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A STUDY ON THE PHYSICO-CHEMICAL PROPERTIES AND HEAVY METAL CONTENT IN CRUDE OIL CONTAMINATED SOIL OF DULIAJAN, ASSAM, INDIA

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ABSTRACT
The redevelopment of contaminated land is becoming increasingly necessary under sustainable-development legislation. Metal migration from the soil to ground water presents an environmental risk that depends on the physicochemical properties of the contaminated soils. The crude oil contaminated soils near oil collecting stations were assessed for heavy metal content. Soil samples were collected from crude oil contaminated areas over a period of six months and heavy metal content was analyzed and compared with standard permissible limit of world health organization (WHO). The average heavy metal concentrations in the soil were found to be high in case of Cr, Pb, Cd, Hg, Fe, Se and As. Some metals *e.g.* Zn, Cu, Ni and Mn were found to be within the prescribed WHO limits. Remediation of these contaminated sites is now becoming necessary in order to rehabilitate the environment.

KEY WORDS: Contaminated soil, multiple pollutants, environment

INTRODUCTION
Anthropogenic sources of hydrocarbons and heavy metals are polluting the environment. Heavy metal pollution from the biosphere has accelerated rapidly since the onset of the industrial revolution and heavy metal toxicity poses major environmental problems (Gisbert *et al*., 2003). Drilling and mining activities generate large amounts of waste rocks and tailings, which are deposited on the land surface. These wastes are often very unstable and become source of pollution of the air, soil and water. This may eventually lead to a loss of biodiversity, amenity, and economic wealth (Bradshaw, 1993) and human health. The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury and arsenic. These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the WHO (Järup 2003). When the elements necessary for human beings, flora and the environment exceed a certain level, they may have toxic effects. There is a potential threat when these contaminants enter in to the food chain through bioaccumulation. It is, therefore, very important to assess the extent of heavy metal pollution in contaminated areas, and also to remove heavy metal from the contaminated land (Wong, 2003) and an understanding of reactive transport in porous media is necessary to predict the fate of pollutants in soils and aquifers (Hu *et al*., 2007). The aim of present study is an attempt to determine the level of chromium, zinc, lead, copper, cadmium, nickel, mercury, iron, manganese, selenium and arsenic in certain crude oil contaminated areas of Duliajan under the district of Dibrugarh, Assam, India, to generate reliable database for safe future use and to help in implementing remedial policies to improve environmental conditions.

MATERIALS AND METHODS
Duliajan (22° 21′ 21.64″ N 95°18′ 22.68″ E), one of the oldest oil fields of Assam is situated in between East and West block of upper Buridihing Reserve Forest. Exploration, refining, and transportations are going on there. Varieties of flora and fauna grow there balancing the toxic effects of crude oil, heavy metals and other components of nature. The area experiences climate with a mean annual rainfall of 1800mm, mean relative humidity of 78% and minimum temperature of 6^{O}C and maximum temperature of 38^{O}C (http:in.weather/India/ assam/ duliajan. html).
Field surveys were conducted from June 2009 to June 2010. Five contaminated sites were surveyed and soil samples were collected (by random sampling technique) in sterile polythene bags and carried to the laboratory. At least three replicates were collected from each sampling site at depths 0-15, 15-30 and 30-45cm. Soils were air dried, grinded and sieved through a sieve (2mm mesh size). Analysis of physico-chemical characteristics were done according to American Public Health Association (APHA, 1998). For the analysis of chromium, zinc, lead, copper, cadmium, nickel, mercury, iron, manganese, selenium and arsenic 1g of from each soil sample was acid digested (4:2:1; H_2SO_4: HCl: HNO_3) and the readings were taken in atomic absorption spectrometer (Thermofisher Scientific iCE 3000 series). Arsenic, selenium and mercury were analysed with VP 100 vapour

system (Thermo Scientific). Three replicated were analysed from each sample.

RESULTS AND DISCUSSION

The result of physico-chemical analysis of crude oil contaminated soil is shown in table 1. The soil was acidic. pH range during the course of the experiment was 4.4 to 4.8. Hydrocarbon contaminated soil usually have a high carbon content. The organic carbon estimated during the experimental period was very high (2.5-2.8%) which might be due to contamination of crude oil. The range of total nitrogen was 0.05 to 0.08%. The range of phosphorus was 5.4 to 5.6ppm. The soil showed moderate range of Na (7-8.5ppm) and K (15-18ppm). Macronutrients such as Ca and Mg were found to be between 59-68ppm and 14-16ppm respectively. It was observed that the moisture content of the soil was between 2.3 to 2.6% during the experimental period. Water holding capacity of soil ranged from 5 to 5.5% during the study period. The conductivity of soil was 230 to 245 µS. The texture is sandy-loam.

TABLE 1. Physico-chemical analysis of crude oil contaminated soil during summer, monsoon and winter season

Parameters	Values		
	Summer	Monsoon	Winter
*p*H	4.8 ± 0.5	4.4 ± 0. 4	4.7 ± 0.06
Organic Carbon [%wt]	2.5 ± 0.45	2.8 ± 0.5	2.7 ± 0.3
Total N [%wt]	0.05 ± 0.003	0.08 ± 0.004	0.06 ± 0.003
Total P [ppm]	5.6 ± 0.08	5.5 ± 0.08	5.4 ± 0.05
K [ppm]	17 ± 1.5	15 ± 1.5	18 ± 1.4
Na [ppm]	8.5 ± 0.65	7 ± 0.5	8 ± 1
Ca [ppm]	68 ± 3.5	59 ± 4	65 ± 5
Mg [ppm]	14 ± 1.8	16 ± 2	16 ± 1.5
Moisture Content (%)	2.5 ± 0.055	2.3 ± 0.2	2.6 ± 0.5
Water Holding Capacity (%)	5.5 ± 1	5 ± 0.8	5.5 ± 0.5
Conductivity (µS)	245 ± 3.5	230 ± 4	240 ± 5
Texture	Sandy loam		

Results represent mean ± SD of three replicates

The result of heavy metal analysis is presented in table 2. Metals such as Cr, Pb, Cd, Hg, Fe, Se and As were found beyond the permissible limit of WHO and APHA. These heavy metals cause potential threat to human health through drinking water when reach to ground water. The range of Cr is 1.2 to 1.5ppm. Exposure of too much Cr can cause serious health effects, irritations in nose and throats and skin rashes. The range of Pb found in soil during the course of experiment was 0.85 to 0.945ppm.

TABLE 2. Heavy metal analysis of crude oil contaminated soil during summer, monsoon and winter season in comparison to Maximum Permissible Limit (MPL) (WHO, APHA)

Elements	MPL (ppm)	Summer (ppm)	Monsoon (ppm)	Winter (ppm)
Chromium (Cr)	0.05	1.2 ± 0.08	1.15 ± 0.07	1.3 ± 0.04
Zinc (Zn)	15.00	7.8 ± 0.85	8.5 ± 0.75	7.5 ± 0.8
Lead (Pb)	0.05	0.9354 ± 0.05	0.85 ± 0.007	0.94 ± 0.05
Copper (Cu)	1.50	1.5 ± 0.04	1.5 ± 0.05	1.3 ± 0.02
Cadmium (Cd)	0.003	0.067 ± 0.007	0.06 ± 0.005	0.07 ± 0.006
Nickel (Ni)	0.02	0.019 ± 0.006	0.02 ± 0.003	0.02 ± 0.004
Mercury (Hg)	0.001	0.002 ± 0.001	0.002 ± 0.001	0.002 ± 0.001
Iron (Fe)	1.00	1.9 ± 0.075	1.5 ± 0.06	1.8 ± 0.05
Manganese (Mn)	0.50	0.37 ± 0.036	0.4 ± 0.005	0.45 ± 0.03
Selenium (Se)	0.01	0.02 ± 0.004	0.025 ± 0.006	0.22 ± 0.004
Arsenic (As)	0.05	0.055 ± 0.005	0.062 ± 0.003	0.08 ± 0.005

Results represent mean ± SD of three replicates

Lead above the permissible level in water can cause severe health problems among the flora and fauna in the area. The range of Cd was between 0.06 to 0.075ppm. Cadmium above the permissible limit can potentially cause nausea, vomiting, diarrhoea, muscle cramps, salivation, sensory disturbances, liver injury, convulsions, shock and renal failure along with kidney, liver, bone and blood damage from a lifetime exposure. Hg level was 0.0025ppm and that of Fe was between 1.5 to 1.95ppm. Bioaccumulation of methyl mercury causes minamata disease. Elemental Hg causes emotional changes, insomnia, neuromuscular changes, headaches etc. At higher exposure it also causes kidney effects, respiratory failure and even death. Although iron occurs naturally in groundwater, the higher concentration of iron has negative impact for human and animals. Se and As were also encountered in high concentrations. The range of Se was between 0.2 to 0.25ppm and that of As was between 0.55 to 0.8ppm respectively. Chronic exposure of Arsenic via drinking water causes various types of skin lesions such as melanosis, leucomelanosis and keratosis. Other manifestations include neurological effects, obstetric problems, high blood pressure, diabetes mellitus, diseases of the respiratory system and of blood vessels including cardiovascular and cancers typically involving the skin, lung, and bladder. The skin seems to be quite susceptible to the effects of As. Arsenic-induced skin lesions seem to be the most common and initial symptoms of arsenicosis. Some elements such as Zn, Cu, Ni and Mn were found to be within the permissible limits of WHO and APHA.

The presence of organic and inorganic contaminants in soils of Duliajan sites provides a major challenge to the redevelopment of land in line with sustainable development requirements. Bioremediation as well as phytoremediation provides a potential low-cost solution to this problem. Remediation of such soils with microorganisms and plants capable of degrading and transforming pollutants when present in soils containing multiple pollutants is the best way compared to other physical and chemical remediation technologies for long term ecological restoration of contaminated sites. In general, bioremediation as well as phytoremediation must be managed by using indigenous plants and microbes especially those surviving in the contaminated sites, instead of foreign or genetically modified species. To find out plants and microbes capable of degrading multiple pollutants in soil has also become an emerging challenge. Besides decontamination of pollutants this green technology provides erosion control and has a great aesthetic value. However, the soils of present study area must be decontaminated in order to rehabilitate environment.

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