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Original Research Paper

Effect of Dissolved Organic Carbon (DOC) on Heavy Metal Mobility in Soils

T. Sherene
Department of Soil Science and Agricultural Chemistry, Tamilnadu Agricultural University, Coimbatore-641 003, T.N., India

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ABSTRACT

Dissolved organic carbon plays an important role in both carbon cycling and chemistry of soils, through its influence on acidity, nutrient availability, metal toxicity and transport. Addition of biological waste materials such as sewage sludge, poultry and animal manures increases the amount of DOC in soils. The effect of DOC on heavy metal mobility was well recognized in this study. In organic matter rich soils, solubilization of organic matter leads to production of more amount of DOC which combines with heavy metals in soils and, thus, causes contamination to groundwater. The organic acids present in the DOC can act as chelating agents and enhance the mobilization of toxic heavy metals. In another way, it is beneficial that the toxic heavy metals are mobilized away from the root zone, thus, preventing accumulation of heavy metals in usable parts of the plants.

INTRODUCTION

Contamination of the environment has become serious in areas of intense industrial and agricultural activities, where large concentrations of heavy metals might reach the soil by atmospheric deposition, animal manure, artificial fertilizer and waste disposal (sewage sludge). The contaminated soil poses a risk to the quality of groundwater and domestic water supply. The total heavy metal content of the soil is commonly used to indicate the degree of contamination, but the heavy metal concentration in solution mostly determines the actual environmental exposure or risk. Several important soil factors, controlling the distribution of heavy metals between soil and solutes, have been identified (Sposito, 1989). Since, copper is immobile in soil, dissolved organic carbon enhances Cu mobility in soil by forming Cu-DOC complexes which ultimately affect the groundwater quality. Hence, the present work has been undertaken to study the effects of DOC on heavy metal mobility in soils.

MATERIALS AND METHODS

Extraction of DOC: Distilled water and 0.5M K_2SO_4 were used as the extractants for the extraction of DOC from the soil, manure and sludge sources. Although number of studies have used distilled water as an extractant for the measurement of DOC (Barriuso et al. 1992) in studies involving soil microbial biomass. 0.5M K_2SO_4 is used as an extractant to measure biomass carbon (Tate el al. 1988). Zhu & Alva (1993) reported that in K_2SO_4 amended soil, the DOC concentration in leachate is more, since K_2SO_4 is a strong DOC extractor.

Five soil samples differing in their organic carbon contents (Ukkadam Sewage Farm, Nanjundapuram, Sanganur Pallam, Thulukanur and Peelamedu) were used for the extraction and estimation of DOC. Ten g of sample was equilibrated with 100 mL of 0.5M K_2SO_4 in 150 mL shaking bottle. The samples were shaken in an end over end shaker for 1 hour and the solution was centrifuged at 8000 rpm for 10 minutes. The solution was filtered through Whatman No. 40 filter paper and again centrifuged at 8000 rpm for 10 minutes. The solution was stored at 4°C before analysis as per Bolan et al. (1996).

Estimation of DOC: Various methods are used in DOC estimation. The most frequently used method involves the measurement of absorption of light by the DOC using spectrophotometer. The second method involves wet oxidation of samples containing DOC and the subsequent measurement of either the CO_2 released or the amount of oxidant consumed. The third method involves dry oxidation of DOC to CO_2 at higher temperature in the presence of a stream of oxygen. The applicability of light absorption method to estimate DOC concentration is dependent on the nature of organic compounds and the presence of coloured inorganic compounds such as iron. Preliminary studies have shown that absorbance of light by DOC decreased with increasing wavelength. Absorbance at low wavelength is likely to be more sensitive indicator of DOC than the higher wavelengths. So, absorbance at 250 nm was selected to obtain a relationship between the absorbance and the concentration of DOC. The initial analysis like bulk density, pH, electrical conductivity, organic carbon, texture, CEC, $CaCO_2$, Al_2O_3, Fe_2O_3 and DTPA-heavy metals and final analysis of heavy metals in DOC extract and pH of the DOC extract were also done.

DOC-Standard preparation: Analytical grade potassium hydrogen pthalate $C_8H_5KO_4$ (2.125mg) was taken in distilled water with 30 g NaCl and the volume was made up to 1000 mL (l mL = l µg of carbon). This gives 1000 µg C. From this, various working standards were prepared.

Working carbon solution: Standard solution of 50 mL volume ranging from 1-100 µgC/L (1, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100) was prepared as given by (Ramesh & Anbu 1996). The regression equation observed was as below.

$$\text{DOC} = \frac{\text{Absorbance} - 0.21497}{0.00234}$$

Leaching study: The column experiment was carried out to study the effect of DOC on heavy metal mobility. The PVC pipes of 4.2 cm in diameter and 35 cm long were filled with 250 g of soils from study area. A muslin cloth and funnel at the bottom of the column held the soil particles in place. The columns were saturated with double distilled water to prevent air inclusion. Then from the top of the column, the DOC extract was added and the filtrate was collected in the beaker, which was kept below the funnel. About 30-45 mL of filtrate was collected and subjected to metal analysis.

RESULTS AND DISCUSSION

Effect of pH and organic carbon on DOC extraction: In soils, pH and organic carbon are considered to be the most important factors influencing the concentration of DOC. It has often been observed that an increase in pH through liming and fertilizers addition to soil increases the concentration of DOC. This was akin to the results obtained in this study (Table 2).

The pH of the Ukkadam sewage farm soils was high (8.78) that leads to higher content of DOC (164.75 mg/kg). This might be due to higher solubility of humic substances in alkaline conditions that are believed to be caused by the conversion of acidic components into ions and subsequent formation of a physical solution in aqueous solution. Similarly, the higher organic carbon in Ukkadam sewage farm soils (5.36%) represented the higher amount of DOC. This might be due to higher pH Leading to greater solubilization of organic matter.

Table 1: Initial characteristics of the soil samples.

	Soil samples	pH	EC (dS m^{-1})	CEC c moles $P^{+}kg^{-1}$	Al_2O_3 (%)	Fe_2O_3 (%)	$CaCO_3$ (%)	Bulk density Mg m^{-3}	Organic carbon (%)	Tex-ture
1	Ukkadam	8.78	1.25	37.3	14.45	1.51	14.8	0.90	5.36	sc
2	Nanj undapuram	7.62	0.65	13.6	10.11	1.05	7.3	1.30	1.50	scl
3	Sanganur Pallam	8.34	1.62	30.5	13.10	1.42	4.3	0.80	3.83	cl
4	Thulukanur	7.19	0.39	9.5	12.21	1.04	7.7	1.05	0.60	sl
5	Peelamedu	8.18	0.27	21.9	12.95	1.20	8.8	1.60	1.70	cl

Table 2: Estimation of DOC in soils.

	Soils	DOC Absorbance			DOC mg kg^{-1}	pH
		Rl	R2	Mean		
l	Ukkadam	0.5966	0.4891	0.5429	164.75	8.30
2	Nanjundapuram	0.6130	0.5881	0.6005	89.20	8.08
3	Sanganur Pallam	0.4960	0.3791	0.4376	140.14	8.09
4	Thulukanur	0.4157	0.4317	0.4237	16.44	7.04
5	Peelamedu	0.2966	0.2103	0.2535	95.12	8.78

Table 3: DTPA-heavy metals (ppm) in soil samples.

	Soils	Zn	Fe	Mn	Cu	Pb	Ni	Cd	Cr
1	Ukkadam	6.92	18.21	17.96	11.92	10.42	3.14	0.37	0.60
2	Nanjundapuram	1.33	13.05	14.17	1.77	4.98	0.81	0.03	0.93
3	Sanganur Pallam	12.76	7.18	16.87	3.76	12.11	2.91	0.04	0.31
4	Thulnkanur	6.60	43.60	27.00	4.06	3.00	0.96	0.15	0.48
5	Peelamedu	7.28	17.90	30.00	7.44	9.66	2.60	0.22	1.02

Table 4: Heavy metal content in DOC extracts of the soil samples.

	Soils	Fe	Mn	Zn	Cu	Pb	Ni	Cd	Cr
1	Ukkadam	0.6860	3.91	0.4974	1.540	6.52	1.658	0.256	-
2	Nanjundapuram	0.2600	1.37	0.2600	0.152	4.27	3.168	-	-
3	Sanganur Pallam	0.3266	2.87	0.3266	0.098	6.02	1.240	0.020	-
4	Thulukanur	1.1720	3.95	1.1720	0.074	2.32	1.368	0.001	-
5	Peelamcdu	0.2738	5.67	0.2738	0.158	5.64	3.568	0.215	-

Table 5: Heavy metal content in the filtrate after leaching the soil column with DOC extract (ppm).

	Soils	Cu	Pb	Ni	Cr	Cd
1	Ukkadam	2.03	2.95	2.81	4.35	0.15
2	Nanjundapuram	0.81	0.07	1.31	0.81	0.81
S	Sanganur Pallam	1.81	2.31	2.95	2.83	2.83
4	Thulukanur	0.07	0.90	0.98	0.03	0.03
5	Peelamedu	1.50	1.34	1.53	1.03	1.03

The lowest DOC concentration was noticed in Thulukanur soils since the pH and organic carbon content of these soils were 7.19 and 0.42% respectively. This is in conformation with the results of other workers who observed a decrease in DOC concentration due to low organic carbon content of the soils. This might be attributed to the changes in the proportion of hydrophobic and hydrophilic compounds in the DOC.

Effect of DOC on metal extraction: The initial available heavy metal status of the soils is given in Table 3. The higher amount of Cd (0.38 mg/kg) was seen in Ukkadam soils followed by Peelamedu soils since these places are highly concentrated with Cd platters and sewage water irrigation practices. The higher amount of readily available Pb was seen in soils of Sanganoor pallam followed by Ukkadam soils. The reason might be that these places are dense in traffic and low lying areas.

The Peelamedu soils recorded higher amount of available Ni since this place is mushroomed with electroplating units mainly of Ni platters. This is followed by Ukkadam soils wherein a severe Ni pollution was noticed. The Cr availability is not very much pronounced in the studied soils since the textile/hosiery units are very few in the area.

The Cu pollution is abundantly seen in Ukkadam soils followed by Peelamedu soils. Though Cu is essential to plants, the presence of higher amounts may produce adverse effects to crops and animals. The Zn platters are largely seen in Sanganoor pallam nearby Ganapathy area. This can be very well understood by the highest content of Zn (12.76 mg/kg) in soils of Sanganoor pallam followed by Peelamedu soils.

The DOC extracts of Ukkadam soils are rich in metals like Pb, Ni, Cd, and Cr followed by Sanganoor pallam. Though, the Cr availability is low, the Cr in DOC extract is high. This may be due to the extracting power of the DOC for metals from unavailable sources (Table 4).

The effect of DOC on heavy metal mobility in highly contaminated soils: Since Cu and Pb are immobile in soil, the effect of DOC on their mobility was recognized well by their highest content (6.52 mg/kg Cu and 7.51 mg/kg Pb) in filtrate of Ukkadam sewage farm followed by Peelamedu soil filtrate. Temminghoff et al. (1998) reported that, for Cu in particular organic matter, both solid and dissolved can affect its mobility substantially (Table 5).

The concentration of DOM is partly controlled by Ca by sorption. Calcium can act as a bridge between negatively charged soil particles, both clay minerals and oxides (Spark et al. 1997). The least metal content was noticed in the filtrates of Thulukanur and Najundapuram.

Giusquians et al. (1998) reported that pig sludge liquid fraction application increases the ground water pollution hazard due to Cu-DOC complex mobility. The highest metal contaminated places in Coimbatore district among the study area are Ukkadam sewage farm and Sanganur pallam. Because of high organic carbon and pH, the extracted DOC was high. Moreover, the metal extracted along with the DOC extract was also high. This showed, that DOC plays a major role in mobilizing heavy metals in a severely contaminated soils, that ultimately affect the groundwater quality.

CONCLUSIONS

Addition of biological waste materials such as poultry and animal manures and sewage sludge increased the amount of DOC in soils. The effect of DOC on heavy metal mobility was well recognized in this study. Also the soil, where there is higher organic matter, the contamination due to heavy metals in groundwater is also more due to the production of dissolved organic carbon. The organic acids present in the DOC can act as a chelating agent and thereby enhance the mobilization of toxic heavy metals. But in another way it is beneficial that the toxic heavy metals are mobilized away from the root zone, thus, preventing the accumulation of heavy metals in usable parts of plants.

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