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The Role of Paraquat (1,1-dimethyl-4,4-bipyridinium chloride) and Glyphosate (n-phosphonomethyl glycine) in Translocation of Metal Ions to Subsurface Soils.

Rhoda O. Mbuk[1], Rufus Sha'Ato[2*] and Nnadozie N. Nkpa[2]

[1]*Chemistry Department, Federal College of Education, Obudu, Cross River State, Nigeria.*
[2]*Department of Chemistry and Centre for Agrochemical Technology University of Agriculture,*
Makurdi, Benue State, Nigeria, 970001

Abstract

We investigated the role of paraquat (1,1'-Dimethyl-4,4'-bipyridinium dichloride) and glyphosate (N-(phosphonomethyl) glycine), on the translocation of some metals (K, Mg(II), Mn(II), Fe(II), Pb(II), Cu(II) and Cd(II)) in soil, using a topsoil (Aquic Ustifluvent: USDA Soil Taxonomy, 2000) sampled at the University of Agriculture Makurdi Crop Farm, in Central Nigeria (7° 47'N, 8° 32'E). Employing column leaching experiments with water only on native soil and soil spiked with the metals and different levels of glyphosate or paraquat treatment, leachates were collected and analyzed for their metal contents. Results showed that in the presence of paraquat the transport of Fe(II) and Mn(II) by leaching in the soil was suppressed while that of Cu(II), K and Pb(II) was enhanced. Glyphosate, similarly suppressed Mn(II) and to some extent Fe(II) translocation in the soil; however, it enhanced the mobility of Cd(II), Cu(II), Mg(II), Pb(II) and K under similar treatment. While paraquat seemed to enhance the translocation of Mg(II) at low application rates of the herbicide, glyphosate promoted its transport only at high application rates; there was no evidence that paraquat affected the movement of Cd(II) in the soil. Our results show that the long-term use of these pesticides in the field may result in the depletion of Cu(II), K and Mg(II) in agricultural soils, and that the use of glyphospate may present the additional risk of possible groundwater contamination with Cd(II) and Pb(II).

Keywords: Herbicide; Pesticide, Soil; Leaching; Leachate; Metal ion mobility; Glyphosate; Paraquat; Pollution; Nigeria.

Introduction

Modern agriculture relies heavily on chemical technologies for overall success: fertilizers for improved yield and pesticides for protection against losses on the field and in storage [1, 2]. While fertilizers, largely inorganic in chemical nature, have a narrow spread in terms of chemical class and composition, pesticides cover a wide range of known classes of (largely organic) compounds - carbamates, acetanilides, organophosphates and organophosphonates, organochl-orines, etc., alongside their additives [2]. Although, overall, the use of these chemicals poses varying degrees of threat to environmental media quality, it is envisaged that their use will continue to grow, especially in poor countries if the food security of an ever expanding population is to be assured [3].

On the field, co-application of fertilizers and pesticides is common practice as it is necessary. To date, however, not much focus has been given to how these chemicals interact on the field, following application even though some of the pesticides have functional moieties suitable for donor-acceptor behaviour with metal ions. In addition to inputs from fertilizers and other anthropogenic activities, metals occur naturally in soils in various stages of oxidation. Often, the mobility or fixation of these in soil is influenced by the organic matter, clay minerals and hydroxy-oxides constituent in the soil, mostly in conjunction with pH effects; there is paucity of data on the role that pesticides (may) play in the translocation of metals in soil as well.

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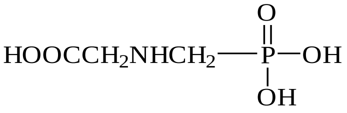
*Corresponding Author Email: rshaato@chemsocnigeria.org

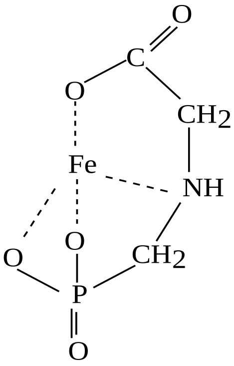
However, there is evidence that many cations adsorbed on clay minerals in soil are capable of coordinating with organic pesticides and some industrial contaminants containing N, O, and P. For example, glyphosate (N-(phosphonomethyl)glycine) shown in structure **(I)**



$$HOOCCH_2NHCH_2{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}{-}OH$$

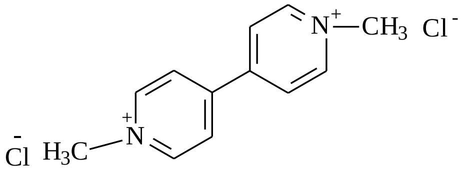
(I)

and its principal metabolite, aminoethylphosphonic acid (AMAP) form complexes with Fe^{3+} and Al^{3+} through the phosphonic acid moiety, with the participation of one of the carboxylic acid oxygen as in structure **(II)** [4, 5].



Structure of Fe-glyphosate chelate
(II)

Metal ions associated with organic matter and or clay surfaces can also interact with ionic organic pesticides such as paraquat **(III)** by an ion-exchange mechanism.



Paraquat dichloride (1,1`-Dimethyl–4, 4`–bipyridinium dichloride)
(III)

For example, Ca-Smectite exchanges with paraquat as indicated [6]:

$$\text{Paraquat}_{(aq)} + \text{Ca-Smectite}_{(s)} \rightleftharpoons \text{Paraquat-Smectite}_{(s)} + Ca^{2+}_{(aq)}$$

Nevertheless, studies by Moure et al. [7] and Spark and Swift [8] provide evidence that paraquat interaction with soil minerals is a chemical complexation (e.g., through H- bonding) rather than an ion exchange process. Whichever mechanisms are operative, the foregoing suggests that these herbicides interact with metal ions and soil surfaces in a manner that could affect the overall fate, including transport, of such metal ions in the soil environment. In addition a number of field studies show that many pesticides, including glyphosate can be transported to a depth of up to one metre, and probably beyond, e.g. [9, 10, 11], thereby posing a risk to groundwater reservoirs alongside whatever non-pesticide contaminants they mobilize and carry in the process.

Soils in Nigeria’s Benue Valley have been used for arable agriculture since the area was inhabited. Over the years, the soils have become impoverished in mineral nutrients and often require generous applications of inorganic fertilizers, supplemented with micronutients such as Zn for optimum crop production [12]. More recently, owing to pressure on farmland and a reduction in farm hands due to rural-urban migration, the practice of shifting cultivation is giving way to intensive use of land and with increasing use of pesticides, particularly insecticides and herbicides, including glyphosate (Roundup®) and paraquat (Grammoxone®).

The aim of this study, therefore, was to investigate the influence, if any, of glyphosate and paraquat on the translocation of metal ions in soils. Translocation is used here to mean transport of metal ions through soil by leaching with infiltrating water. The expectation was to shade light on the long-term effect of the use of these herbicides on farmlands with respect to their metals content and associated groundwater risk assessment.

Materials and Methods

Sampling and soil analysis

The soil sample (an Aquic Ustifluvent by USDA Soil Taxonomy Classification [13]) was collected from the University of Agriculture Makurdi Crop Farm, in Central Nigeria (7° 47’N, 8° 32’E), in the Lower Benue Valley. The farm is on an alluvial deposit on the bank of the River Benue. Topsoil up to 33 cm depth was collected, air-dried for 2 weeks, then gently crushed loose and sieved with 2 mm mesh sieve and the < 2 mm soil fraction retained for this study. Some relevant soil physicochemical properties were determined using routine methods as follows: pH by glass electrode method, organic matter by the Walkley-Black wet oxidation method and CEC by the 1.0 N sodium acetate extraction method (with determination of exchangeable cations by atomic absorption spectrometry-AAS) [14, 15].

Design of leaching experiments

The translocation of water-soluble metal ions was studied in six sets of plastic columns (12cm x 7cm, i.d.). The first set consisted 250 g of native soil only; the second contained additions of each of K^+, Mg^{2+}, Mn^{2+}, Fe^{2+}, Cd^{2+}, Cu^{2+} and Pb^{2+} (as nitrates) to 250 g soil to give 8ppm concentration of each metal in the soil; this doubled as a test for their recovery by simple leaching with pure water.

***Table 1.* Summary of the compositions of columns used in the leaching experiments*.**

Col: Set	Amount of soil	Concentration of metal ion spike	Concentration of Herbicide Spike	Herbicide Concentration Code
1	250 g	0	0	-
2	250 g	8.0 ppm	0	-
Native soil + Paraquat				
3	250 g	0	55ppm	PARQ 1
	250 g	0	110ppm	PARAQ 2
	250 g	0	165ppm	PARAQ 3
	250 g	0	220ppm	PARAQ 4
Native soil + Metal on spike + Paraquat				
4	250 g	8.0ppm	55ppm	PARQ 1
	250 g	8.0ppm	110ppm	PARAQ 2
	250 g	8.0ppm	165ppm	PARAQ 3
	250 g	8.0ppm	220ppm	PARAQ 4
Native soil + Glyphosate				
5	250 g	0	72ppm	GLYFOS 1
	250 g	0	144ppm	GLYFOS 2
	250 g	0	216ppm	GLYFOS 3
	250 g	0	288ppm	GLYFOS 4
Native soil + Metal ion spike + Glyphosate				
6	250 g	8.0ppm	72ppm	GLYFOS1
	250 g	8.0ppm	144ppm	GLYFOS2
	250 g	8.0ppm	216ppm	GLYFOS3
	250 g	8.0ppm	288ppm	GLYFOS4

* All leaching was by deionized distilled water (DDW) only.

The third set of columns consisted of four different treatments of paraquat (Grammoxone®) to give approximately 55, 110, 165 and 220 mg paraquat/kg soil (respectively, PARAQ1, PARAQ2, PARAQ3 and PARAQ4). The fourth set of columns received the metal additions to give 8ppm concentrations, plus the paraquat treatments. The fifth and sixth set of columns had glyphosate (Roundup®) replacing paraquat with the active ingredient at applications of 72, 144, 216 and 288 mg glyphosate/kg soil, as appropriate (respectively, GLYFOS1, GLYFOS2, GLYFOS3 and GLYFOS4). These summarized in Table 1.

Prior to commencement of the leaching experiments, each column was first saturated with distilled deionized water (DDW), pH 7 and allowed to stand for 24 hours. This operation ensured that all the voids within the soil were completely filled with water and for the soil to attain distribution equilibrium with added chemicals, where relevant. Subsequently more DDW (pH 7) was added and 100mL of leachate at 2.5 mL/min collected from each column and analyzed for K, Mg, Fe, Mn, Pb, Cu and Cd using a Unicam 969 Atomic Absorption Spectrophotometer (AAS). For each treatment duplicate columns were used and their leachates collected and analyzed individually; the results are the average of these. As a data quality assurance measure, the stock solutions of glyphosate and paraquat dichloride were also analyzed for K, Mg, Fe, Mn, Pb, Cu and Cd; results showed negligible amounts of the metals compared to that in the leachates.

Results and Discussion

Soil properties and metal ion recovery from the soils

The soil pH in water and electrolyte ($CaCl_{2aq}$) suspensions was 5.95 and 5.39, respectively. Its particle size distribution was 89% sand, 7% clay and 4% silt, while the organic matter content was 0.75 ± 0.03% and CEC 20.8 mmol(+)/kg soil (Table 2). Metal ion recoveries in the spiked soil, using DDW, are presented in Table 3. The general low recovery observed is attributed to sorption to the soil [16]. Nevertheless, since the translocation study is focused on water-leachable (mobile) ions, the experimental design as presented is considered valid enough to meet the aim of the study. Furthermore, the negligible amounts of the metals of interest in the experimental stock solutions, gives us confidence that the elevated amounts of the metals in leachates obtained from herbicide-spiked soils was due to their enhanced mobility as influenced by the herbicides.

***Table 2.* Some physico-chemical properties of the soil used.**

pH		**Particle size Distribution (%)**			**Organic carbon**	**Organic matter**	**Fe_2O_3**	**Exchangeable Al**	**Cation exchange capacity (CEC)**
H_2O	$CaCl_2$ aq.	Sand	Silt	Clay		(%)		**(mg/kg)**	**mmol(+)/kg soil**
5.95	5.39	89.0	4.0	7.0	0.46 ± 0.02	0.75 ± 0.03	0.24	6.14	20.8

***Table 3.* P*er cent* recoveries of metals from spiked soil samples by leaching with distilled deionized water (DDW).**

Fe	Mn	Cu	Mg	Pb	Cd	K
64.4	2.97	0.67	21.7	0.62	0.0	49.3

Metal-ion content in soil leachates

Fig. 1 shows metal ion concentrations in the leachates from native soil and native soil treated with the various concentrations of paraquat and glyphosate; while Fig. 2 shows similar results for 8ppm metal-spiked soil. The soil employed being a sandy alluvial soil is well drained allowing for easy infiltration of percolating water. Use of deionized water for the leaching experiments ensured that any metal ions detected in the leachates originated from the soil solution and not through any process of desorption initiated by the water. Where there were changes in the concentrations of the metal ions following pesticide applications, these changes were attributed to the influence of the pesticides, by any mechanism.

Thus, the figures demonstrate the influence of paraquat and glyphosate on the mobility of Fe^{2+}, Mn^{2+}, Mg^{2+}, Pb^{2+}, Cd^{2+} and K^{+} in the soil. The native soil (soil without pesticide application) generally, but not unexpectedly, gave low concentrations these metals in the leachate. This is consistent with the occurrence of free metal ions in the soil solution. The low recoveries recorded in Table 2 also indicate a strong tendency for the soil to adsorb metal ions input into it. Of special interest is Cd which was not detected in either the native soil leachate or that from the Cd-spiked soil, suggesting strong adsorption of the added Cd(II) in this soil. Generally, only ultra-trace to trace amounts of Cd are expected in uncontaminated soils.

Metal-ion translocation in the presence of paraquat

There was a strong suppression of the translocation or leachability of Fe^{2+} and Mn^{2+} in the presence of paraquat. Translocation of Pb^{2+} was also somewhat suppressed by paraquat in the native soil, although there was an apparent enhancement of mobility at the higher levels of paraquat application. Similarly, Mg^{2+} mobility seems to be more favorable at higher paraquat treatments. However, there was no evidence that treatment of soil with paraquat would enhance the movement of Cd^{2+} in the soil Fig. 1 and Fig. 2. Only in the case of Cu^{2+} and K^{+} was it clear that paraquat could facilitate translocation in the soil as both figures show. The foregoing trend is generally repeated in the soil sample with *ab initio* additions of the metal ions. As Fig. 2 shows, despite strong adsorption of added Cu^{2+}, the presence of paraquat did, indeed, aid its leaching from the soil.

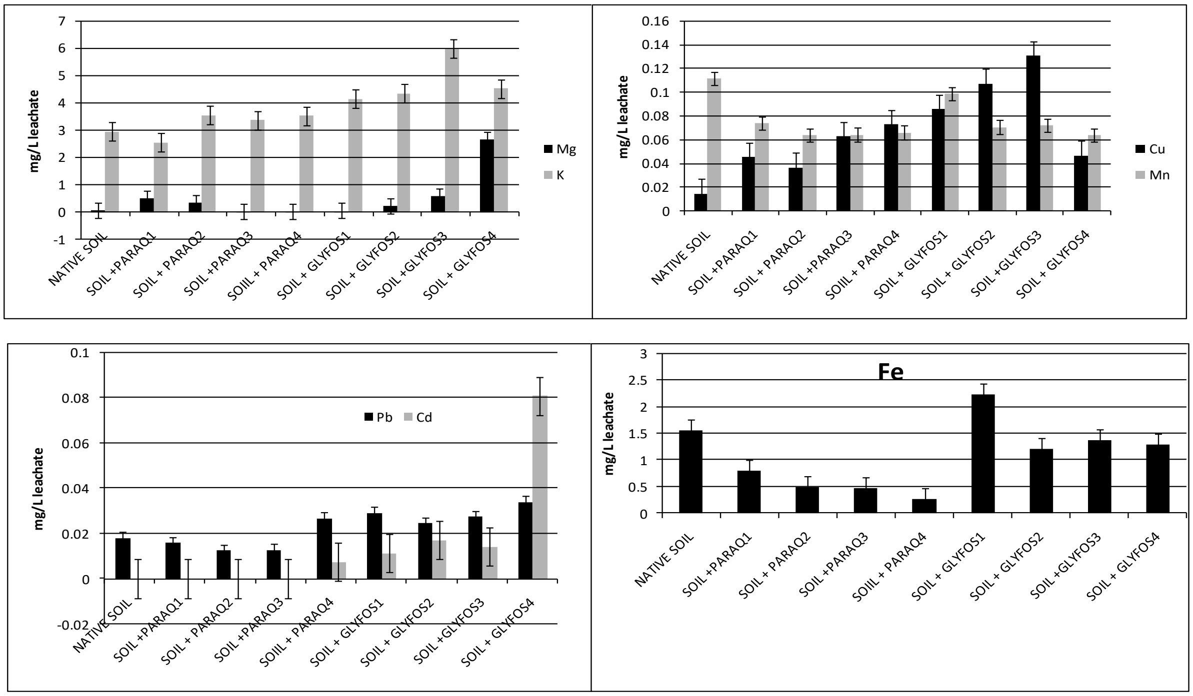


***Figure 1.* Concentrations of Cd, Cu, Fe, K, Mg, Mn, and Pb in aqueous leachates obtained from a native and glyphosate- and paraquat-treated alluvial soil from the Lower Benue Valley, Central Nigeria.**

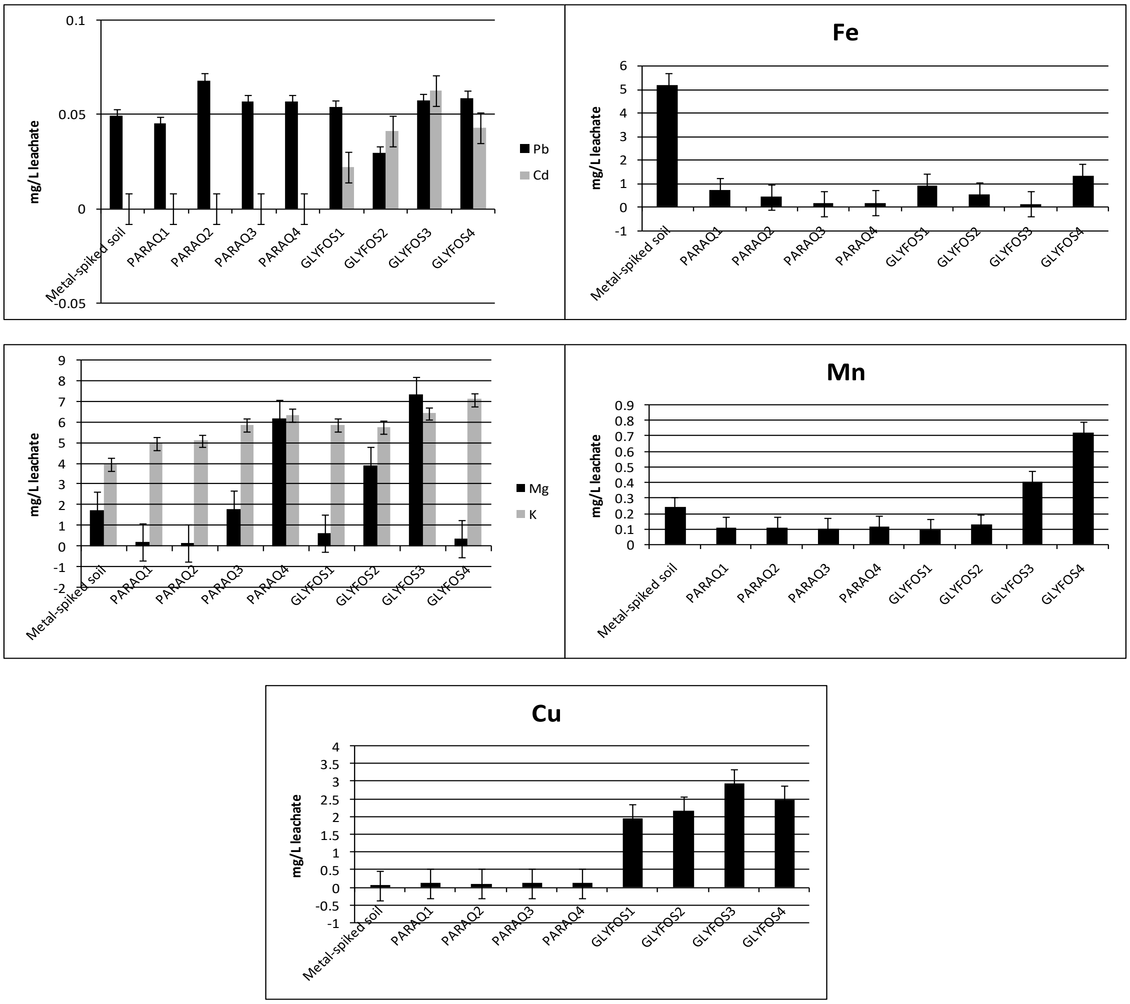


Figure 2. **Concentrations of Cd, Cu, Fe, K, Mg, Mn, and Pb in aqueous leachates obtained from a native and glyphosate- and paraquat-treated alluvial soil from the Lower Benue Valley, Central Nigeria, spiked with the metals *ab initio* to 8 ppm.**

Whereas the mechanism by which paraquat contributes to K^+ and Cu^{2+} mobility in soil, as evidenced in this study, is most likely to be by ion-exchange [6], while entertaining the possibility of competitive adsorption by surface complexation, in the case of Cu^{2+} [7, 8], that by which it suppresses the mobility of the other metals is less clear. However, paraquat is known to adsorb predominantly to negatively charged soil colloids via ionic and charge transfer bonds [17, 18]; perhaps, by this adsorption, paraquat, in some way, presents surfaces favorable to Fe^{2+} and Mn^{2+} adsorption, to prevent their movement with infiltrating water.

Metal-ion Translocation in the Presence of Glyphosate

Although not as clearly demonstrated as with paraquat, leachability of Fe^{2+} and Mn^{2+} in soil treated with different levels of glyphosate appeared to be suppressed, although Mn^{2+} appeared to have been transported with glyphosate at the higher levels of its application in the metal-spiked soil (Fig. 2). Given that glyphosate forms complexes with Fe^{2+} (as shown in structure **(II)**), it is possible that similar complexes could be formed with Mn^{2+} [5, 6, 19, 20]. While these metallo-glyphosate complexes might be expected to be water-soluble given the pH of the soils and so be easily transported with percolating water [20, 21], the fact that the metals were not so transported, suggests that any complexes formed may have become strongly adsorbed to soil surfaces, (given the high tendency of glyphosate to adsorb soils, including tropical soils, with Kd values up to 900 L kg^{-1}) [5, 18, 22], or they may even have precipitated in the soil. This could be a plausible explanation for Fe^{2+} and Mn^{2+} 'retention' in soil in the presence of glyphosate.

All the other metal ions considered (Cd^{2+}, Cu^{2+}, Mg^{2+}, Pb^{2+} and K^+) showed enhanced mobility in the glyphosate-treated soil. In these cases, it may be reasoned that any metallo-glyphosate complexes formed were more water-soluble than those formed with Fe^{2+} and Mn^{2+} and so were more easily transported with percolating water. Alternatively, it is possible that competitive adsorption of glyphosate on surface sites in soil minerals between glyphosate and metal ions is responsible for their enhanced mobility (especially for Cu^{2+}) in addition to metal ion-glyphosate complexation [7, 8] or adsorption of glyphosate to soil colloids could have triggered cation exchange or other desorption reactions involving these metal ions and protons in solution [5, 6, 19]; either way their mobility in the soil would be enhanced.

Conclusion

The findings of this study show that paraquat can enhance the translocation of Cu^{2+}, K^+ and to some extent (at high levels of pesticide treatment) Mg^{2+} and Pb^{2+}, in soils containing low organic matter, low clay contents and significant amounts of these metals. However, the mobility of Fe^{2+} and Mn^{2+} is definitely suppressed under the same conditions. In glyphosate-treated soils, movement of Fe^{2+} and Mn^{2+} was similarly suppressed, albeit less so as in paraquat-treated soil, compared to the control, while mobility of Cu^{2+}, Cd^{2+}, Mg^{2+}, Pb^{2+} and K^+ was enhanced to different extents and at differing levels of glyphosate application. The conclusion is that applications of these herbicides, especially glyphosate, on field could eventually lead to depletion of the water-soluble K^+ and Mg^{2+} content of the soil due to leaching. On the other hand there could be suppression of the levels of the water-soluble contents of the plant nutrients Fe^{2+} and Mn^{2+} due to sorption. Where the soil is contaminated with the toxic Cd^{2+} and Pb^{2+}, their water-soluble content would be elevated above what would be in their absence, with the attendant environmental and health implications.

Specifically, mobile cations which are non-adsorbed on soil are available for plant uptake. Therefore, intensive use of these herbicides will make these metals more available for plant uptake so that plants grown on such soils will eventually contain elevated amounts of these metals with deleterious consequences. We recommend that the work be extended to include more pesticide types and wider range of soils with widely different properties, in order to better understand this phenomenon.

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