

THE ROLE OF SOIL AS A SINK FOR CONTAMINANTS: (A Review)

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ABSTRACT

Soil is a complex heterogeneous system containing varying amounts of primary and secondary minerals. This paper describes the adsorption behaviour soil components.

The inorganic pollutants reach the soil surface as a result of deposition from the atmosphere or placement, and are also deposited on vegetation foliage. The inorganic pollutants can be sorbed to the various sites on soil mineral surfaces, or can be volatilized from the soil to the atmosphere, which usually occurs only after the elements has been converted to an organometal form. These inorganic pollutants can be washed away in surface water run-off and have the potential to be absorbed into the foliage and the root system of plants, and can ultimately enter and become dispersed in the groundwater.

المخلص

تحتوي التربة على أنواع عديدة من المعادن الأولية والثانوية وبدرجات متفاوتة في التركيز. هذه الورقة تشرح كيفية امتصاص المكونات المختلفة في التربة. معرفة قابلية الامتصاص للمكونات المختلفة للتربة تؤدي إلى تقدير مدى امتصاص النبات للعناصر النادرة وتقدير حركتها خلال التربة. مثلاً تصل المكونات غير العضوية عادةً لسطح التربة نتيجة الترسيب من الغلاف الجوي. هذه المكونات غير العضوية يمكن امتصاصها على الأسطح المختلفة لمعادن التربة أو يمكن أن تتبخر من التربة للغلاف الجوي، وهذه الحالة تحدث فقط بعد أن يتحول معدن التربة إلى حالة عضوية. هذه المكونات غير العضوية يمكن أن تتساقط مع الجريان السطحي للمياه وتدخل المجموع الخضري والجذري للنبات، ويمكن أيضاً أن تتساقط خلال المياه الجوفية.

TRACE ELEMENTS IN SOIL

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Soil is a complex, heterogeneous system containing varying amounts of primary and secondary minerals, hydrous oxides, and organic matter, each possessing its own metal-sorbing properties. Knowledge about the adsorption behavior of various soil components, coupled with soil composition data, is needed to predict qualitatively, the migration and plant availability of trace elements (Korte *et al.*, 1976).

Heavy metals is a general collective term applied to the group of metals and metalloids with an atomic density greater than 6 g/cm^3 . It is usually applied to the elements such as Pb, Zn, Ni, Cu, Cd and Hg, which are commonly associated with pollution and toxicity problems. Alternative name applied for these elements is 'trace elements' but it is not as widely used. Unlike most organic pollutants, such as organohalides, heavy metals occur naturally in rock-forming and ore minerals and so there is a range of normal background concentrations of these elements in soils, sediments, water and living organisms. Pollution gives rise to anomalously high concentration of the metals relative to the normal background levels, therefore presence of the metals is insufficient evidence of pollution, the relative concentration is all important (Alloway and Ayres, 1997).

Trace elements are normally present at relatively low concentration in soils or plants, and obviously include a large number of elements with widely varying chemical characteristics.

Trace elements in soils can be divided into three broad categories based on their expected chemical form in soil solutions (Pierzynski *et al.*, 1993):

- 1- Cationic Metals: these are metallic elements for which the predominant form in the soil solution would be a cation. Examples are Ag^+ , Cd^{2+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Hg^{2+} , Ni^{2+} , Pb^{2+} , and Zn^{2+} .
- 2- Oxyanions: These are elements that combine with oxygen with an overall negative charge such as AsO_4 , $\text{B}(\text{OH})_4^-$, CrO_4^{2-} , MoO_4^{2-} , and SeO_4^{2-} .
- 3- The halogens which are the members of group VII in the periodic table and are present as anions in the soil solution which include F^- , Cl^- , Br^- , and I^- .

The trace element concentrations in soils can be determined by soil chemical analysis, it is difficult to determine if such concentrations reflect a contamination problem since the natural variability in soil trace element concentrations is quite high (Pierzynski *et al.*, 1993).

The table below shows some normal soil concentrations for selected trace elements and some geochemical concentrations:

Table (1): The Normal Rang and Metal-rich for Some Trace Element Concentrations in Soil

Element	Normal Range (mg/Kg)	Metal-rich Range (mg/Kg)
As	<5 - 40	Up to 2,500
Cd	<1 - 2	Up to 30
Cu	2 - 60	Up to 2,000
Mo	<1 - 5	10 - 100
Ni	2 - 100	Up to 8,000
Pb	10 - 150	10,000 or more
Se	<1 - 2	Up to 500
Zn	25 - 200	10,000 or more

Source: Bowie and Thornton, 1985.

The Behavior of Pollutants in Soil: The concentration of pollutants in air or rivers tend to be diluted fairly rapidly while in the case of soils many pollutants tend to accumulate. Soils act as a sink for pollutants through the adsorption processes, which bind inorganic and organic pollutants with varying strengths to the surface of the soil profile to the water table, reduces their bioavailability to plants and, effect their rate of decomposition. The mineral constituents of soil include: particles of weathering rock and diskrete rock-forming minerals (such as quartz), clay mineral, hydrous oxides Fe, Al, Mn, and calcite. The humic substances, clay minerals and hydrous oxides are bonded together in various ways forming the colloidal adsorption complex which plays an important role in determining the behavior of pollutants. Several different types of adsorption reactions can occur between the surfaces of organic and mineral colloids and the pollutants (alloway and Ayres, 1997).

Gao *et al.* (1997) stated that the transport and mobility of heavy metals in soil depend on concentration, speciation and solubility in soils is controlled by reaction with solid phases. They mentioned that components that partition more strongly to the solid phase exhibit

low mobility in soils while those that partition more strongly to the liquid phase have greater mobility and may ultimately contaminate the groundwater. They found that the adsorption of Pb, Cu, Zn, Cd, and Ni was higher at pH 6.5 than at pH values, fig (1) shows processes governing mobility, solubility and availability of elements in soils.

Sorption-Desorption of Heavy Metals by Soils: Scheidegger and Sparks (1996) defined desorption as the release of adsorbed species, while adsorption is defined as the accumulation of a substance or material at an interface between the solid surface and the bathing solution. It is strictly a two dimensional process and doesn't include three dimensional processes such as surface precipitation, co-precipitation and diffusion into the crystal would all be examples of sorption, a general term that should be used when the retention mechanism at a surface is unknown.

The soil has substantial capacity to sorb heavy metals from solution and to a great extent, their concentrations in solution are controlled by sorption-desorption reactions at the surface of both organic and inorganic soil colloids. (Swift and McLaren 1991). Tessier *et al.* (1979) developed a fractionation procedure that separated the total metal content into the exchangeable, associated with organic matter and carbonate, Fe and Mn oxide, and residual forms.

The distribution and chemical fractionation of heavy metals retained in mangrove soils receiving waste water was studied by Tam *et al.* (1996) and found that a significantly higher percentage of Mn, Zn, and Cd in the water-soluble and exchangeable fractions. Copper appeared to be more strongly adsorbed in mangrove soils than the other heavy metals. Their findings suggest that whether the heavy metals retained in mangrove soils becomes a secondary source or a permanent sink would depend on the kinds of heavy metals and also the type of mangrove soils.

A laboratory study with a brackish marsh sediment contaminated by several trace and toxic metals to determine the effect of a range of pH,

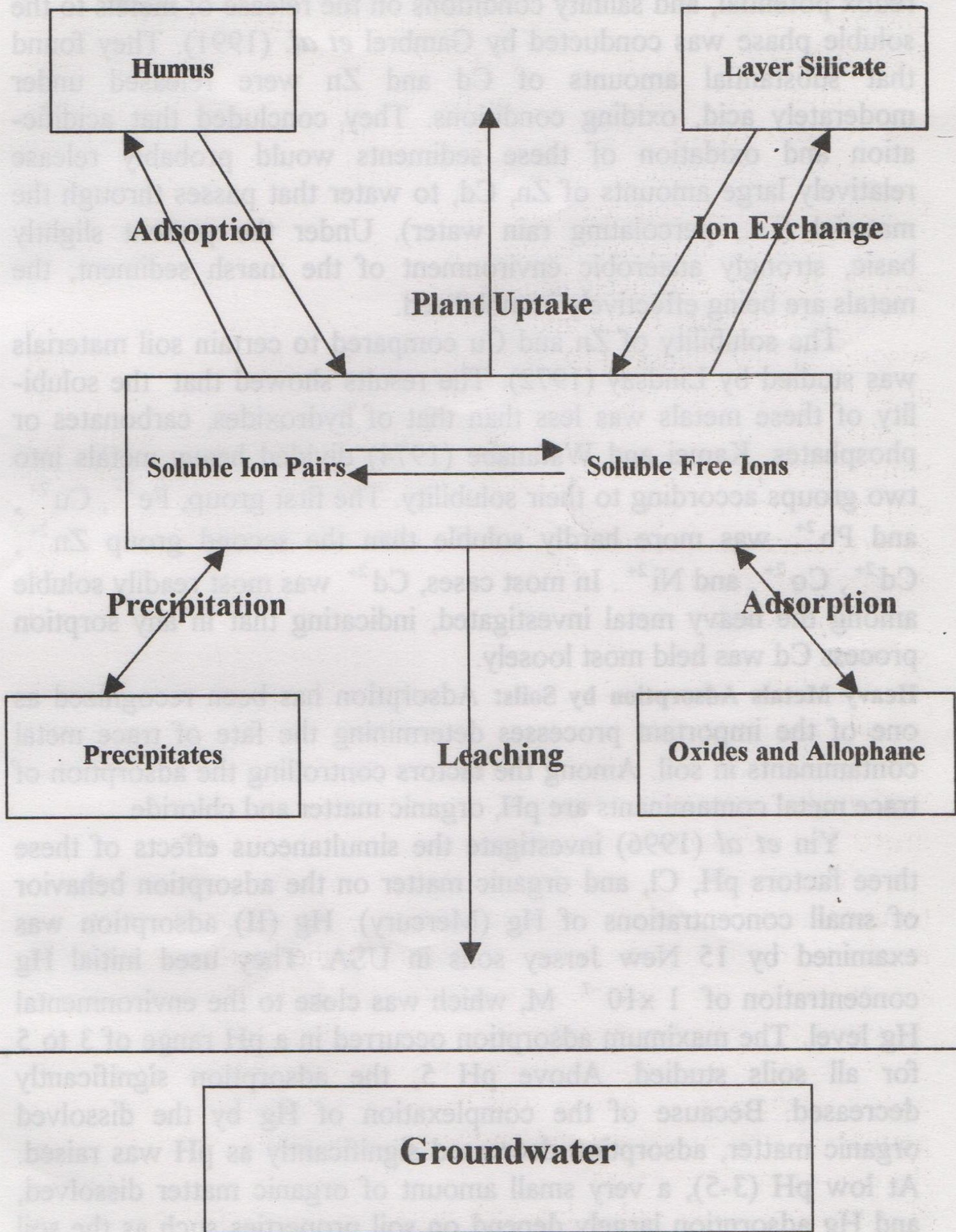


Fig (1): Dynamic interactive processes governing solubility availability, and mobility of elements in soils (After, McBride, 1994)

redox potential, and salinity conditions on the release of metals to the soluble phase was conducted by Gambrel *et al.* (1991). They found that substantial amounts of Cd and Zn were released under moderately acid, oxidizing conditions. They concluded that acidification and oxidation of these sediments would probably release relatively large amounts of Zn, Cd, to water that passes through the material (i.e., percolating rain water). Under the present slightly basic, strongly anaerobic environment of the marsh sediment, the metals are being effectively immobilized.

The solubility of Zn and Cu compared to certain soil materials was studied by Lindsay (1972). The results showed that the solubility of these metals was less than that of hydroxides, carbonates or phosphates. Kamei and Watanabe (1974) divided heavy metals into two groups according to their solubility. The first group, Fe^{3+} , Cu^{2+} , and Pb^{2+} was more hardly soluble than the second group Zn^{2+} , Cd^{2+} , Co^{2+} , and Ni^{2+} . In most cases, Cd^{2+} was most readily soluble among the heavy metal investigated, indicating that in any sorption process Cd was held most loosely.

Heavy Metals Adsorption by Soils: Adsorption has been recognized as one of the important processes determining the fate of trace metal contaminants in soil. Among the factors controlling the adsorption of trace metal contaminants are pH, organic matter and chloride.

Yin *et al* (1996) investigate the simultaneous effects of these three factors pH, Cl, and organic matter on the adsorption behavior of small concentrations of Hg (Mercury). Hg (II) adsorption was examined by 15 New Jersey soils in USA. They used initial Hg concentration of 1×10^{-7} M, which was close to the environmental Hg level. The maximum adsorption occurred in a pH range of 3 to 5, for all soils studied. Above pH 5, the adsorption significantly decreased. Because of the complexation of Hg by the dissolved organic matter, adsorption decreased significantly as pH was raised. At low pH (3-5), a very small amount of organic matter dissolved, and Hg adsorption largely depend on soil properties such as the soil surface area which was found to be the most important factor affecting the adsorption. They found that the presence of chloride in soil had no effect on Hg (II) adsorption by any soil under alkaline

conditions, because only a small amount of Hg-Cl complexes were present. Under acidic conditions, the effect of chloride on Hg adsorption depended on the soil organic matter content; the presence of chloride could significantly reduce Hg (II) adsorption.

Harter, (1983) studied the adsorption and desorption from pH-adjusted soils. Surface and subsurface horizon samples of two soils were equilibrated with varying amounts of $\text{Ca}(\text{OH})_2$ prior to metal addition. The amounts of all four metals retained was dependent upon pH of the soil sample, with retention dramatically increasing above pH 7.0 to 7.5 with the exception of Ni, at least 70 to 75% of the retained metals was extractable, with that sorbed by the highest pH soils being the least extractable. Based on subsequent extractability, the soil used appears to have specific adsorption sites for Pb, Ni, and Cu but little or none for Zn.

Cadmium, which is an important soil and water pollutant, is generally acknowledged to be one of the critical environmental chemicals, which gains entry into many biological and chemical processes (Fishbein, 1984). Cadmium may accumulate in agricultural soils through the application of soil amendments like phosphatic fertilizers and sewage sludges which are known to contain levels of 7.3-170 ppm (Lisk, 1972) and <1-3410 (Alloway, 1990) respectively.

Ramachandaran and Souza (1998) studied the adsorption behaviour and chemical speciation in two contrasting soil types of India i.e., Vertisol and Ultisol. Their investigation indicated that the adsorption capacity of Ultisol was very much lower (30 times) than that of Vertisol, indicating thereby the possibility of higher amounts of Cd in soil solution of Ultisol. They found the adsorption capacity of Vertisol is ($\mu\text{g Cd g}^{-1}$ soil).

The pollution by tailings from metalliferous mining, particles of ore minerals in the soil, such as PbS , ZnS , and CuFeS_2 become oxidized releasing metal cations such as Pb^{2+} , Cu^{2+} , Zn^{2+} , and Cd^{2+} into the soil solution where they undergo adsorption reactions (Alloway and Ayres 1997).

Allard *et al.* (1991) studied the distribution of Cu, Zn and Cd within an illitic clay formation located beneath an old deposit of sulfidic mine tailings. They found that total concentrations of metals

have been quantified as a function of depth. The distribution between the pore water and the solid phase has been measured. Qualitative information have been obtained by an operational leaching procedure. Field measurements were validated with batch adsorption experiments. The result suggests that transport of metals originating from the tailings is diffused controlled. Apparent diffusivities as well as distribution coefficients were estimated. They concluded from their study that the adsorption in the lower pH range has a limited quantitative impact on the mobility of Cu, Zn and Cd. As the pH exceeds five they are almost quantitatively immobilized in the order Cu, Zn, Cd, which suggests a retardation mechanism related to the degree of hydrolysis.

The effect of iron oxide removal on heavy metal sorption by acid subsoils was studied by Elliott et al.(1986). They investigate the adsorption of Cd, Cu, Pb and Zn from 0.025M Na Cl O₄ solutions by two ferruginous subsoils. The results showed that under acidic conditions, selective dissolution and removal of the Fe oxide soil component by dithionite-citrate-bicarbonate (DCB) generally increased heavy metals adsorption by the soils. This effect was attributed to increased electrostatic attraction of cations to the DCB-washed soils as evidenced by substantial reduction in the zero point of charge (ZPC) for the Dothan soil following DCB extraction.

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