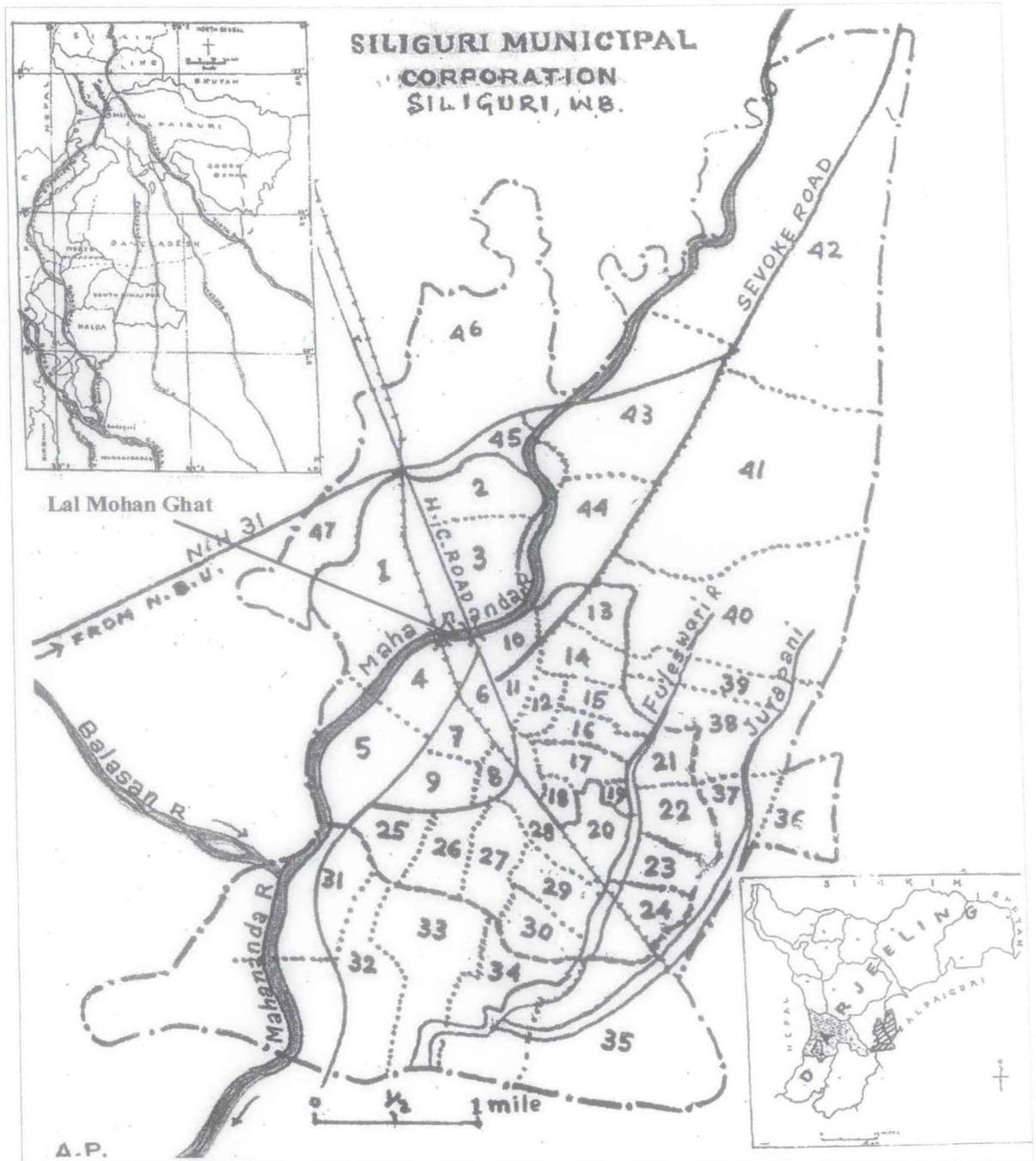


Figure 5.1.2 Map of the Northern Part of West Bengal

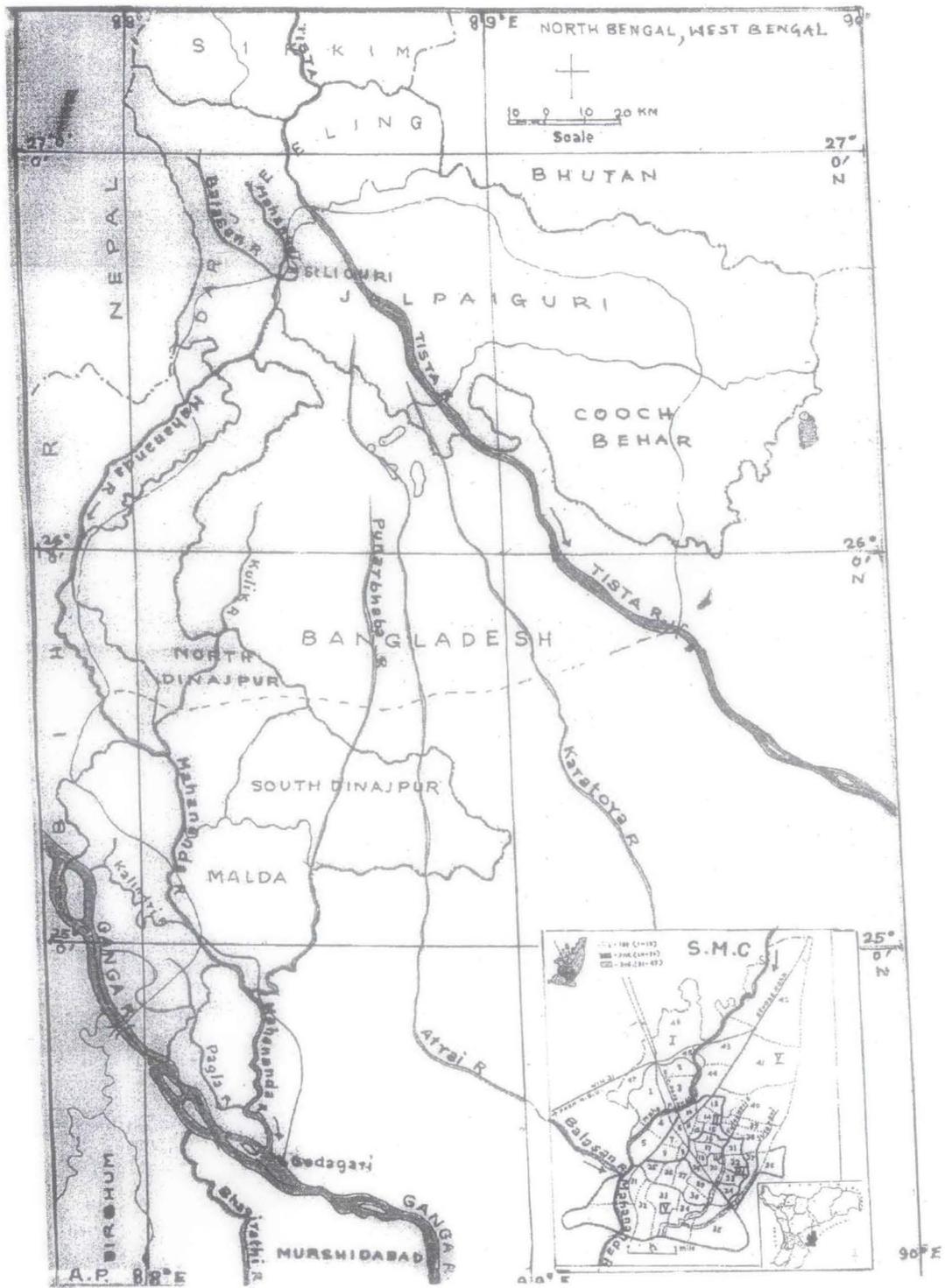
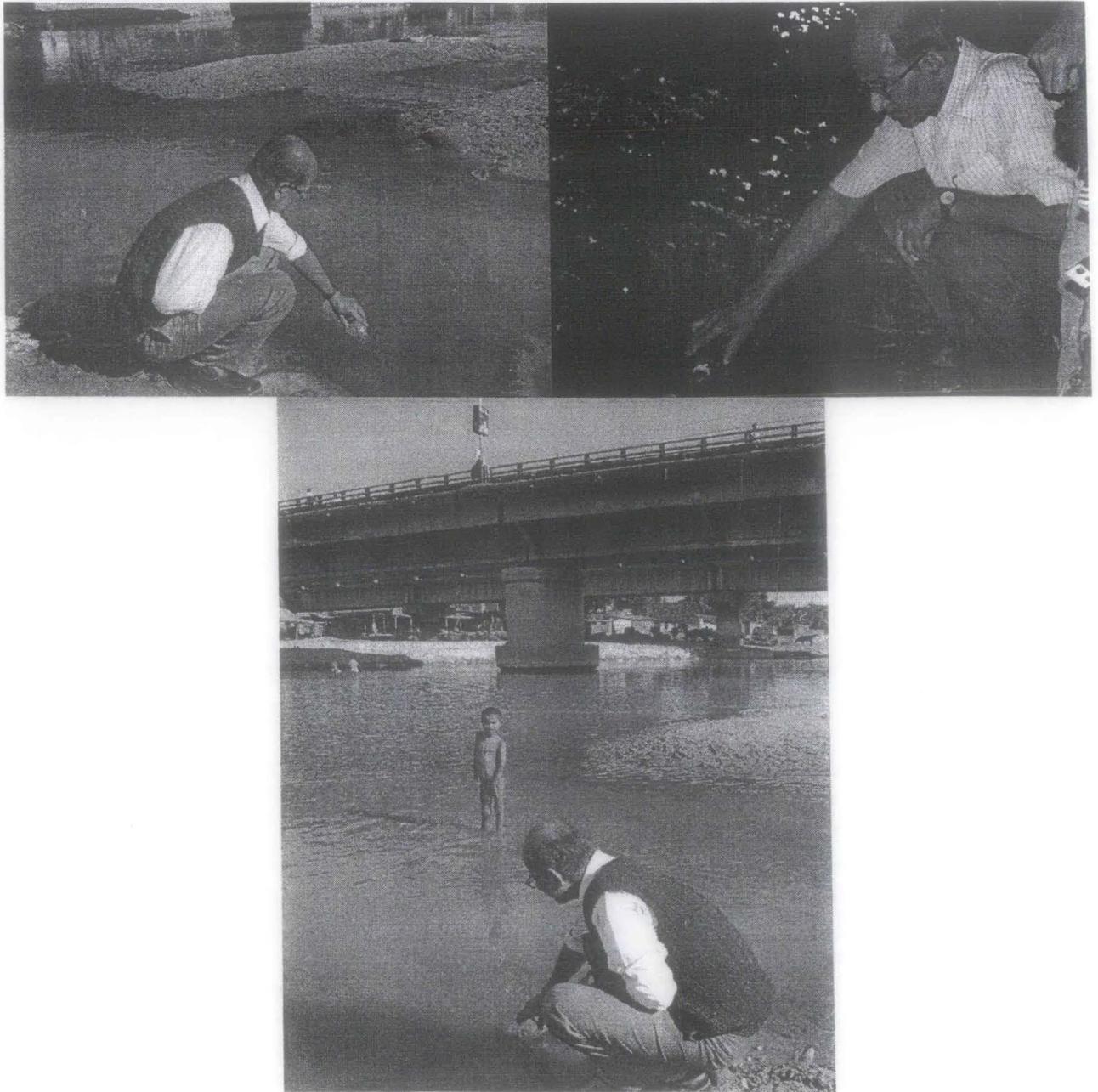


Figure 5.1.3 Water Collection on 17-10-2010 and 18-10-2010



5.3 Results and discussion:

The data obtained for water analyses (Tables 5.1.1 to 5.1.3) clearly brought about an indication of high levels of contamination after the immersions of the idols. Analyses with compound **9** for the sample 1, i.e, before the immersions – Pb(II) ions present was in low concentration ($2.35 \mu\text{g L}^{-1}$)(Indian standard- 0.05 mg L^{-1} , drinking water, WHO – 0.01 mg L^{-1}) whereas the Cr (III) ions (for Cr(VI)-Indian standard- 0.05 mg L^{-1}) was present below its detectable limit. However, for samples 2 and 3 the concentrations of both the ions were found to be considerably high indicating a risk of water pollution if the amount of pollution load continue to increase. When compared with the above results (Table 5.1.1) with the results presented in (Table 5.1.2) for water samples without digestion the concentrations of the free ions were found to be lower as expected.

The data on the soil analyses (Table 5.1.3) confirmed the presence in increased concentrations for both Pb (II) and Cr(III) in the soils of the river bed.

5.4 Conclusion:

The investigation indicated the real situation of Mahanada river in Siliguri during the Durga idol immersions. Both the soils and water got polluted though yet not alarming for a large population for heavy metal related problems. It is to be noted that the synthesized solid supports compounds **4** and **9** worked efficiently during these studies.

Industrial waste water analysis and separation of Pb(II) ions by Pyridine Carboxaldehyde thiosemicarbazone resin, 5 -amino 1, 3, 4 - thiadiazole- 2- thiol resin and 2-hydroxy naphthaldehyde thiosemicarbazone resin.

5.5 Introduction :

Industrial waste water disposal has been a problem of heavily industrialized area. Many heavy metals are released in the environment through the waste water of industrial effluents. Metal industries such as electroplating, paints, dyes and lead battery industries released Cr, Cd, Pb metals into the environment through the effluent. Living organisms are damaged by these metals even at low concentrations for the various toxic metals and can affect human population in a large scale. Lead is particularly harmful to humans, plants and animals.

The lead poisoning can cause hypertension, nephritis, abdominal pain, constipation, cramps, nausea, vomiting, behavioral changes, learning disabilities, reading problems, development defects and language difficulties [9, 10]. As mentioned, major lead pollution has been through the manufacture of storage batteries, painting pigments, ammunition, solder, plumbing fixtures, automobiles, cable coverings and radioactivity shields. Lead ions concentrations approach 200–500mg L⁻¹ in the industrial waste waters. This value is very high in relation to the water quality standards and it should be reduced to a range of 0.1–0.05mgL⁻¹.

There are several methods for the separation and estimations of Pb ions. Among these methods, sorption using functionalized solid supports has proved to be one

of the most feasible, simple, selective, cost-effective, ease of operation and high efficient process for the removal of heavy metals from polluted sources.

Therefore, an investigation was undertaken to determine the level of Pb (II) ion pollution in an adjoining industrial area of Siliguri township (West Bengal). In this industrial area several factories including lead battery factories are housed. Hence there is a possibility of Pb (II) hazard in the drinking water and the agricultural soils of the locality. We, therefore, have undertaken an investigation to study the level of Pb (II) pollution in the water collected from the drains of the industrial estate through which the discharges from all the factories flow.

5.6 Methodology:

All the required chemicals used were procured from commercial sources as mentioned earlier. The names of the instruments and their manufactures are mentioned in Chapter III.

5.6.1 Sampling :

To investigate Pb metal ion contaminations, water samples were collected in the month of May 2010 from three drains (5 liter from each location) where effluents were discharged from lead cells / battery and lead metal and other industries located at the Dabgram Industrial Growth Centre. Dist. Darjeeling, West Bengal, India.

Column operation :

Collected water samples (1 - 3) were filtered twice by using whatman filter paper (No. 42) and 10ml each of filtered sample 1 and sample 2 were diluted to 100ml by distilled water. These two samples (both of sample 1 and sample 2) were then passed through two separate columns of compound 7 which was pre-adjusted to pH- 6. The sorbed metal ions were eluted by 1M HNO₃ from the two columns. In another experiment 5ml of collected samples (sample 3) was diluted to 100ml by distilled water and then the total volume was passed through the column of compound 8, the column was adjusted to pH- 6. After washing with distilled water the sorbed metal ion was eluted by 2M HCl. Similarly 100ml diluted sample 3 was passed through another column of compound 6 (pH adjusted to 6). The column was then washed with distilled water and the sorbed metal ions was desorbed by 2M HNO₃. All the eluted metal ion solutions were collected into four separate 50ml volumetric flasks.

Lead ion concentration was measured by the standard AAS method. The results are presented in the Table5.4.1

Table 5.6. I Concentration of Pb(II) ions in industrial water

Sample No. for Three locations	Resin Compound Studied	Lead Metal ion found $\mu\text{g L}^{-1}$
1	7	286.5
2	7	293.5
3	8	566.0
3	6	585.5

Figure 5.6. J Main Entrance of Dabgram Industrial Growth Centre



5.7 Results and discussion

The results showed that the Pb(II) metal concentrations are much higher in the discharged water. The selected compounds worked well for the study. There is a trend of increasing level of water contamination which can be accumulated in the soil or water sources where it will be finally discharged.

Soil analysis of Khoribari and Haldibari Block area by Salicylaldehyde thiosemicarbazone resin, Pyridine carboxaldehyde thiosemicarbazone resin, 2-mercapto isothiocyanate resin and 2, 4, 6- tri hydroxy benzoic acid resin.

5.8 Introduction :

Metals like Cu, Zn, Fe, Co, Mo, Mn are essential components for normal growth of plant and fertility of soil. However, excess amount of these metals if accumulated in the soil can lead to a number of problems, such as soil contamination, surface and ground water contaminations etc. [6, 7]. Khoribari is a small block of Siliguri Mahakuma Parishad, Dist. Darjeeling, West Bengal [Figure 5.8.1]. This area cultivates many cash crops, vegetables like bringal, cauliflower, cabbages, cucumber, chili etc. for many years. The soil is very fertile not only for vegetable production but also for producing other agricultural crops.

Haldibari is a small area of Coochbehar District, West Bengal [Figure 5.8.1] and it is situated near Bangladesh Border area in the east.

The vegetables which are produced from this area are distributed throughout the northern part of West Bengal. The unique fertile character of the soil allows the production of many important crops throughout the year.

Besides natural cycle, metal concentrations are increasing many folds in the agricultural land for the indiscriminant use of chemical fertilizers, pesticides and insecticides. So it is an important area to investigate - the level of metal concentrations of the cultivable agriculture lands specially for preservation of soil fertility.

We under took a study to investigate the level of concentrations of Cu(II),Zn(II) and Fe(III) in the soils of these fertile areas of the North Bengal to enable to understand the conditions of soil fertility. We report here in the results of our studies.

5.9 Methodology

All the required chemicals used were procured from commercial sources as mentioned earlier. The names of the instruments and their manufactures are mentioned in Chapter III.

5.9.1 Soil Sampling and Digestion :

Top soil samples (from 0 – 10 cm depth) were collected from two spots of Khoribari and Haldibari area each during the month of October 2010.

- 1) The soil samples collected from paddy field of Haldibari was marked SH-1 and from cucumber field was marked as SH-2.
- 2) The soil samples collected from Khoribari were marked as follows:

SK – 1 Cauliflower cultivated land and

SK – 2 Cucumber cultivated land

The cultivated land for paddy and cucumber are shown in the figure [Figure 5.6.2]. After the collection of the samples foreign detritus and lithogenic shells were removed by hand picking. Then all the samples were air dried. 1gm each of soil samples was placed in four 50ml conical flasks. To this 10ml (10 : 1 HClO₄ : H₂SO₄) acid was added and heated on an oil bath (200-210⁰C) until the HClO₄ was evaporated off. All the mixtures were heated for 1 hour. The mixture were then cooled down - diluted and filtered. The filtrates were transferred to 100ml volumetric flasks for analysis of the metal ions (stock solutions), the white residues left for each of the samples was transferred and rejected.

Column operation

10ml of metal solution from the stock solutions of SK – I was passed through the column of compound 6 (pH – 6). The column washed by distilled water and the sorbed metal ions were desorbed by 15ml 1M HCl.

In the another experiment 10ml metal solution from the stock solution of SK – 2 was passed through the column of compound 1 adjusted to pH – 6. The sorbed metal ions were desorbed by 15ml 1M HCl.

Further 10ml digested soil from the stock solution of SH -1 was passed through the column of compound 3 (pH – 4) – the sorbed metal ion was desorbed by 15ml 2M HCl.

Finally 10ml from the stock solution of the digested soil sample SH – 2 was passed through the column of compound 4 (pH adjusted to 6). After washing with distilled water, the sorbed metal ion was desorbed with 15ml 2M HCl. The concentrations of all the eluted metal ions of the two soil samples were measured by following standard AAS method. The results are tabulated in Table 5.1.

Table 5.1 Result of Soil analysis

	Place	Sample	Compound	Metal	(μg)g ⁻¹ of soil sorption
1	Khoribari	SK – 1	6	Cu	28.00
				Zn	99.50
				Fe	1690.0
		Sk – 2	1	Cu	18.52
				Zn	60.50
				Fe	1675.00
2	Haldibari	SH – 3	3	Cu	20.50
				Zn	65.50
				Fe	1570.0
		SH – 4	4	Cu	16.50
				Zn	50.50
				Fe	1605.00

Figure 5.6.1 The Map of West Bengal

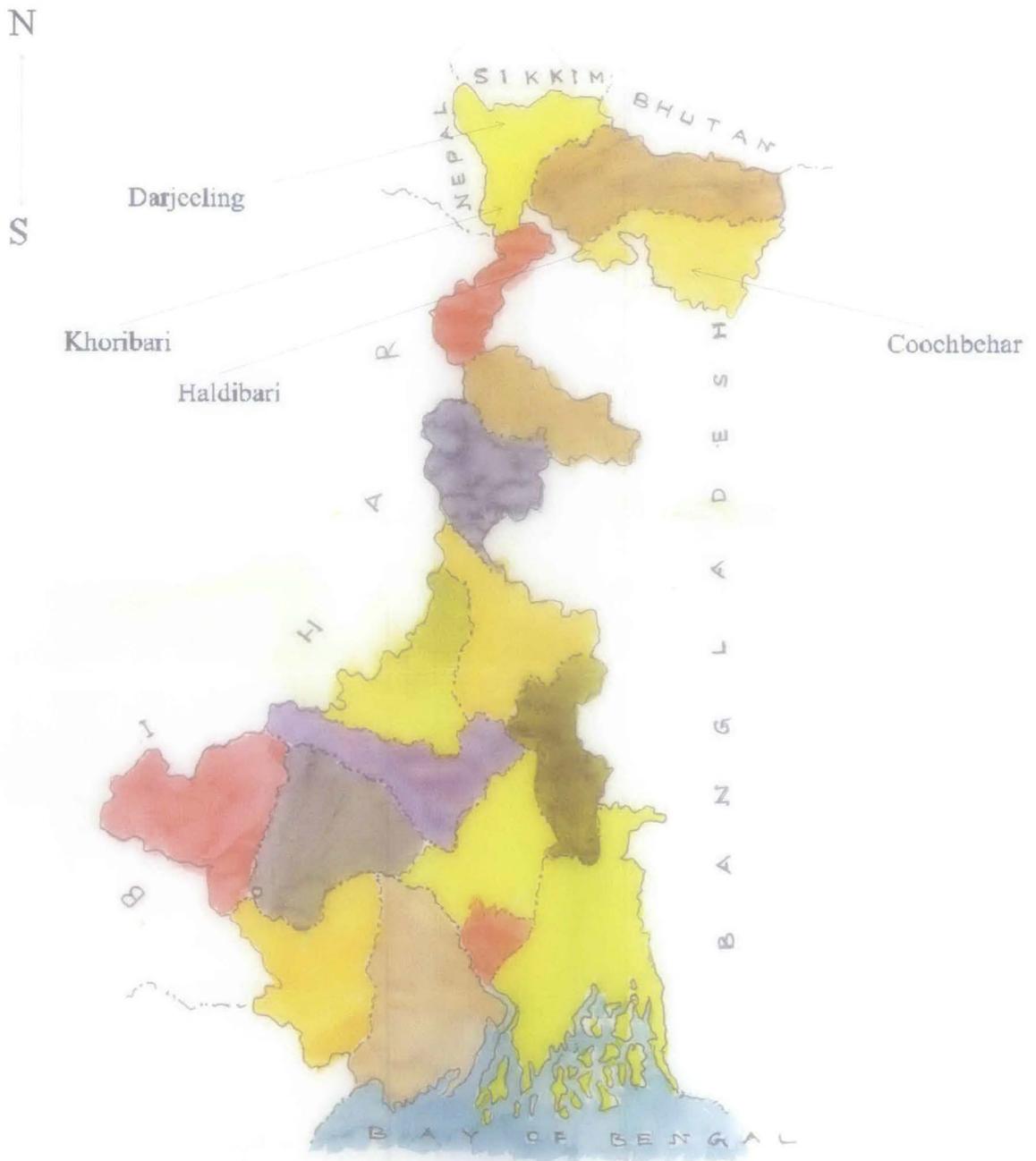


Figure 5.2 Cultivated land of Cucumber and Paddy land of Khoribari and Haldibari



5.10 **Results and discussion**

It is evident from the estimation and the obtained results that none of the metal ions under study are present in these soils in high concentrations. On the contrary the iron concentration is low than usual [6]. However, it is helpful if the concentrations of these metal ions in the soils be monitored at a regular interval of times.

5.11 **Conclusion**

A selection of the synthesized compounds from **1-9** may be effectively utilised to estimate the concentration levels of various metal ions in industrial waste water, river water and agricultural soils. The monitoring of such metal concentration should be an essential part which will ensure a safe and disease free environment to sustain.

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Publications and Seminar

1. G. C. Dey and A. Roy, Synthesis and Application of Functionalised Resins in the separation of Heavy Metal ions, Chemistry in North Bengal (Annual Journal) 1, (2007) 1.
2. G. C. Dey and A. Roy, Synthesis and Characterisation and application of a series of Functionalised Resins for separation and Pre-concentration of Cu(II), Zn(II), Co(II), Ni(II), Pb(II), Cd(II), Mn(II) and Hg(II) metal ions, Chemistry in North Bengal (Annual Journal). 2, (2008) 1.
3. G. C. Dey and A. Roy, Application of Functionalised Resins for the separation and Pre-concentration of Cu(II), Zn(II), Pb(II), Cd(II), and Cr(III) metal ions, Chemistry in North Bengal (Annual Journal). 3 (2009) 1.
4. Seminar : Oral presentation :
 - (i) West Bengal State Science and Technology Congress – 2008 at Bengal Engineering and Science University. “The Application of Functionalised Resins in Heavy Metal Separations.”
 - (ii) West Bengal State Science and Technology Congress – 2010 at West Bengal University of Animal and Fishery Sciences, Kolkata. “Application of Functionalised Resins in Heavy Metal Separations.”
 - (iii) West Bengal State Science and Technology Congress – 2011 at Ramkrishana Mission Residential College, Narendrapur, Kolkata. “Application of Functionalised Resins in the Pre-concentration and Separation of Heavy Metal ions discharged in the River Mahananda at Siliguri from paints and colours of immersed Durga idols.”
5. G. C. Dey and A. Roy, Synthesis and characterization of Merrifield Resins Functionalized by N, S, O donor ligands – its application for the separation and Pre-concentration of Cu(II), Zn(II), Pb(II), Cd(II), and Cr(III) metal ions. Paper communicated to Journal of Hazardous Materials.

