

EFFECT OF TRACE METALS DISTRIBUTION ON SOME GREEN PLANTS AND GROUND WATER/ SOIL COLUMNS IN ARIYALUR CEMENT INDUSTRIAL ZONES

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ABSTRACT

To evaluate the impact of the cement's dust and waste released by the cement industries and find the influences of cement waste on the ground water, surface and bottom soil, and two different plant samples of Ariyalur cement industrial zones (V.Kaikatti - S1, Keelapazhur - S2 and Kallankuruchi - S3) with in 1.5 km approximately. For control study, the samples were collected from Jamal Mohammed College (C1), Tiruchirappalli, Tamil Nadu. The physiochemical (pH, EC, TDC, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , CO_2^- , HCO^- , Cl^- and SO_4^{2-}) and trace metals (Cd, Cr, Cu, Fe, Ni, Pb and Zn) were analyzed from the water and soil samples, and the phytochemical (total chlorophyll, Chlorophyll a and b, total carotenoids, free amino acids, soluble sugars, phenols and lipids) and trace metals were studied from plant samples. The ranges of EC in surface sediment and bottom sediment of study area were 449.4 – 828.6 $\mu\text{s}/\text{cm}$ and 343.3 – 469.8 $\mu\text{s}/\text{cm}$, while TDS ranges were 283.0

– 522.0 mg/L and 216.3 – 296.0 mg/L, respectively which might be due to waste water effluents of cement industry. The average Cd concentration in water and sediment was 0.15 mg l⁻¹ and 0.73 mg kg⁻¹, respectively. The higher concentrations of phytochemical parameters were observed in control site plants than study site plants. Metal contents of plant samples Cd, Cr, Cu, Fe, Ni, Pb and Zn concentrations are between BDL – 0.06, BDL – BDL, BDL – 0.22, 0.04 – 0.54, BDL – BDL, BDL – 0.05 and 0.06 – 0.52 mg kg⁻¹, respectively. But in control site, the Cd, Cr, Cu, Fe, Ni, Pb and Zn concentrations were BDL – BDL, BDL – BDL, BDL – 0.04, 0.04 – 0.06, BDL – BDL, BDL – BDL and 0.06 – 0.10 mg kg⁻¹, respectively. Most of the parameters concentrations were higher in the study area (2 – 20

fold) than the control site samples. The most contaminated site area found within the 0 to 500 m of the cement factory. The concentrations of phytochemical constituents were higher in control site than study area which indicate that the cement dust/ waste were strongly affects the growth and productivity of plants.

KEYWORDS: Cement industrial zone, Heavy metal, *Croton bonplandianum*, Physiochemical parameters.

INTRODUCTION

Rapid urbanization and industrialization releases enormous volumes of wastewater, which is increasingly utilized as a valuable resource for irrigation in urban and peri-urban agriculture. It drives significant economic activity, supports countless livelihoods particularly those of poor farmers, and substantially changes the water quality of natural water bodies. Soil pollution is developed due to constant fall of cement dust, resulted in the formation of colloidal gels of calcium silicate and calcium aluminate. The cement dust, produced by cement manufacturing units is considered one of the most hazardous pollutants which affect the surrounding environment. These particles can enter into soil as dry, humid or occult deposits and can undermine its physicochemical properties. Wastewater may also contain various heavy metals including Zn, Cu, Pb, Mn, Ni, Cr, Cd, depending upon the type of activities it is associated with. Continuous irrigation of agricultural land with sewage and industrial wastewater may cause heavy metal accumulation in the soil and vegetables (Sharma et al., 2007).

The environmental pollution as a result of cement industry could be defined as an undesirable process that is responsible to pollute water, air and land through its various activities, right from the mining activity of the raw material (limestone, dolomite etc.) to its crushing, grinding and other associated processes in cement plant. Plant intake trace metals from the environment through air, water and food. Excessive content of heavy metals in plants can have a negative influence on their development. In the contaminated areas, plants produced adaptive and defensive mechanisms that involve precipitation of excess metal in crystalline form or salt deposition on the tips of the leaves. The effective can be explained by the improper size and form of plants in comparison with those grown in uncontaminated areas. Since most of plant roots are located in the soil, they can play an important role in metal removal via filtration, adsorption and cation exchange, and through plant-induced chemical changes in the rhizosphere (Wright and Otte, 1999). Especially, the role of cement pollutants

causing injury to plants either by direct toxic effect or modifying the host physiology and biochemical nature rendering it more susceptible to infection (Gupta and Mishra, 1994).

Some trace metals are essential in plant nutrition, but plants growing in a polluted environment can accumulate trace elements at high concentrations, causing a serious risk to human health (Vousta *et al.* 1996). The main sources of trace metals to plants are the air and soil from which metals are taken up by the root or foliage. The uptake of metal concentration by roots depends on speciation of metal and soil characteristics and type of plant species *etc.* Consequently, metal mobility and plant availability are very important when assessing the effect of soil contamination on plant metal uptake, as well as translocation and toxicity or ultra-structural alterations (Chandra Sekhar *et al.*, 2001). The consequence of trace metals in foods such as vegetables and tubers have been a considerable interest because of their toxicity effect which are important in human beings (Asaolu, 1995).

Metals-accumulating plants are directly or indirectly responsible for much of the dietary uptake of toxic heavy metals by humans and other animals. While some heavy metals are essential, excessive accumulation in living organisms is toxic. All heavy metals at high concentrations have strong toxic effects and regarded as environmental pollutants. Intake of heavy metals through the food chain by human populations has been widely reported throughout the world (Muchuweti *et al.*, 2006). The non-biodegradable and persistent nature, heavy metals are accumulated in vital organs in the human body such as the kidneys, bones and liver and are associated with numerous serious health disorders (Duruibe *et al.*, 2007). Individual metals exhibit specific signs of their toxicity. Lead, As, Hg, Zn, Cu and Al poisoning have been implicated with gastrointestinal (GI) disorders, diarrhoea, stomatitis, tremor, hemoglobinuria causing a rust-red colour to stool, ataxia, paralysis, vomiting and convulsion, depression, and pneumonia. The nature of effects can be toxic (acute, chronic or sub-chronic), neurotoxic, carcinogenic, mutagenic or teratogenic (European Union, 2002).

The overall objectives of this research were: 1) To study the concentrations of physiochemical of parameters of the surface and bottom soil, and ground water samples of three different cement industrial zone of Ariyalur district; 2) To assess the phytochemical properties of two different plants in the three contaminated sites; 3) To determine the concentrations of seven different trace metals in two different plant biomass growing on a contaminated site. Information obtained from this study should provide insight for using

native plants to remediate metal contaminated sites and also the impacts of cement factory on the ecosystems.

MATERIALS AND METHODS

Sampling and processing

In Premonsoon (June - August) 2014, surface (0-5 cm)/ bottom (10 – 15 cm) soil and water samples from three different areas were collected at cement industrial zone of Ariyalur district. The sampling sites of V.Kaikatti (S1), Keelapazhur (S2) and Kallankuruchi (Kaliyaperumal kovil) (S3) were approximately 0-500 m, 500-1000 m and 1000-1500 m away from the cement industry, respectively (Figure 1). For control study, the soil and water samples were collected from Jamal Mohammed College (JMC), Tiruchirappalli (C1 = Control site - non-industrial area), Tamil Nadu. At each location, a ground water and two soil samples (soil depth: surface soil = 0-5 cm; bottom soil = 10-15 cm) were collected by 2,500 mL sterile container and sterile spatula, respectively. The soil samples were stored in sterile plastic bags. Physicochemical parameters i.e., pH, electrical conductivity (EC) and total dissolved solids (TDS) were measured using field kit (Thermo Orion 5-Star pH Multi-Meter) (Vignesh 2012a; 2012b) on the site and other parameters were measured in the laboratory using the standard procedure (Vignesh *et al.*, 2013; 2014). All samples were kept in iceboxes and processed within 12 h of collection. For heavy metal analysis, one liter of ground water sample was acidified immediately with concentrated nitric acid (HNO₃) and was filtered with 0.45 µm nitrocellulose filter paper by using vacuum filtration unit.

The common and frequently available plants such as *Croton bonplandianum* and *Cassia auriculata* were collected from the three different locations (wide reference above) of Ariyalur district and the control site is JMC, Tiruchirappalli. The leaves were carefully removed and washed with sterile distilled water to remove the dust particles. About 1g of leaves were cut into small pieces in a mortar ground with a pinch of quartz sand and a total of 10 mL of absolute acetone. Initially, add only a small amount of acetone to begin the grinding process. It is much easier to grind the leaves if the extract is a pasty consistency. Add more solvent in small increments while continuing to grind the leaves. For some species may need to add more than the suggested 10 mL of acetone. Pour the extract into a 15 mL centrifuge tube and centrifuge in the bench top centrifuge at 5000 rpm for 3 to 5 min. Remove the extract to a 10mL graduated cylinder using a Pasteur pipette. Transfer an aliquot of the clear leaf extract (supernatant) with a pipette to a 1-cm-pathlength cuvette and take absorbance

readings against a solvent blank in a UV-VIS spectrophotometer at 662, 645, 470, 435 and 415 nm wavelength to determine the concentrations of photosynthetic pigments like chlorophyll-a, chlorophyll-b and carotenoids. This extract was also used to quantify the other phytochemical parameters.

Trace metal analysis

Water samples were filtered by Whatman No.1 filter paper and were used for analysis. Both soil samples were air-dried and gently crushed and sieved through a 2 mm sieve and stored for further analysis. The concentrations of soluble cations and anions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , CO_2^- , HCO^- , Cl^- and SO_4^{2-}) were determined according to the method described by APHA (1998). The total concentrations of trace metals such as Cd, Cr, Cu, Fe, Ni, Pb and Zn were analyzed from the water, soil and plant samples. The 1 g of soil and plant samples was treated with aqua-regia mixture (hydrochloric acid + nitric acid) in Teflon bomb and was incubated at 140 °C for 2-3 days. After incubation, the reaction mixture was filtered with nitrocellulose (0.45 μm) filter paper by Millipore vacuum filtration unit. The water samples were treated with APDC + MIBK solvent and were used for trace metal analysis. The extraction of the studied metals in the solutions was determined by the atomic absorption spectroscopy (AAS), GBC SensAA, Australia.

Quality control and data analyses

Due care was taken to avoid metal contamination in the process of sampling, extracting and analysis. Before analysis, the devices were rinsed with acidified water (10% HNO_3) and weighted to dissolve metals. Also, all equipments and containers were soaked in 10% HNO_3 for 24 h then rinsed thoroughly in de-ionized water before use. Moreover, quality control was assured by performing duplicate analyses on all samples and by using reagent blanks and standards. Also the values of the studying metals below the detection limits of the atomic absorption spectroscopy (AAS), GBC SensAA were refused.

RESULT AND DISCUSSION

People on globe are under tremendous threat due to undesired changes in the physical, chemical and biological characteristics of air, water and soil. These are related to animal and plants and finally affecting on it. Industrial development results in the generation of industrial effluents, and if untreated results in water, sediment and soil pollution. In ground water samples, the concentration of pH in S1, S2 and S3 were 7.2, 6.9 and 6.8 respectively. But in surface sediment, the concentration of pH in S1, S2 and S3 were 7.6, 7.2 and 7.5, and

similarly the concentration of bottom sediment is 7.3, 7.0 and 7.2 respectively (Figure 2). The pH of the water, surface and bottom soil in the control site were 6.7, 7.5 and 7.4, respectively. Water and soil pH is important because it influences the availability and plant uptake of micronutrients including heavy metals. In the ground water, the EC ranged from 246.6 – 327.2 $\mu\text{S}/\text{cm}$ while the TDS concentrations ranged from 155.5 – 206.1 mg/L during the study.

The ranges of EC in surface sediment and bottom sediment of study area were 449.4 – 828.6 $\mu\text{S}/\text{cm}$ and 343.3 – 469.8 $\mu\text{S}/\text{cm}$, while TDS ranges were 283.0 – 522.0 mg/L and 216.3 – 296.0 mg/L, respectively which might be due to waste water effluents of cement industry. But in control site, the EC and TDS ranges were 159.0 $\mu\text{S}/\text{cm}$ – 100.2 – 167.3, respectively. The range of Cl concentrations in water, surface and bottom soil samples were 14.7 – 17.7 mg/L, 35.5 – 97.4 mg/g and 17.7 – 45.2, respectively. But in the Na concentrations at water, surface and bottom soil samples were 3 – 3.2 mg/L, 28 – 89.2 and 11.0 – 35.3 mg/g, respectively. In the ground water, the Ca ranged from 19.1 – 22.0 mg/L while the Mg concentrations ranged from 3.8 – 6.0 mg/L during the study. The ranges of Ca in surface sediment and bottom sediment of study area were 16.0 – 21.0 mg/kg and 11.0 – 19.1 mg/g, while Mg ranges were 2.4 – 16.2 mg/kg and 2.3 – 9.4 mg/kg, respectively. In water, the concentrations of SO_4 , N- NO_2 and O- PO_4 ranges were 70.7 – 126.0, 1.9 – 2.1 and 2.8 – 3.1, respectively. In sediment, the concentrations of K, HCO_3 and H_4SiO_4 ranges were 5 – 22.1, 24.4 – 179.3 and 3.6 – 18.8 mg/kg, respectively. The concentrations of physiochemical parameters were high (2-10 fold) in Ariyalur industrial zone than in control site.

Having mainly excessive amounts of heavy metals such as Pb, Cr and Fe, as well as heavy metals from industrial processes are of special concern because they produce water or chronic poisoning in animals and plants. In water, concentration of Zn was found in the range from 0.26 – 0.74 mg l^{-1} and its minimum concentration was detected in S3W1 and the maximum concentration was in S1W1. For soil samples, Pb concentration ranged from 0.18 – 1.36 mg kg^{-1} . Unfortunately, the nil value of trace metals was not observed in any sampling sites as well as both the water and soil samples. The concentration of Fe in water, surface sediment and bottom sediment ranged from 486.0 – 930.0 mg l^{-1} , 842.0 – 1548.0 mg kg^{-1} and 618.0 – 1058 mg kg^{-1} , respectively. The Cu concentrations of water and sediment ranged from 0.32 – 0.72 mg l^{-1} and 0.36 – 2.56 mg kg^{-1} , respectively. The average Cr concentration in water and sediment was 0.045 mg l^{-1} and 0.20 mg kg^{-1} , respectively. The average Cd concentration in

water and sediment was 0.15 mg l^{-1} and 0.73 mg kg^{-1} , respectively. In water, Ni concentrations were in the range of $0.04 - 0.14 \text{ mg l}^{-1}$ with an average of 0.09 mg l^{-1} while in sediment average was 0.31 mg kg^{-1} (Figure 3). Heavy metals and chemicals are a main group of soil pollutants and their contamination in environment affects all ecosystem components (White and Claxton, 2004). With the exception of iron, all heavy metals above a concentration of 0.1% in the soil become toxic to plants and therefore change the community structure of plants in a polluted habitat. However, each plant species has a specific threshold value for each heavy metal where it exerts toxicity. When close to rivers, the heavy metals are gradually washed off leading to the diminution of the heavy metal vegetation with special concern about the risk of losing endangered plants (Becker and Dierschke 2008; Lucassen *et al.* 2010).

The higher concentrations of phytochemical parameters were observed in control site plants than study site plants (Figure 4). The amount of heavy metals taken up by a plant is dependent on the concentration of heavy metals in the polluted soil. In most plants, heavy metals are predominantly accumulated in roots. The shoot/root ratio is generally below unity in most plants but not in metallophytes. In some heavy metal plants, the concentration of heavy metals in shoots and leaves can be particularly high and the partitioning of heavy metals between shoots and roots differs from one metallophyte to the next and with each individual heavy metal (Kramer, 2010). Metals in contaminated sites may influence the plant growth, which are able to accumulate the high concentrations of metals. The metals can accumulate in the roots of plants due to the direct water and soil contact. But the metal deposition on the upper ground level of the plants were water transportation inside the plants and air pollution. The concentrations of metals in the plant samples analyzed are reported in Figure 5. Metal contents of plant samples Cd, Cr, Cu, Fe, Ni, Pb and Zn concentrations are between BDL – 0.06, BDL – BDL, BDL – 0.22, $0.04 - 0.54$, BDL – BDL, BDL – 0.05 and $0.06 - 0.52 \text{ mg kg}^{-1}$, respectively. But in control site, the Cd, Cr, Cu, Fe, Ni, Pb and Zn concentrations were BDL – BDL, BDL – BDL, BDL – 0.04, $0.04 - 0.06$, BDL – BDL, BDL – BDL and $0.06 - 0.10 \text{ mg kg}^{-1}$, respectively. Metals such as Cu, Zn, Mn and Fe are essential for plant growth, other metals do not have any significant role in the plant physiology (Gupta and Mishra, 1994). The uptake of these heavy metals by plants is an avenue of their entry into the human food chain with harmful effects on health (Muchuweti *et al.*, 2006).

The degree of tolerance of plants to heavy metals was divided into the three categories: hypo-tolerance, basal tolerance, and hyper-tolerance (Ernst et al., 2008). A hyperaccumulator may be defined by the threshold value which is approximately a 10 times higher concentration of a heavy metal in the aerial parts compared to the content in a non-hyperaccumulator growing on the same polluted habitat and approximately 400 taxa worldwide are hyperaccumulators (Bert et al., 2002). The metal concentrations in study area samples were 2 – 20 fold higher than the control site samples. As per the above category, the study and control site were referred as hyper and hypo tolerance sites. The presence and consecutive addition of these metals would reduce the plant productivity and soil fertility and ground water quality.

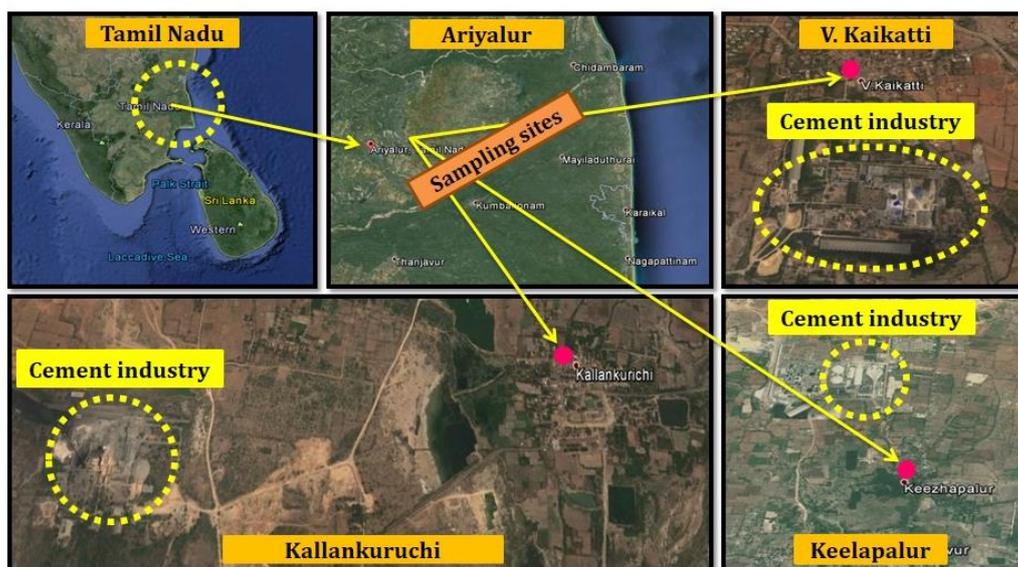


Figure 1. Sampling site of the study area

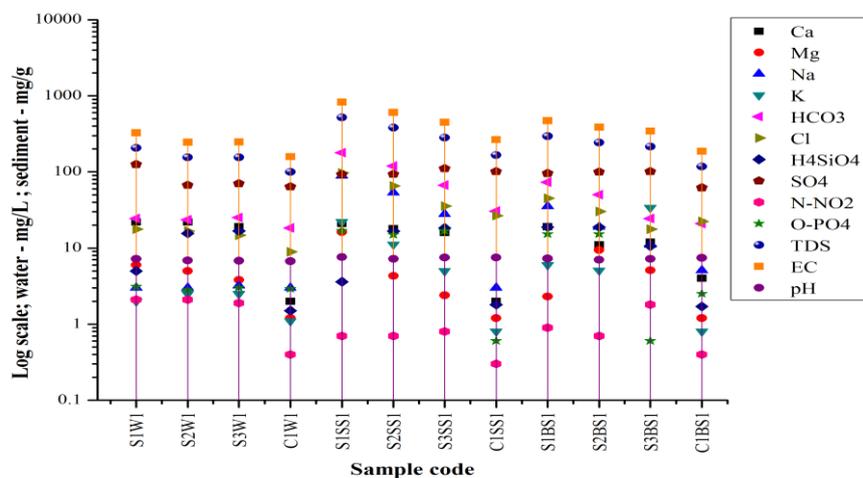


Figure 2. Concentration of physiochemical parameters in water and soil samples of three different stations during premonsoon season.

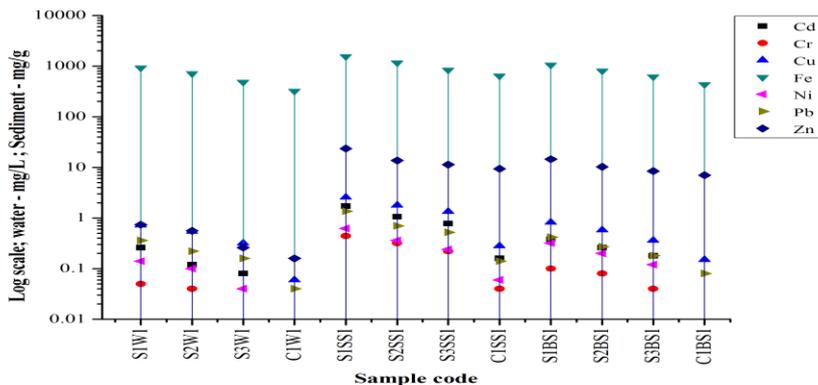


Figure 3: Concentration of Trace metals in water and soil samples of three different stations during premonsoon season.

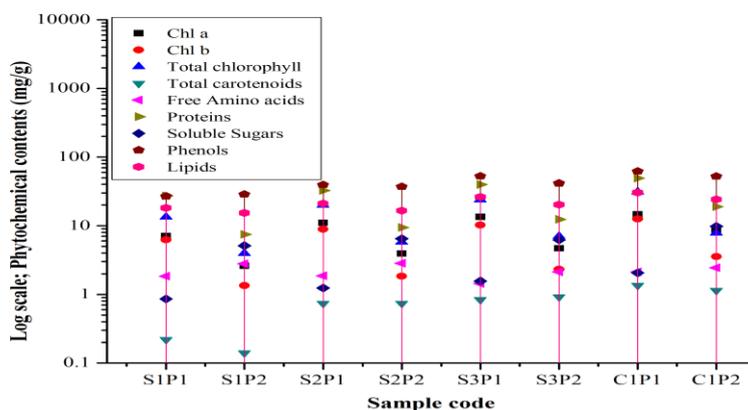


Figure 4. Concentration of biochemical content in two different plant samples of three different stations during premonsoon season.

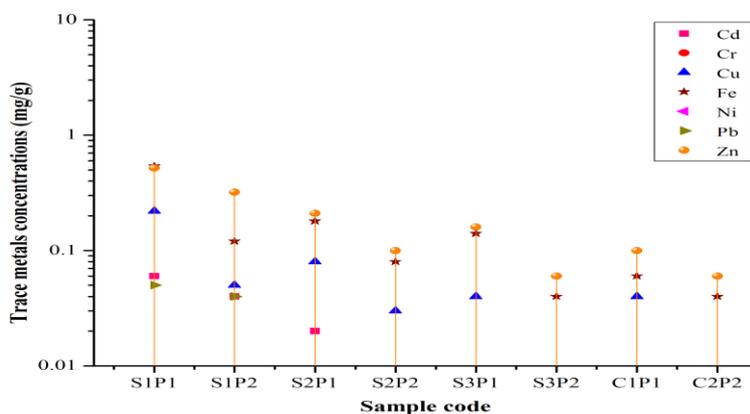


Figure 5. Concentration of trace metals in two different plant samples of three different stations during premonsoon season

CONCLUSION

The main objective of this study is to find the trace metal concentrations in three different samples (water, surface and bottom soil and 2 plants) of three different regions of cement industrial zones in Ariyalur district. The physiochemical parameters were high in surface soil than bottom soil and ground water. Interestingly, the phytoconstituents results indicated that the control sites plants got higher amount of chl a, b, c, amino acid, protein and etc. than Ariyalur site plants due to the accumulation of heavy metals. The cement industries released lot of waste materials to the land side without any sort of treatment leads to cause the serious infections to the human and indirectly it accumulates continuously in water/ soil and plants. The results of pollutions reveal the order of samples are Sediment > water > plant. The necessary monitoring is need to be maintain the environment in spick and span level.

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