

**HOW AGRICULTURAL CHEMISTRY CAN CONTRIBUTE TO DEALING
WITH PROBLEMS OF ENVIRONMENTAL POLLUTION**

**CONTRIBUTION DE LA CHIMIE AGRICOLE À LA PROBLÉMATIQUE
DE LA POLLUTION DE L'ENVIRONNEMENT**

**IL CONTRIBUTO DELLA CHIMICA AGRARIA ALLE
PROBLEMATICHE DELL'INQUINAMENTO AMBIENTALE**

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Abstract

Soil is a complex heterogeneous system whose physical, chemical and biological properties regulate interactions with the chemical species which reach its surface. Soil chemistry is an essential tool for understanding and predicting these interactions. Soil is able to immobilize and transform organic and inorganic molecules by different mechanisms, such as complexing and redox reactions. This behaviour gives soil detoxifying capacities towards pollutants which accumulate in the environment. Pollution by heavy metals is regulated by their solubility in soil solution which in turn depends on soil pH and redox properties and metal speciation. Organic and inorganic colloidal soil fractions can promote the immobilisation, degradation, and diffusion of organic molecules such as agrochemicals, solvents, hydrocarbons and other chemicals which reach the soil by anthropic activities. Predicting the fate of xenobiotics in soil, water, air, and plant ecosystems, the recycling of biomass and the decontamination of polluted soils are of major concern to soil chemistry.

Keywords: *soil chemistry; heavy metal pollution; redox and complexing reactions; xenobiotic degradation*

Résumé

Le sol est un milieu complexe et hétérogène dont les propriétés physiques, chimiques et biologiques règlent les interactions avec les espèces chimiques qui arrivent sur sa surface. La chimie agricole est un instrument indispensable pour comprendre et prédire ces interactions. Le sol peut immobiliser et dégrader les molécules organiques et inorganiques au moyen de mécanismes différents comme les réactions d'oxydo-réduction ou de complexation; cette capacité permet au sol de se détoxifier des polluants qui s'accumulent dans l'environnement. La pollution due aux métaux lourds est réglée par leur solubilité dans la solution du sol qui à son tour dépend du pH et des propriétés redox du sol et de la spéciation des métaux. Les fractions colloïdales du sol (organiques et inorganiques) peuvent favoriser

l'immobilisation, la dégradation et la diffusion des molécules organiques provenant de l'activité anthropique comme les produits agrochimiques, les solvants, les hydrocarbures et les autres produits liés aux activités anthropiques qui arrivent sur le sol. La prédiction du destin des xenobiotiques dans les divers compartiments de l'environnement comme le sol, l'eau, l'air et le règne végétal, le recyclage des biomasses et la décontamination des sols pollués sont parmi les problèmes majeurs auxquels la chimie agricole s'intéresse.

Mots-clés: *chimie agricole; pollution des métaux lourds; réactions de oxyde-réduction et de complexation; dégradation des pesticides*

Riassunto

Il suolo è un sistema complesso ed eterogeneo le cui proprietà fisiche, chimiche e biologiche regolano le interazioni con le specie chimiche che pervengono sulla sua superficie. Lo studio della chimica del suolo è uno strumento essenziale per comprendere e predire queste interazioni. Il suolo è in grado di immobilizzare e trasformare le molecole organiche ed inorganiche mediante meccanismi differenti come le reazioni di complessazione e di ossido-riduzione. Questa capacità rende il suolo un mezzo con proprietà autodepuranti nei confronti degli inquinanti che si accumulano nell'ambiente. L'inquinamento da metalli pesanti è regolato dalla loro solubilità nella soluzione di suolo che a sua volta dipende dal pH del suolo, dalle sue proprietà redox e dalla speciazione dei metalli. Le frazioni colloidali del suolo di natura organica ed inorganica possono promuovere l'immobilizzazione, la degradazione e la diffusione delle molecole organiche provenienti dalle attività antropiche come gli agrofarmaci, i solventi, gli idrocarburi e le altre specie chimiche che raggiungono il suolo. Predire il destino degli xenobiotici nei vari comparti ambientali come il suolo, le acque, l'aria ed il regno vegetale, il riciclo delle biomasse e la decontaminazione dei suoli inquinati sono oggi tra i temi di maggiore interesse della chimica agraria.

Parole chiave: *chimica agraria; inquinamento da metalli pesanti; reazioni redox; complessazione; degradazione xenobiotici*

Introduction

Agricultural chemistry deals with the effects of anthropic activities on natural systems, namely in environmental compartments such as soil, water, air, and plants. Agricultural Chemistry was introduced as a subject matter on courses at Agriculture Faculties several years after Justus von Liebig proposed his mineral nutrition theory. In 1843, this matter was still absent from the programme at the Agricultural Faculty of Pisa (Italy). Although, in Bologna it appeared in 1903 as a biennial subject in the Agriculture University program, research activities in the

field of Agricultural Chemistry concerning the use of inorganic fertilizers for plants had already begun in 1870 with the publication of Liebig's results.

In the 20th century, specific knowledge on soil chemistry and fertility made an exceptional advance starting from an intuition which today seems banal but is not. Research has focused on the energy involved in the behaviour of water in soil, demonstrating that water is not free but, on the contrary, is retained by the soil solid phase and its free energy decreases by reducing soil humidity; the availability of water depends on its thermodynamic status and hence, plant roots compete against soil surfaces for water. Similar competition between plants and soil occurs for all chemical species, whether useful or toxic. Soil is able to immobilize and detoxify all substances which reach it using different degradation mechanisms. Initially, when problems due to the environmental pollution were unknown, research in the field of Agricultural Chemistry was mainly focused on the study of nutrients. After the 2nd World War, it became increasingly concerned with pollutants. Nowadays, Agricultural Chemistry can be considered a subject with an enormous value for the environmental field and, in this context it has developed and in the future may continue to develop over a number of research areas which deal with the main problems caused by the pollution of ecosystems. The following topics can be indicated as items of actual particular scientific interest:

- 1) the fate of organic and inorganic xenobiotics and their behaviour in the environment; their metabolism in plants and their accumulation along the food chain; the contamination of surface and deep waters; their diffusion in the atmosphere or in confined systems as greenhouses; the risks run by agricultural workers who use pesticides;
- 2) the recycling of biomasses: this topic has strong environmental value since it is connected to the needs of modern society to eliminate materials with potentially highly polluting characteristics and to restore the soil organic matter level which is continuously depleted by intensive cropping;
- 3) the recovery of polluted soil and the development of new technologies for detoxification purposes.

Soil pollution with heavy metals

Heavy metals are naturally contained in rocks and sediments and are released at a faster or slower rate as a result of pedogenetic processes. Anthropogenic activities, as well as organic fertilization, the atmospheric fallout of fumes from industrial sources, mining activities and so on can determine an increase in heavy metal concentrations in soil. Nowadays, the level of metals in the environment raises a problem which is still under debate: at what level can metal accumulation be considered a matter of concern for ecosystems and human health? In soil metals are partitioned between solid and liquid phases. The fraction which is retained by the soil solid phase can be considered immobilised for different periods of time owing to the type of interaction developed between metals and solid phases: i)

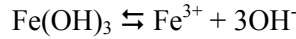
Adsorption; ii) Inclusion as a part of the crystalite mineral network; iii) Precipitation; iv) Entrapment in cell structures or biopolymers. In the liquid phase, metals can be found as complexed by water or other inorganic and organic species. The main ionic species present in soil are reported in table 1.

Table 1 - Main inorganic constituents in soil. *Components commonly found at concentration < 10^{-6} mol L⁻¹ with the exception of polluted sites

Chemical species	Major constituents (10 ⁻⁴ –10 ⁻² mol L ⁻¹)	Minor constituents (10 ⁻⁶ –10 ⁻⁴ mol L ⁻¹)	Others*
Cations	Ca ²⁺ , Mg ²⁺ , Na ⁺ , K ⁺	Fe ²⁺ , Mn ²⁺ , Zn ²⁺ , Cu ²⁺ , NH ₄ ⁺	Cr ³⁺ , Ni ²⁺ , Cd ²⁺ , Pb ²⁺
Anions	HCO ⁻ , Cl ⁻ , SO ₄ ²⁻	H ₂ PO ₄ ⁻ , F ⁻ , HS ⁻	CrO ₄ ²⁻ , HMoO ₄ ⁺
Moleculars	Si(OH) ₄ ⁰	B(OH) ₃ ⁰	

Metal ions and their equilibrium in soil. The activity of metal ions Mⁿ⁺ in the liquid phase (whose value for diluted solutions coincides with its concentration [Meⁿ⁺]) and their tendency to precipitate, can be defined by the solubility product constants of the compounds formed by precipitation. In soil, metal ions precipitate mainly as hydroxides, carbonates and phosphates but they may give rise to other solid phases by forming complexes with several organic and inorganic legands, comprising humates and fulvates.

Let us consider the following precipitation reaction for iron (III) hydroxyde:



given that:

$$K_{sp} = [\text{Fe}^{3+}] [\text{OH}^-]^3 = 10^{-39.30}$$

The activity of Fe³⁺ can be obtained as follows:

$$\begin{aligned} \log [\text{Fe}^{3+}] + 3\log [\text{OH}^-] &= -39.30 \\ \log [\text{Fe}^{3+}] &= -39.30 - 3\log [\text{OH}^-] \\ \log [\text{Fe}^{3+}] &= -39.30 - 3\log (10^{-14} - [\text{H}^+]) \\ \log [\text{Fe}^{3+}] &= -39.30 - 3(-14+\text{pH}) \end{aligned}$$

In this form, the relationship shows the dependence of Fe³⁺ activity on the pH. At pH = 5 for example, it will be:

$$\log [\text{Fe}^{3+}] = -39.30 - 3(-9) = -12.30$$

Similarly, the activity of the metal in aqueous systems in equilibrium with other oxides and hydroxides can be calculated. In figure 1, the trend of Fe³⁺ activity in the presence of Fe(III) oxides and soil-Fe as a function of pH is reported.

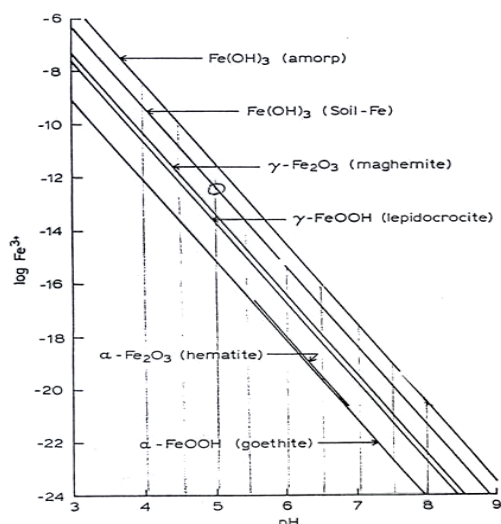
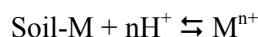
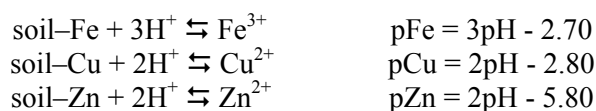


Figure 1
The activity of Fe³⁺ maintained by Fe(III) oxides and soil-Fe as a function of pH (Lindsay, 1979).

In soil, several heavy metals cannot be isolated and identified as discrete mineral phases (predominantly oxides and hydroxides), due to their extremely low concentration. In these cases, their activity can be determined directly in soil by considering soil as a homogeneous entity which can complex the metal (M) in the soil-M form (e.g. soil-Fe, soil-Cu; soil-Zn). In other words, the soil-M form is not considered as a crystalline phase but an amorphous phase in which the degree of structural order is higher than that of the freshly precipitated metal hydroxide. Systems of this type are described by the equilibrium:



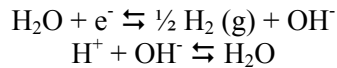
and the metal activity trend as a function of pH can be obtained by the following expressions (Lindsay, 1979) where function “p” stands for “-log”:



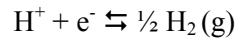
Unfortunately, these expressions are only theoretical since metal activity is the resultant of phase solubility where metals are present and varies depending on the redox, complexing and sorptive properties of soils together with their pH. A more comprehensive description of the equations concerning the activity of heavy metal in soils as a function of soil properties have been reported in the paper by Brümmer et al. (1983) and the lecturers interested in this topic are invited to refer to it for a better comprehension of such a complex phenomena.

Redox effect on metal concentration. Thanks to their metabolic activities, living organisms release electrons into the soil; under conditions of insufficient aeration, electron activity can cause a reduction in certain chemical species and so modify the solubility of some compounds, giving rise to real phase transformations. If redox potential is expressed in terms of pe (- log electron activity) it is possible to treat electrons in the same way as other chemical species and hence to describe both the chemical and electrochemical equilibria with a single equilibrium constant.

The term pe used in combination with pH (pe + pH) is an expression of a redox parameter of particular interest. In aqueous systems the value of pe + pH ranges from 0 to 20.78 (Figure 2) (Larsen 1983) owing to the fact that, in almost all soils, the dissociation of water to H₂(g) or O₂(g) defines the redox properties of the soils. In reducing environments, it will be:



from which the following equation results:



from which it is possible to obtain the equilibrium constant (K⁰):

$$K^0 = \frac{[\text{H}_2]_g^{1/2}}{[\text{H}^+][\text{e}^-]}$$

The expression when transformed into logarithmic form becomes:

$$\log K^0 = \frac{1}{2} \log [\text{H}_2]_g + \text{pe} + \text{pH}$$

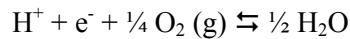
The equilibrium constant K⁰ for this reaction is defined as equal to 1 under standard conditions ([H⁺] = 1 mol L⁻¹; H₂(g) partial pressure = 1 atm) from which the following can be obtained:

$$\text{pe} + \text{pH} = -\frac{1}{2} \log [\text{H}_2]_g$$

when H₂(g) = 1 atm:

$$\text{pe} + \text{pH} = 0$$

Under oxidizing conditions, the following reaction will take place:



whose equilibrium constant is:

$$K^0 = \frac{[H_2]_g^{1/2}}{[H^+][e^-][O_2]_g^{1/4}}$$

The value of K^0 obtained from the tabulated standard Gibbs free energy of formation is equal to 20.78. In a diluted aqueous system, the water concentration is near to the unit and therefore the equilibrium when expressed in logarithmic form becomes:

$$pH + pe = 20.78 + 1/4 \log [O_2]_g$$

when $O_2(g) = 1 \text{ atm}$:

$$pe + pH = 20.78$$

The two calculated values (0 and 20.78) define the redox limit of the natural aqueous systems (figure 2).

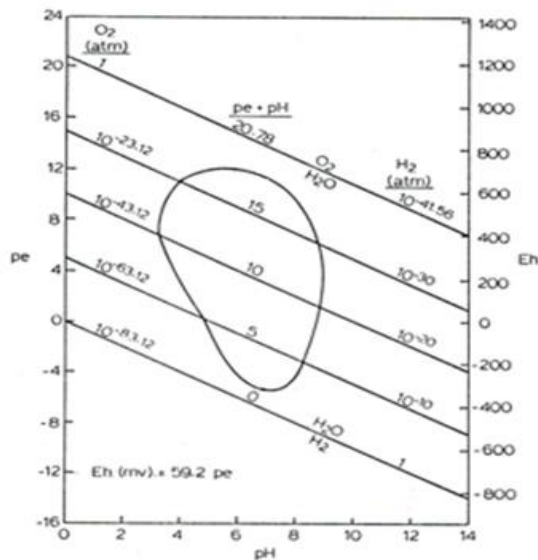
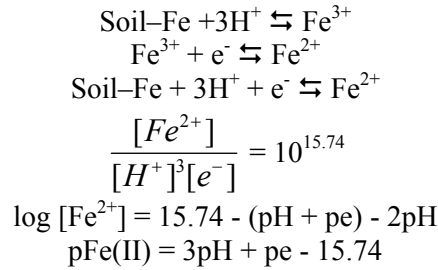


Figure 2

Equilibrium redox relationships of aqueous systems. The circumscribed area is representative of most soils (Lindsay, 1979).

At pH 7 and under oxidizing condition, the pe of soils generally ranges from +7 to +13; on the contrary, under reducing conditions it ranges from -2 to -6. In addition, the solubility of soil components and hence the activity of heavy metals in liquid phase is affected by its soil redox state.

Considering the following equilibria:



For (pe + pH) values which are lower than +16, Fe(II) activity is higher than that of Fe(III) and this is what should usually occur in soils (figure 3).

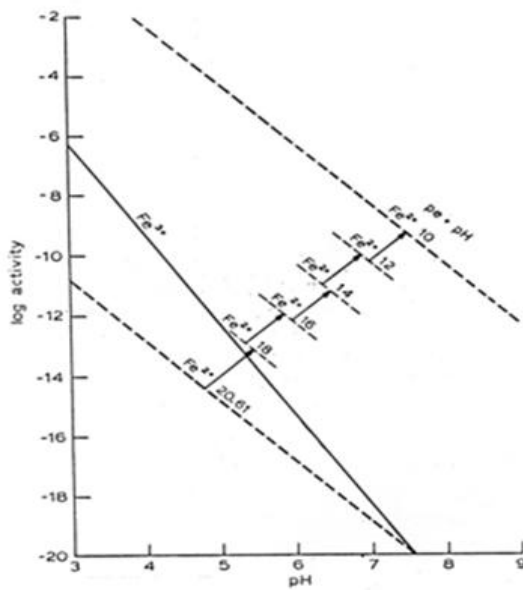


Figure 3

The effect of redox and pH on Fe(II) activity in equilibrium with Soil-Fe as a function of pH (Lindsay, 1979).

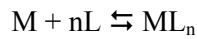
The effect of redox potential on metal activity can result as being very complicated: at alkaline pH the solubility of Zn, Cu, Cd and Pb is favoured by a reducing medium owing to the formation of soluble and stable complexes with carbonates, hydroxilic ions, and organic matter. Conversely, at soil acid pH values, reducing conditions disadvantage the solubility of the metals usually due to the formation of sulphites or other insoluble organo-mineral complexes. The effect of metal pollution is hence a function of metal speciation, pe + pH value, and the amount and type of legands in the soil.

Effect of complexation reaction on metal concentration. In soils, metal interact with both high and low weight organic molecules, including humic and fulvic acids. Soil organic matter contains endogenous and exogenous chelants and

legands able to complex metal ions. Complexation reactions reduce the precipitation of the metals by increasing the total amount of pollutant in the soil liquid phase (apparent solubility). In fact, legands, acting as carrier agents, mobilize metals along both the soil profile and water bodies. Nevertheless the concentration, and hence the toxicity, of the hydrated form of metal ions can be notably reduced by complexation with organic molecules. In addition, the formation of the complex may induce redox reactions resulting in the modification of the oxidation state of the metal and hence of its activity in the aqueous media. The effect of the complexation reaction on ion solubility depends on the stability of the complexes which have been formed. Let us consider a series of metal-legand (L) equilibria with unitary activity coefficients whose equilibrium constants are K_n :



This system can be also described by the equilibrium:



T

he ratio $ML_n / M \cdot L^n$ describes a new constant called β which, as it is easy to demonstrate, can be obtained by the following equation:

$$\beta_n = K_1 K_2 \dots K_n$$

from which if $n = 1$, $\beta_1 = K_1$.

β is known as the total formation constant. The total concentration of the metal will be equal to:

$$[M]_{\text{tot}} = [M(H_2O)_x]^{z+} + \sum_{i=1}^n [ML_i]$$

Therefore, metal concentration in the soil liquid phase is controlled by the concentration of all the different legand species in solution and by the stability of the complexes which have been formed.

The mobility of such complexes in the soil depends in turn on the charge of the different free and complexed species, whose distribution continuously vary along the soil profile according to the physical and chemical characteristics of the horizons which are passed through.

Natural detoxification processes in soil. Soil is a natural system with self-depurating capacities. These properties are mainly due its colloidal organic and inorganic fraction. Often research is focused on the activity of discrete soil

components such as clay minerals or humic substances instead of soil as a whole, in order to better understand the depurating mechanisms of soil depuration processes. Some experimental findings can give an idea of the complexity of the real systems and mechanisms acted on degrading inorganic and organic hazardous pollutants.

An interesting example from an environmental point of view is represented by the $\text{Cr}_2\text{O}_7^{2-}$ -galacturonate system: galacturonic acid is a hydrolysis product of pectins, the building blocks of plant walls which are continuously released into soils from plant roots and which accumulate in the rizosphere to form root mucigel.

The redox reaction to Cr(III) by Cr(VI) in the $\text{Cr}_2\text{O}_7^{2-}$ -galacturonate system shows very slow kinetics, whereas the same reaction speeds up in the presence of Cr(III) or Cu(II) (Deiana et al., 1991). This system represents one of the Cr(VI) detoxification mechanisms; in fact, while Cr(III) is produced, the system improves its capacity to control the concentration and diffusion of one of the most hazardous anionic species in the environment (figure 4).

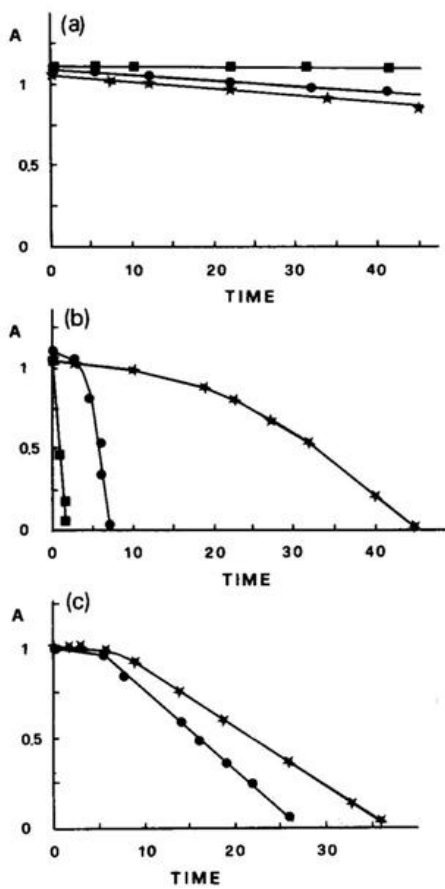


Figure 4

Kinetics of the reduction of Cr(VI):

A) Cr(VI)-HGAL system;

B) Cu(II)-Cr(VI)-HGAL system;

C) Cr(III)-Cr(IV)-HGAL system.

() pH = 3.2; (•) pH = 4.2;*

(▲) pH = 5.0

(Deiana et al., 1991).

HGAL: polygalacturonic acid.

Most substances employed in agriculture for plant protection end up in the soil where they may have the same fate as other organic compounds generated by human activities.

In the soil liquid phase, the main organic constituents are carboxylic acids, amino acids and monosaccharides (concentration range from 10^{-3} to 10^{-5} mol L⁻¹); minor constituents may be considered as all those organic species in concentrations lower than 10^{-5} mol L⁻¹, such as proteins, phenols, alkaloids and even herbicides, fungicides, insecticides, polychlorobiphenils (PCBs), polycyclic aromatic hydrocarbons (PAHs), hydrocarbons, solvents, and all substances which reach the soil as a consequence of human activities. These compounds are distributed within soil solid, liquid and gaseous phases where they may be involved in:

- 1) immobilisation processes (adsorption, precipitation, etc...);
- 2) biotic and abiotic degradation processes;
- 3) environmental diffusion (leaching, erosion, volatilisation, root uptake...).

Factors affecting the retention and degradation of agrochemicals in soil are connected to the chemical and physical characteristics of the pollutants (solubility, volatility, n-octanol/water partition coefficients – K_{OW} , acidic constant – K_a) and to those of soil (pH, texture and organic matter content).

a) Quinalphos-montmorillonite interaction. In the following example it is interesting to note how the type of metal at the interlayer of an expandable clay can influence and modify the mechanism and rate of degradation of an insecticide owing to the formation of different complexes between metal and insecticide. The catalytic activity of montmorillonite towards quinalphos (*O,O*-diethyl *O*-quinoxalin-2-yl phosphorothioate) insecticide is only expressed when montmorillonite is exchanged with Cu, Na and K. The reaction induced by Cu-montmorillonite on the adsorbed insecticide is different from that induced by Na- and K-clay either with regard to the identity of the degradation products or the kinetics of the degradation process (Figure 5) (Pusino et al., 1988).

Two different degradation pathways have been proposed for quinalphos (Figure 6). Na-clay, quinalphos is hydrolysed by the nucleophilic attack of water (or hydroxide ions) on the phosphorus atom followed by displacement of an ethoxyl group to give *O*-ethyl *O*-quinoxalin-2-yl thiophosphoric acid. In Cu-clay, the proposed mechanism requires the initial coordination of the exchangeable ion to form a six-membered chelate complex involving the nitrogen ring and the phosphorothioate sulphur of quinalphos.

This interaction increases the electrophilic character of phosphorous and simultaneously weakens the P-O-quinoxaline bond, facilitating the cleavage of this bond by the nucleophilic attack of water. The degradation product, 2-hydroxyquinoxaline, which is formed in the clay interlayer remains absorbed therein. The slower rate of decomposition observed for Fe- and Al-clay may be ascribed to the lower tendency of these cations to form complexes via (S,N)-coordination.

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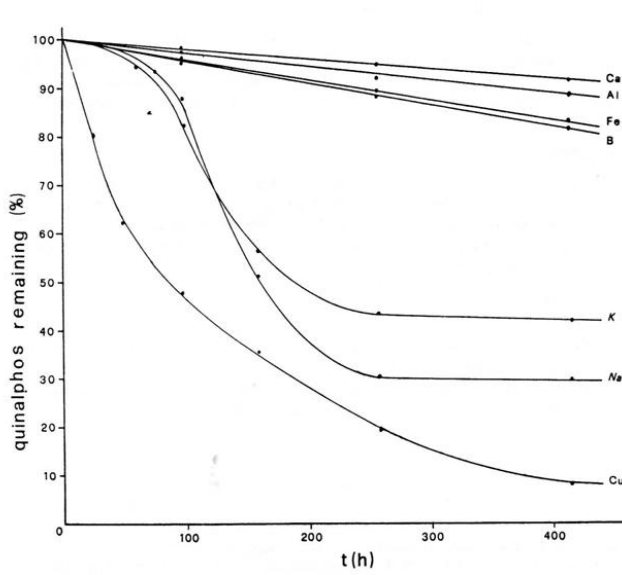
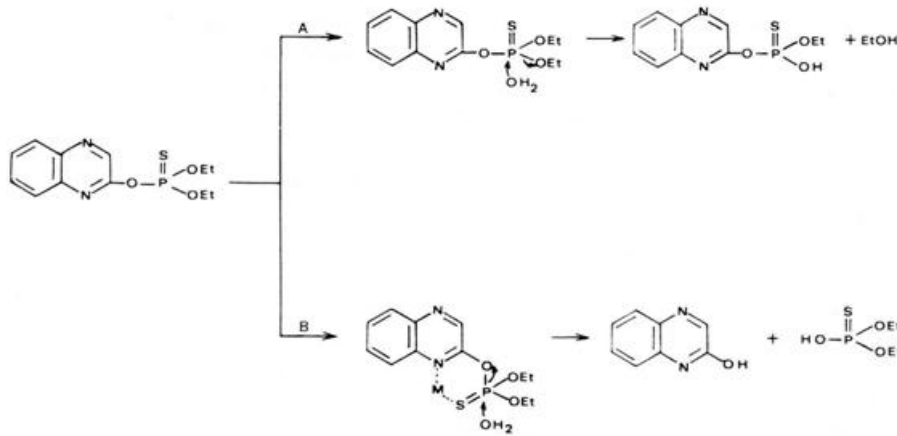


Figure 5

Effect of cations on the hydrolysis of quinalphos by clays exchanged with different metals (Pusino et al., 1988).

Figure 6 - Proposed mechanisms for hydrolysis of quinalphos (Pusino et al., 1988).



b) Effect of undesalted dissolved organic matter from compost on the persistence, adsorption, and mobility of cyhalofop herbicide in soil. Cyhalofop-butyl (butyl (R)-2-[4-(4-cyano-2-fluorophenoxy)-phenoxy]propionate), is a pro-herbicide for the post-emergence control of weeds in rice. It is an acetyl CoA carboxylase inhibitor. Its active form is the cyhalofop-acid (figure 7): in soil, cyhalofop-butyl is easily hydrolyzed to its acid form. The effect of dissolved organic matter (DOM) from two composts on the behaviour of cyhalofop, in both buthyl ester and acid form, has been investigated in paddy field sediment and in forest soil at low (TOC 4.1%) and high organic matter content levels (TOC 7.3%), respectively.

The degradation of cyhalofop-butyl in the sediment was slow, giving cyhalofop-acid as the only metabolite, whereas in forest soil, the process was faster, and three byproducts were detected (cyhalofop-acid, cyhalofop-amide, cyhalofop-diacid, figure 7). The degradation of cyhalop, in both its buthyl ester and acid form, is mediated by soil microorganisms as confirmed by the stability of these species in sterile soils.

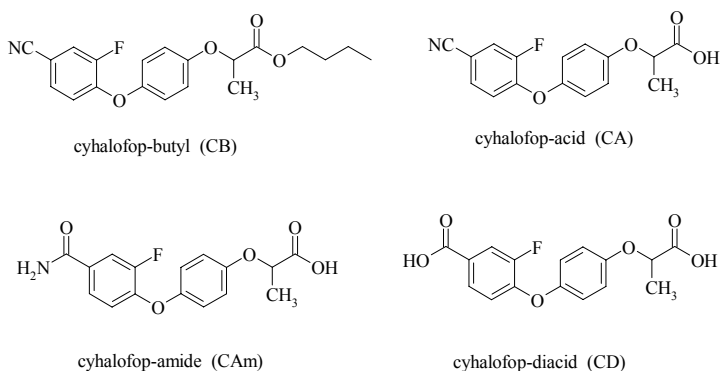


Figure 7

Structure of cyhalofop-butyl and its hydrolysis by products.

Cyhalofop-butyl solubility in DOM solution at pH 6.0 results as similar to that in water at the same pH. Its unchanged solubility in the presence of DOM indicates that no interaction occurs between hydrophilic DOM and lipophilic pro-herbicide. On the contrary, the doubled solubility of cyhalofop-acid at pH 6.0 suggests an interaction of the anionic form of cyhalofop-acid (pH_a 3.8) with the acidic groups or metal cations which DOM is rich in.

Table 2 - Cyhalofop-butyl and cyhalofop-acid solubility in the presence of DOMs at pH 6 (Blasioli et al., 2008). ^a Solution at maximal solubility. DOM_A and DOM_M , respectively, from a compost formed of winery byproducts and urban plant trimmings and a compost formed of municipal solid waste and lignocellulosic material.

Solvent medium	cyhalofop-butyl solubility (μM)	cyhalofop-acid solubility (μM)
Water solution	0.83 (\pm 0.21)	322.0 (\pm 3.9)
DOM_A solution ^a	0.89 (\pm 0.28)	638.0 (\pm 4.7)
DOM_M solution ^a	0.85 (\pm 0.26)	554.0 (\pm 18.1)

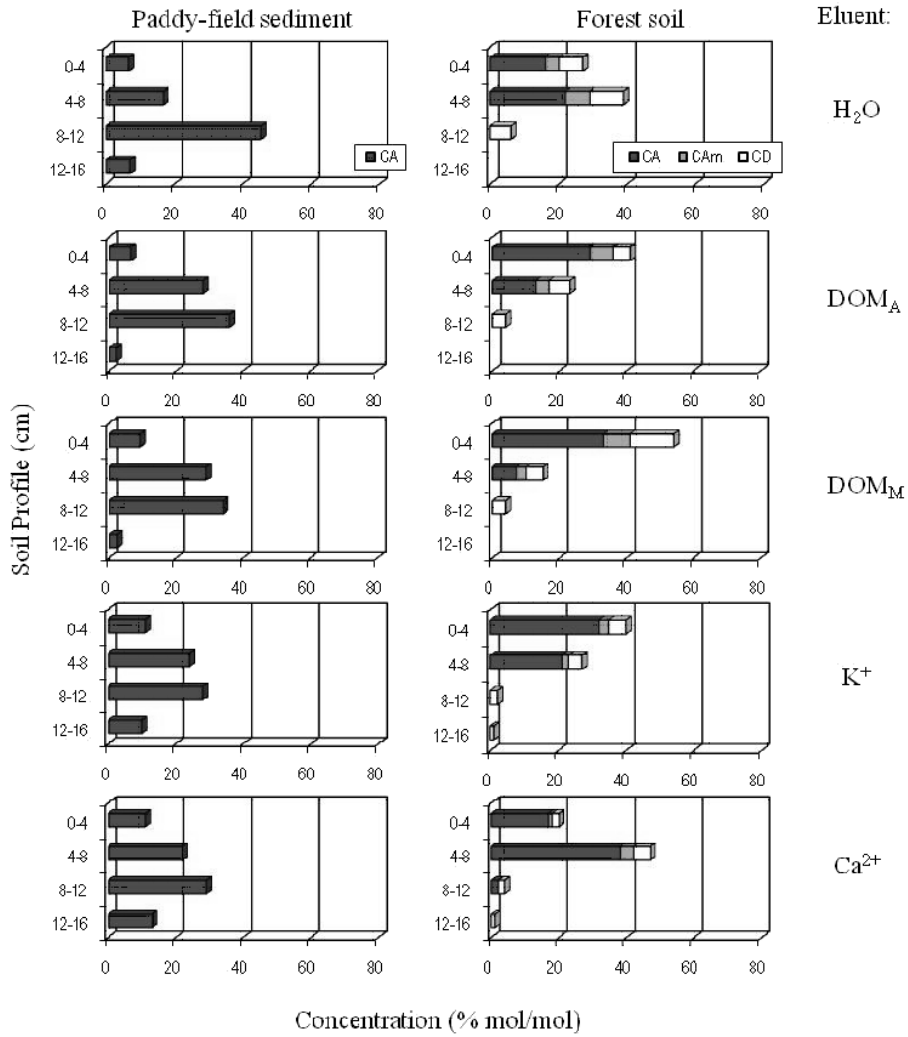
The adsorption of cyhalofop-butyl and cyhalofop-acid is higher in forest soil than in the paddy-field sediment. Soil pre-treatment with DOMs significantly decreases the adsorption of cyhalofop-butyl, whereas it increases that of cyhalofop-acid. The adsorption of cyhalofop-acid is reversible on paddy-field sediment but irreversible on forest soil. Reversible-type adsorption is due to polar-ionic interactions: DOM, in fact, on interacting with soil, increases either the number of organic sites available for interaction with cyhalofop-acid or increases the base metal saturation

degree, resulting in the formation of additional cations and water bridges which are able to retain the cyhalofop-acid.

On the contrary, irreversible-type adsorption results from hydrophobic interactions between DOM and cyhalofop-acid: metal ions contained in DOM, after complexation with soil organic matrixes, reduce negative electrostatic repulsion and favour hydrophobic interactions.

This interpretation of adsorption/desorption results are confirmed by mobility experiments made on soil columns (figure 8).

Figure 8 - Mobility of cyhalofop-acid and byproducts along the profile of soil columns leached with DOM or metal solutions (Blasioli et al., 2008)



The presence of DOMs in the eluting solution reduces cyhalofop-acid mobility along both soil profiles in comparison to soils eluted with distilled water.

In paddy-field soil, which is poor in organic matter, the increase in the degree of base metal saturation on soil surfaces, brought on by DOM, favours the creation of cation and water bridges with the carboxylate moiety in cyhalofop-acid.

In forest soil, with higher organic matter content, the base metals contained in the DOM solutions, by decreasing the repulsive forces between the negative charges of both soil organic matter and the carboxylate groups of cyhalofop-acid and other acid byproducts, reduces their movement along the soil profile (figure 8).

In this context, bivalent and monovalent cations in the DOM solutions play different roles in the mobility of the herbicide along the soil profile. In fact, the presence of K^+ ions in the eluting solution reduces the mobility of cyhalofop acid in soils, whereas the effect of Ca^{2+} ions is not so marked.

Such differences can be explained by the formation of inner sphere metal bridges between the cyhalofop-acid carboxylate group and the K^+ ion and of the outer sphere water bridge with the Ca^{2+} ions.

Since the former type of interaction is stronger, the metal bridge reduces the leaching of carboxylic acids along the soil to a greater extent than is found for the water bridge.

Hence, the different strengths of formed complexes are a function of the different dimensions of K^+ and Ca^{2+} ions and can be considered responsible for the difference in cyhalofop-acid mobility at different soil depths.

In the light of the findings presented herein, it is possible to conclude that the metal component of DOM, which is not usually considered in studies on the fate of agrochemicals in soil, has to be taken into account especially with negatively ionisable pesticides, in order to predict and to describe their mobility in soil.

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