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The Effects of Mn^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+} and Zn^{2+} Ions on Pesticide Adsorption and Mobility in a Tropical Soil

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Abstract The adsorption behaviour of DDT in a tropical silt-clay soil from Kenya showed that addition of increasing metal ion concentrations from 10 to 100 μg/g of soil, reduced the % DDT adsorption in the soil by factors ranging from 6.1% to 15.4% depending on the type of metal ion. The inhibition of adsorption by metal ions was most observed in the lower ranges of metal ion concentrations in soil, i.e. up to 100 μg/g, beyond which additional increase in metal ion concentration did not result in any further increase in % adsorption. In the standard adsorption test procedure with different soil samples saturated with 100 μg/g of metal ions, the rate of adsorption of the pesticide varied with the type of metal ion and the equilibrium maximum adsorption of DDT was lowered with addition of metal ions, with the % adsorption of 78.4% (control) being reduced to lower values in the range of 67%–77.4%, depending on the type of metal ion. The data for control and samples fitted well into the Freundlich adsorption model and showed that addition of metal ions lowered the K_f values compared with control. The results suggested that in the natural soil–water environments where there was no disturbance, aggregation of humic substances-pesticide molecule complexes altered the observed lowering of adsorption caused by inhibition by metal ions, and enhanced binding to solid soil phase occurred instead. In the leaching experiments, DDT was found to leach more extensively in soils with lower %OC content and the extent of leaching in soil columns saturated with metal ions at 100 μg/g was found to be inhibited compared with control and depended on the type of metal ion.

Keywords Metal ions effects · DDT soil adsorption and mobility

The more rapid dissipation of pesticides in tropical soils compared with temperate soils has mainly been attributed to faster rates of volatilization in different soils caused by adverse tropical weather conditions, including intense solar radiation and rainfall as well as high soil temperatures and low % air humidities (Lalah et al. 1994, 2001). However, the dissipation rates from soil are also influenced by adsorption/desorption and leachability which are in turn controlled by pesticide binding to soil clay minerals and organic matter (Calderbank 1989; Lalah et al. 2001). Organic matter and clay minerals are the components most often implicated in pesticide adsorption in soil. However, clay and organic matter move as a unit rather than as separate entities and the relative contribution of organic and inorganic surfaces to adsorption will depend upon the extent to which clay is coated with organic matter (Calderbank 1989). The relative rates of adsorption of pesticides such as DDT in different soils have been shown to decrease with decreasing organic matter content in the order peat > clay soil > sandy loam soil (Vollner 1991). Pesticides of various types are variously adsorbed by clay as well as by organic matter and the adsorption mechanisms involved include one or a combination of hydrophobic interactions or van der Waals forces of attraction, hydrogen bonding, charge transfer and ion-exchange mechanisms

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(Calderbank 1989; Lalah et al. 2001). The fate and degradation of pesticides in soil is also affected by dissolved organic matter (DOM), which constitutes only 1% of total organic carbon in soils and is the most mobile soil organic matter or humus fraction (Nierop et al. 2002).

Although pesticide structure and its physical chemical properties including its hydrophobicity, volatility, vapour pressure, water solubility, polarity, acidity and polarizability allow molecular estimation of its adsorption behaviour (Calderbank 1989), the presence of competitive or non-competitive binding factors existing in the soil environment such as heavy metal ions can make predictions of their adsorption and mobility to be more complex (Parr and Smith 1974; Kayyali et al. 1998; Kamiya and Kameyama 2001; Yang et al. 2006). These metal ions get adsorbed to soil clay minerals and organic matter just like pesticides as has been reported in studies with dissolved organic matter (Kamiya and Kameyama 2001). Because of differences in concentration and types of metal ions in soil, adsorption of pesticides is influenced by competitive or non-competitive complexation of heavy metal ions to soil clay minerals and organic matter (Parr and Smith 1974). The complexation of heavy metals with dissolved organic matter and clay minerals influences their solubility, mobility and degradation in soils and sediments and this complexation is reported to be more significant for Cu and Pb than for Cd, Zn and Ni (Ryan et al. 1983; Kamiya and Kameyama 1998; Kamiya and Kameyama 2001). Pesticide degradation The influence of pesticide degradation is influenced by soil organic-matter-pesticide-metal ion interactions is charactrized by saturation-type inhibition effects of metal ions with humic acids varying with limiting concentration of the complex, and the inhibition effects have been found to increase in order Cr(III) < Co(II) < Mn(II) < Cu(II) (Ryan et al. 1983; Weng et al. 2002; Green-Ruiz 2005; Schwab et al. 2005; Banks et al. 2006; Kyziol et al. 2006).

Although earlier studies done in temperate soils predicted that DDT is strongly adsorbed to soils with little leaching (Sleicher and Hopcraft 1984), contamination of ground water was also reported and significant leaching potential demonstrated in laboratory experiments with certain temperate soil types (Sleicher and Hopcraft 1984; Vollner 1991). The studies reported in this paper were conducted to determine the effect of metal ions on adsorption and leachability of ^{14}C-p,p′-DDT in three different tropical soils from Kenya.

Materials and Methods

Uniformly labelled ^{14}C-p,p′-DDT (specific activity: 24.95 mCi/mmol) was obtained from the IAEA, Vienna. Non-labelled p,p′-DDT, p,p′-DDE and p,p′-DDD, all 99% pure by TLC, were obtained from Greyhound Chromatography and Allied chemicals, UK. Crystalline 2,5-diphenyloxazole (PPO; from Fisher Chemicals, USA), 2,2-p-phenylbis (4-methyl-5-phenyloxazole; dimethyl POPOP) from Eastman Kodak Co., USA and Triton X-100 from ICN Biochemicals, Inc., USA, were used in liquid scintillation spectrometry. A Harvey ^{14}C cocktail for liquid scintillation from R.J. Harvey Instrument Co., USA, was used as a trapping solution during biological material oxidation and subsequently as a scintillator solution in bound residue determination. Mannitol ($CH_2 \cdot OH \cdot (CH \cdot OH)_4 \cdot CH_2OH$) from Kobian, Nairobi was used to enhance combustion during biological material oxidation. Florisil (60–100 mesh) from Machery Nagel Co., Germany, was used for column chromatography clean-up. Analar grade $NiCl_2 \cdot 6H_2O$, fused with $CaCl_2$, $CoCl_2 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, $CuSO_4 \cdot H_20$ and $ZnCl_2$ (from Kobian, Nairobi) were used as metal ion standards. Glass columns (internal diameter: 4.7 cm, length: 40 cm) were used for the leaching experiments. A Tricarb 1000TR liquid scintillation counter (LSC) analyzer and vials were obtained from Packard-Canberra Co. USA and were used for liquid scintillation counting while a biological tissue oxidizer OX-600 from J. R. Harvey Instrument Co. was used in the determination of bound residues. Gas liquid chromatography (GLC) a Packard Model 421 with ECD detector was used for pesticide residue analysis. Glass columns of internal diameter 1 cm and length 13 cm were used for clean-up. The metal ion concentrations were analysed in an atomic absorption spectrophotometer (AAS) instrument A Perkin–Elmer atomic absorption spectrophotometer model 2380 with an air/acetylene flame.

Three different field soil samples were used in this study. The samples were obtained from two sites in Nairobi and one in Mtwapa in the Coast region in Kenya. The plots were prepared by digging (~0.5 m deep) up and removing all weeds and stones, and then surface soil up to a depth of about 6 inches was scooped up by inserting PVC pipes and taken to the laboratory in plastic bags. The soil samples were air-dried separately, then crushed and homogenized in a Mortar and Pestle and finally screened through 1 mm sieve to remove stones and large solid particles. The soil samples were taken for characterization at National Agriculture Laboratories, Kabete, Nairobi.

The adsorption tests were done based on the standard EEC (1988) procedures. In the first experiment, duplicate 10 g portions of soil were weighed and placed in 150 mL glass conical flasks. Then 45 mL portions of different concentrations of the metal ions, Mn^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+} and Co^{2+} (containing equivalent concentrations of 10, 20, 50, 100, 200, and 400 µg/g of soil) were added separately into the flasks. A solution of ^{14}C-p,p′-DDT mixed with non-labelled p,p′-DDT, each constituting 0.28 µg/L p,p′-DDT (equivalent of 439,500 disintegrations per minute (dpm) of radioactivity) was added to each flask. The mixtures were shaken in the mechanical shaker continuously for 6 h then centrifuged for 10 min at 10,000 rpm. The supernatants were analysed by counting aliquots in an LSC instrument after 0.5, 1, 2, 3, 4, 5, and 6 h, respectively, to determine the amount of DDT left in the solution after soil adsorption. One set of controls contained ^{14}C-p,p′-DDT and soil but no metal ion and another set of controls contained ^{14}C-p,p′-DDT and metal ions but without soil. These experiments gave us data on adsorption of DDT in the three different soils with varying concentrations of DDT in μg/g soil expressed as % adsorption. Another similar experiment was done but without agitation and by undisturbed equilibration in the flasks for 10 days. We also determined DDT and its metabolites DDE and DDD in the supernatants and in the soil after 6 h by extraction in *n*-hexane in a separatory flask, clean-up in florisil (40–60 mesh) and GLC analysis. A recovery for DDT was found to be 72.7%.

The leaching experiments were done according to the EEC method (EEC 1988). Glass columns (4.7 cm diameter and 40 cm long) with flow controls at the bottom and plugged with glass wool at the bottom were used for soil column preparation. To each glass column 100 g of soil was added and packed gently to ensure uniform packing. Soil columns were 17 cm in length. Six columns were prepared each time and one control column was prepared (soil without metal ions). Each soil column was saturated with a solution of 0.01 M $CaCl_2$ for uniform ionic strength and with the respective metal ion concentrations. Experiments were done in duplicates. The solution containing metal ions and salt was allowed to move up the soil column by capillary for 12 h and then allowed to drain free overnight by running the same solution through it at the rate of 7–8 mL per hour. Trial runs with metal ion concentrations of 10, 20, 50, 100, 200, 500, and 1,000 μg/g dry soil were done and 100 μg/g was found to give best though slightly higher than environmental concentrations. After saturation of the column with the metal ion, the soil columns were inoculated with ^{14}C-p,p′-DDT mixed with unlabelled p,p′-DDT (equivalent to 0.905 μg/g of soil and 889,340 dpm of radioactivity) for each column. The leaching was done by running continuously with 0.01 M $CaCl_2$ solution and was allowed for 48 h at the rate of 7–8 mL/hr. The leachate was collected in a glass beaker and was analysed for radioactivity by mixing an aliquot of 1 mL with 5 mL of scintillator in a 20 mL vial for analysis by LSC. The soil was then removed from the column and analysed by Soxhlet extraction in thimbles for 2.5 h with methanol. A recovery of 78.8% was obtained for the method. Bound residues were determined in the biological tissue oxidizer by combustion of 1.5 g soil with 25 mg mannitol and counting of trapped $^{14}CO_2$ in a Harvey ^{14}C cocktail in the LSC. The percentage pesticide in the leachate was calculated. The total residues in various sections of the soil column were determined μg/g soil and then expressed as % of applied ^{14}C-residues. The determination of metal ions in the solution that had passed through the columns was done using AAS according to method of Ochieng et al. (2006). The same was done for a blank soil before the actual experiments. Standard solutions of Cu^{2+}, Mn^{2+}, Co^{2+}, and Ni^{2+} were used for calibration curve. The exact concentration of metal ions determined in the solutions exuding out of the columns after equilibration just before the start of the leaching experiments (μg/g) were: Mn (102), Cu (92.2), Co (83.6), Ni (106), and Zn (130).

Results and Discussion

The characteristics of the soil samples used in these experiments are shown in Table 1. The soil characteristics in Kenya vary from region to region and this is due to differences in geology, altitude and climatic conditions. However, most soils in Kenya are loamy, silty clay, clay or sandy. The three samples of soil used in the study represented three soil types. As shown in the table, they had very different clay and organic matter contents which are expected to influence pesticide adsorption and mobility differently.

No appreciable degradation of p,p′-DDT was observed during the 6-h adsorption experiment and 48-h leaching experiments as the metabolites DDE and DDD were not identified by GLC (in adsorption) and were less than 1% of total residues detected in the leaching experiment. However, there was some negligible degradation of DDT to DDE and DDD (<1% of total detected residues) after the 10-day adsorption experiment.

The results showed that raising the metal concentration from 50 to 100 μg/g of metal ion in soil introduced a significant change in adsorption of the pesticide in Chiromo soil (Fig. 1). Minimum change in adsorption expressed as % adsorption was shown with metal ion concentrations ranging from 10 to 50 μg/g and from 100 to 400 μg/g. The 100 μg/g metal-ion concentration would be

Table 1 Physico/chemical characteristics of the soil samples

Source	pH	% Sand	% Silt	% Clay	% OC	% Moisture	Texture
Chiromo	5.7	13.6	41.7	44.7	1.42	9.0	Silt clay
Buru Buru	5.1	8.4	18.2	78.4	4.34	11.0	Clay
Mtwapa	6.2	90	2	7.2	0.54	0.70	Sandy

Note: % OC denotes % organic carbon; soil analysis by the national agricultural laboratories (NAL), Kabete

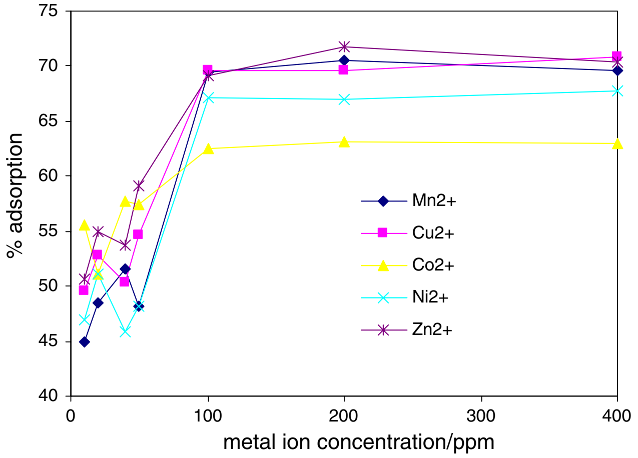

Fig. 1 The effect of increasing metal ion concentration on adsorption of ^{14}C-DDT

the saturation limit for adsorption sites on the clay minerals and organic matter in the soil. Beyond this limit no more adsorption of the pesticide could be increased. The equilibrium % pesticide adsorption (relative to the total initial pesticide concentration in the 0.01 M $CaCl_2$ solution) data obtained with 100 μg/g of metal ion concentration were 69.4% (Mn), 62.5% (Co), 67.2% (Ni), 69.4% (Cu), and 69.1% (Zn) compared with 73.7% adsorption in control.

The presence of various metal ions at 100 μg/g therefore inhibited the adsorption of DDT in this soil as shown by lowering the maximum percentage of adsorbed pesticide. The different extents of % adsorption at 100 μg/g metal ion concentration could be due differences in complexation strengths between the soil colloids and metal ions as there is simultaneous non-competitive inhibition and interaction with pesticide molecules. However, the differences in equilibrium adsorption were not significantly large since all these metals are in the same period of periodic table and are close to one another and their cationic sizes are not so different. We would expect the cationic sizes to decrease as $Mn^{2+} > Zn^{2+} > Co^{2+} > Cu^{2+} > Ni^{2+}$ with atomic masses for Mn, Co, Ni, Cu and Zn being 54.94, 58.93, 58.69, 63.55, and 65.39, respectively. Other factors which affect the stability of metal ions oxidation states and their complexation strengths are also involved, such as the electronic effects due to promotion and movement of electrons in the complex formed (and in this respect one would expect Co to have more variable valencies compared with Cu and Zn), hydration energies and the inner sphere/outer sphere binding mechanisms. To explain the essential forces dominating the inhibition effects of metal ions, previous researchers reported that the greater part of the effects is dependent on complexation strengths of the metal ions and found that the effects were enhanced by Cu(II) ion having high complexation ability (due to its smaller ionic size) which was assigned to the inner sphere binding accompanied by loss of hydration shell (Ryan et al. 1983). In the same report, the inhibition was lowered by Mn(II) and Co(II) ions having relatively not so strong complexation abilities which were assigned to the outer sphere binding without loss of hydration shell (Ryan et al. 1983). Extending this same argument, the lowest inhibition effect of Cr(III) ion is due to the fact that the complexation ability of Cr(III) to humic acids should be weaker than Mn(II) and Co(II) owing to its stronger hydration property resulting from its higher cationic valence (therefore outersphere mechanism of adsorption) and smaller ionic radius making it more difficult to lose its hydration shell relative to those of Mn(II) and Co(II) ions. These mechanistic variations would indicate that to understand metal ion–soil colloid complexation strengths, it is necessary to determine binding constants for specific ions as it is apparently inaccurate to generalize on complexation strengths. However, in general, increasing the concentration of metal ions during the adsorption test showed that 100 ppm was the optimum equilibrium metal ion concentration beyond which further increases would not influence the % adsorption of the pesticide. This could be happening when all the binding sites were saturated and further adsorption was mainly influenced by interactions between soil colloids–metal ions and pesticide molecules. The most effective metal ion concentration on pesticide adsorption was found to be Ni^{2+} and Cu^{2+} which lowered the maximum adsorption capacity of Chiromo soil more than the other metal ions (Fig. 2).

In the second set of experiments, the adsorption behaviour of DDT in Chiromo soil in presence of metal ions, with agitation and following standard EEC (1988) adsorption test procedure was studied. The presence of the metal ions increased the pesticide adsorption rates compared with control initially and up to 4 h before reaching

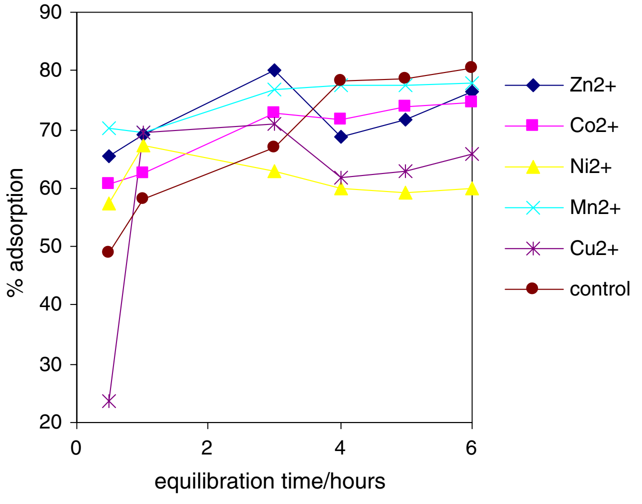

Fig. 2 Adsorption of ^{14}C-DDT (with agitation)

equilibrium concentrations in soil (expressed as % adsorption) of 78.4% after 4 h (control), 78% after 3 h (Zn), 69.4% after 3 h (Cu), 67% after 1.5 h (Ni), 73% after 3 h (Co) and 77.4% after 3 h for (Mn) (Fig. 2). The presence of metal ions in the soil lowered the equilibrium adsorption concentrations and the time taken to start attaining the equilibrium compared with control, with most effects shown with Cu and Ni^{2+} ions. All the metal ions lowered the adsorption over the 6 h interval. The smaller cationic sizes, stronger hydration and outer-sphere complexation strengths would explain the more inhibition effects observed with these two metal ions.

The equilibrium concentration of adsorbed pesticide (expressed as equilibrium % adsorption), fitted well into the Freundlich isotherm model where $Y = K_f X^{1/n}$ with Y being the amount of pesticide in the test solution (in µg/L), X the equilibrium % adsorption and K_f and 1/n being the two Freundlich constants. A plot of $\ln Y = \ln K_f + 1/n \ln X$ was done to obtain the Freunlich constants given in Table 2. The metal ion addition to the soil lowered the maximum equilibrium % adsorbed pesticide in the Chiromo soil, but this did not alter the Freundlich constants significantly as shown in Table 2. The results showed that the % equilibrium concentration of the pesticide was directly proportional to the concentration of the pesticide in the test solution for the control and all the various metal ions-soil samples at a concentration of 100 µg/g of metal ion in soil and in the pesticide concentration range (11, 56, and 280 µg/L, respectively).

Without agitation, the presence of the metal ions Co^{2+}, Ni^{2+} and Mn^{2+} appeared to delay adsorption during the first 3 days compared with control (Fig. 3). Decreased % adsorption of DDT for all metal ions was found to be in the order Ni > Mn > Co after 3 days. After 4 days equilibration equilibrium status began to be attained but enhanced adsorption was shown with addition of all metal ions compared with control which can be explained by clustering or aggregation of particles under undisturbed conditions (Tipping and Ohnstad 1984). Aggregation occured by clustering of ^{14}C-pesticide molecules-dissolved organic matter complexes from the solution onto the solid phase soil matrix. Such undisturbed conditions with soil exposed to flooded contaminated water are rather theoretical. Therefore without agitation the metal ions seemed to inhibit adsorption to Chiromo soil colloids initially during the first 3 days, before aggregation started masking the adsorption effects (Fig. 3).

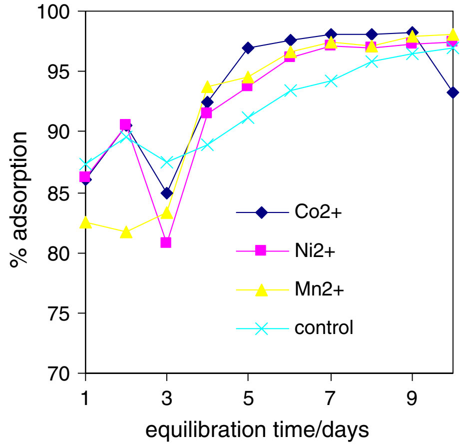

Fig. 3 Adsorption of ^{14}C-DDT (no agitation)

The results showed that DDT leached down the column to varying strengths depending on the metal ion present in the soil column. The different extents of leaching were due to differences in soil composition as shown by differences in their % organic carbon and % clay contents. The least amount of ^{14}C-p,p′-DDT was detected in the effluent from Nairobi clay and silty clay soil columns, respectively, which both had higher organic matter contents (4.34% and 1.42%) as compared with sandy soil from Mtwapa (with 0.54% OC) (Table 3). The results shown in the table (Table 3) indicated that addition of metal ions to the soil columns caused less ^{14}C-DDT leaching in the soil columns as compared with control. Therefore addition of metal ions inhibited DDT leaching and caused greater retention of the pesticide in the soil. The exceptions were Ni^{2+} in Chiromo soil which showed greater leaching compared with control and other soil columns. This exception demonstrates that

Table 2 The effects of increasing the concentration of pesticide (µg/L) in the test solution on its equilibrium concentration in soil (% adsorption) and the Freundlich adsorption constants

Equilibrium % adsorption						
Concentration of pesticide	Control	Zn^{2+}	Co^{2+}	Ni^{2+}	Mn^{2+}	Cu^{2+}
280	78.4	76.3	71.5	60.0	77.4	65.0
56	15.7	15.3	14.3	12.0	15.5	13.0
11	3.08	3.00	2.81	2.36	3.04	2.55
Freundlich contants						
1/n	1	0.9997	1	0.9994	1	1.0003
K_f	280	272	255	214	276	232

Note: 1/n and K_f are Freundlich constants ($r^2 = 1$); metal ions (100 µg/g soil)

Table 3 The % ^{14}C-DDT residues in the leachates

Extent of leaching (expressed as % leached)						
Soil sample	Control	Mn^{2+}	Cu^{2+}	Co^{2+}	Ni^{2+}	Zn^{2+}
Chiromo	1.12	0.95	0.31	0.70	14.59	0.53
Buru Buru	1.35	0.91	0.62	0.94	1.28	1.06
Mtwapa	21.65	8.86	1.18	12.40	1.58	1.57

Note: Control: no added metal ions; concentration of metal ions: 100 µg/g of soil binding of the pesticide was dependent on the strength of the interactions between the pesticide molecules and soil matrix and on the type of organic matter-soil matrix. The results from the leaching experiments were done with soil columns saturated with the metal ions all at a concentration of 100 µg/g of soil. Initially there was binding of metal ions on the soil colloids. There was also non-competitive binding of DDT molecules on soil colloids. As the leaching solution (0.01 M $CaCl_2$ solution) was running through the column, some of the metal ions got dissolved in the water, creating more binding sites for the pesticide molecules. Therefore there was more retention of pesticide molecules in the soil columns saturated with metal ions compared with controls. The relative complexation strengths of metal ions-soil colloids, pesticide molecule-soil colloids and soil colloids–metal ions-pesticides influenced the different leaching extents shown by the results. The factors affecting adsorption which are discussed in the previous section also apply here. The movement of metal ions into the leachates was shown by AAS analysis of leachates in Chiromo soil which gave results of concentration of metal ions (mg/L) as 102 (Mn), 92.2 (Cu), 83.6 (Co), 106 (Ni), and 130 (Zn). The varying extents of leaching in the different soil columns are also shown in Fig. 4.

After each leaching experiment, the soil in the column was analysed to account for the concentration of pesticide in the leachate and to show the retention of the pesticide in the soil column. The retention of ^{14}C-DDT residues was confirmed in all the columns as shown for Buruburu soil (Fig. 5). Substantial amounts of ^{14}C-p,p′-DDT residues were found in the glass wool plugs and these were analysed and accounted for as leachate. A weak negative correlation was shown between the % OC and the % of pesticide detected in the leachate for control soil sample, and for Mn^{2+}-soil sample and Co^{2+}-soil sample ($R^2 = 0.4516$, 0.4656, and 0.4434, respectively) but no correlation for Ni^{2+}, Zn^{2+} and Cu^{2+} ($R^2 < 0.15$) showing that the leaching was influenced by both organic matter content and other parameters such as ionic size and the resultant strength of metal ion–soil matrix bonding as has already been discussed. There was also negative correlation of % clay with %leachate especially for control soil sample, Mn^{2+} and Co^{2+} ($R^2 = 0.768$, 0.7798 and 0.7611, respectively) but correlation was weaker for Cu. and Zn ($R^2 = 0.4336$ and 0.2673, respectively) and Ni showed no correlation at all for %clay versus % leachate.

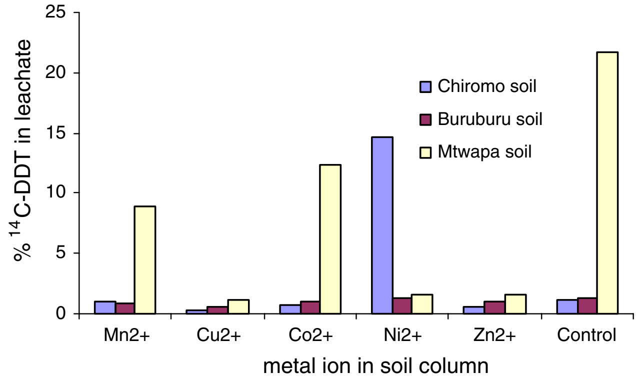

Fig. 4 Leaching extent of DDT in the soil columns

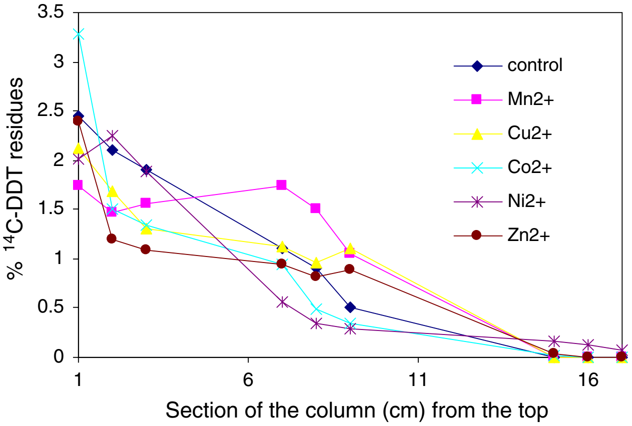

Fig. 5 Distribution of ^{14}C-DDT residues in the soil column (Buruburu soil)

The study showed that depending on the type of metal ion present in the soil and the type of soil, DDT mobility in soil was varied. In this standard leaching test procedure, the mobility of DDT in soil was inhibited by presence of metal ions. There was extensive leaching of DDT especially in sandy soils even in presence of metal ions such as Mn^{2+} and Co^{2+}. The other metal ions (Cu^{2+}, Ni^{2+}, and Zn^{2+}) inhibit its mobility in sandy soil. However, in silty clay and clay soils such as the soil types studied here, DDT leaching is limited and is also influenced by presence of metal ions. It is therefore possible for DDT to leach beyond 17 cm in soil into drainage water and into underground water, although this would depend on field conditions such as soil type, soil characteristics, volatilization and rainfall pattern (Cronan and Aiken 1985; Lalah et al. 2001). Several environmental factors must therefore be considered when interpreting laboratory leaching experiment results. However, our results here confirm both adsorption and leaching of DDT in tropical soils which supports previous reports on DDT where predictions showed strong adsorption (Sleicher and Hopcraft 1984) and laboratory studies showed significant leaching in temperate sandy soils (Vollner 1991).

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