

## Copper soil retention capacity after intensive and repeated pig slurry applications

*Capacité de rétention du cuivre dans un sol soumis à des épandages  
intensifs et répétés de lisier de porc.*

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### Abstract

*The high metal contents of pig slurry spread on agricultural fields can bring large amounts of metals to the environment. This work is part of a large study aimed to determine the impact of land pig slurry applications on soil and water quality, with emphasis to metal distribution and speciation within such systems, and to soil retention capacity. This paper presents the main results of field and laboratory investigations about copper accumulation in a soil after high loads of pig slurry spreading.*

*Samples were regularly collected on an experimental specially equipped field so-called "Solepur". On this field, numerous pig slurry applications were performed from 1991 to 1995, approximately corresponding to the amount which might have been spread over one century. The "Solepur" process can be considered as a simulation model for what happens to metals in pig slurry under normal field conditions over a long period of time.*

*Total concentrations and speciation data of copper were measured during five years within four compartments: pig slurry, soil, drainage water and plants. It was then possible to calculate metal fluxes and budgets.*

*The results showed accumulation of copper in bioavailable form in the soil surface layer, in the same form than in pig slurry, i.e. mainly "bound to organic matter", and very little downward metal movement was observed. Copper concentrations in drainage water were low and confirmed metal retention in the soil.*

*Laboratory experiments carried out on copper soil retention capacity showed an enhanced adsorption of copper in the soil after high pig slurry applications. This result supports the idea that saturation of soil by copper from pig slurry is unlikely.*

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## Résumé

Les teneurs élevées en éléments métalliques contenus dans les lisiers épandus en agriculture peuvent entraîner des apports conséquents à l'environnement. Le but de ce travail est de déterminer le devenir de ces métaux issus des épandages de lisiers et de préciser les éventuels risques de pollutions des sols et des eaux par ces éléments en abordant l'aspect de la spéciation métallique et de la capacité de filtration du sol. Cet article présente les principaux résultats d'un travail au champ et en laboratoire sur l'accumulation de cuivre dans un sol soumis à des doses importantes apportées par les épandages de lisier de porc.

Les échantillons ont été prélevés régulièrement sur un dispositif expérimental appelé SOLEPUR. Sur cette parcelle, de nombreux épandages de lisiers de porcs ont été effectués entre 1991 et 1995, correspondant globalement à ce qui serait épandu en 100 ans.

Les concentrations totales en cuivre ainsi que la spéciation ont été mesurées sur 4 compartiments : lisier de porc, sol, eau de drainage et les végétaux.

Les résultats montrent que l'accumulation du cuivre dans le sol s'effectue sous une forme biodisponible et dans une fraction liée à la matière organique. Il n'est pas observé de migration du cuivre en profondeur. Les concentrations en cuivre dans les eaux de drainage étaient très faibles, ce qui confirme la rétention de cet élément par le sol.

Un essai en laboratoire sur l'évaluation de la capacité de rétention du sol en cuivre montre une capacité supérieure dans le sol soumis à des épandages intensifs.

## 1. Introduction

Intensive pig farming practices engender large volumes of pig slurry with no other solution for farmers than land disposal. This common practice results in serious environmental problems such as nitrate and phosphate contamination in ground waters and rivers.

Another issue less studied is metal pollution: pig slurry actually contains high concentrations of metals such as Cu, Zn, Fe, Mn, Co, Cd (Meeus-Verdinne *et al.*, 1986) and in Brittany a long-term study performed by Coppenet *et al.* (1993) concluded in a regular increase of copper and zinc concentrations in soils.

The present work is a five-year study about copper brought by heavy and repeated pig slurry applications onto agricultural lands (L'Herroux *et al.*, 1997). For this purpose, an experimental field was set up by the Cemagref<sup>1</sup> of Rennes (Martinez, 1997) and pig slurry was regularly spread on it for 5 years. Drainage water was daily sampled, making possible an assessment of metal fluxes. This experimental

procedure appeared as a good model for simulating what happens to metals in pig slurry under normal field conditions over a long period of time.

Metal speciation is known to be more appropriate than total concentrations to assess metal impact on the environment since each fraction of the speciation can provide information on metal mobility and bioavailability. Sequential extractions in soil and slurry were performed according to the procedure described by Tessier *et al.* (1979) for the partitioning trace metals into five fractions likely to be affected by changes in environmental conditions.

Laboratory experiments conducted on soil samples in 1995, after 4 years of pig slurry spreadings, showed the adsorption capacity of the soil in function of pH and depth. Surface sorption can regulate the solubility of metals in the soil solution and influence the uptake of metals by plants.

## 2. Materials and methods

The Solepur treatment unit, detailed in a previous paper (Martinez, 1997), was set up in 1990 in North-Finistère (Brittany) by the Cemagref of Rennes. It consisted of a 3280-m<sup>2</sup> field hydrologically-isolated from the surrounding soil at a depth of 80 cm and equipped to recover all the leachate. Drainage water flowed under gravity and passed through a field laboratory fitted with an on-line flowmeter and an Isco autosampler to collect daily water samples. Repeated high pig slurry applications were performed on the experimental field from 1991 to 1996 at a mean rate of 1000 m<sup>3</sup> ha<sup>-1</sup> yr<sup>-1</sup>, representing 4571 m<sup>3</sup> ha<sup>-1</sup> of slurry over the 5-year experiment. Another smaller field similarly set up and equipped did not receive any spreading and was used as a control plot. *Lolium perenne* was cultivated on both fields and cut down twice a year.

### Sampling

*Soil* : Soil samples were annually collected in March at three depths (per layer: 0-20, 20-40 and 40-60 cm depth) and stored in polyethylene vials at room temperature.

*Pig slurry*: During each slurry application representative slurry samples were collected, stored in polyethylene vials and frozen.

*Drainage water*: One litre of drainage water was daily collected in 250-mL fractions every 6 hours. The water samples were transferred into 125-mL polyethylene bottles, acidified with concentrated HCl to reach a pH of 2 and stored until analysis.

### Total copper

To determine the total copper concentrations in slurry and soil, the samples were digested by a mixture of strong acids (65% HNO<sub>3</sub>, 30% H<sub>2</sub>O<sub>2</sub> and 48% HF).

## Speciation

*Soil and pig slurry* The speciation protocol described by Tessier *et al.* (1979) is based on successive leachings of the samples by different reagents. This procedure enables to split metals into five fractions likely to be affected by changes in environmental conditions (Table 1).

	Metal fractions	Processes responsible for metal release
	(I) "Exchangeable".	Weak complexes, ion exchange
	(II) "Bound to Carbonates".	pH decrease (pH = 5)
Soil	(III) "Bound to Fe or Mn Oxides"	Reduction of metal oxides
	(IV) "Bound to Organic Matter"	Degradation of organic matter
	(V) "Residual".	No possible release, metals hold in mineral structures

*Table 1*  
*Informations obtained from the metal speciation procedure*  
*(Tessier et al. 1979).*

## Copper adsorption experiments

This experiment was conducted to compare copper soil sorption between the two fields (experimental and control) and determine whether copper soil "saturation" can occur. Soil samples used for the experiment were collected from the experimental field in 1995, after 4 years of pig slurry spreading, at 3 depths (0-20 cm ; 20-40 cm and 40-60 cm) and at the surface of the control field (0-20 cm). 100-mL solutions of copper chloride ranging from 0 to 1000 mg L<sup>-1</sup> were added to a 20-g soil sample to determine copper adsorption. The pH was adjusted to 6.0 to reach the initial pH of the surface soil before the beginning of the experiment in 1991. The mixture was shaken at room temperature for 24 hours. Previous experiments showed that equilibrium was reached within this time. The samples were centrifuged, filtered through 0.45 µm membranes and stored in 20-mL Teflon vials.

## Analysis

Copper concentrations in solution were determined using either flame or flameless absorption spectrophotometry, according to the sample concentration; a standard addition technique was used to account for possible matrix effects.

## **3. Results**

*Pig slurry :*

The mean copper concentration in fresh pig slurry over the 5 years of spreadings was  $40 \text{ mg Cu.kg}^{-1}$  (SD=15, n=43). This concentration is in agreement with values reported by other authors (Meeus-Verdine *et al.*, 1986; Bernal *et al.*, 1992). The amount of pig slurry spread on the experimental field after the five years of the experiment was equivalent to  $4571 \text{ m}^3 \text{ ha}^{-1}$ . It resulted in a copper supply of two hundred kilograms.

Results of copper speciation in pig slurry indicated a large percentage of metal in the "Organic" fraction (66%) and in the "Oxides" fraction (28%) The low percentage observed in residual form (<1%) indicated that copper brought by pig slurry was in bioavailable forms.

*Soil :*

Copper clearly accumulated in the soil surface layer ( $38 \pm 8 \text{ mg Cu.kg}^{-1}$ ) and slightly in the middle layer ( $20 \pm 5 \text{ mg Cu.kg}^{-1}$ ) (Figure 1). No significant change occurred in total copper concentration for the deepest layer (40-60 cm), indicating no downward metal movement.

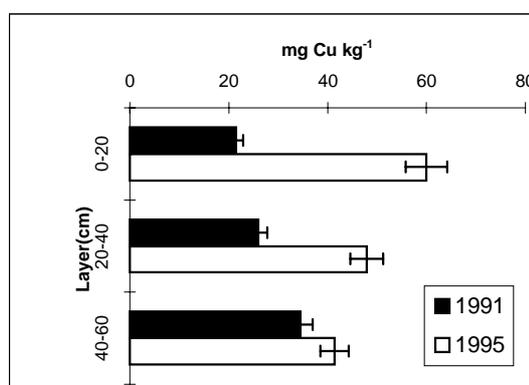
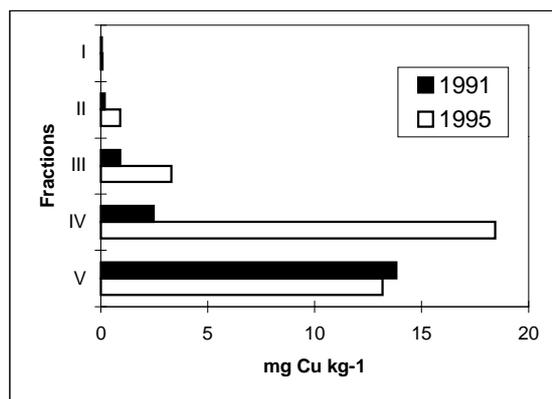


Figure 1. Total copper concentrations in the soil at the three depths in 1991 and 1995. Error bars indicate standard deviation (n = 4).

Soil speciation in the surface layer showed that copper at the beginning of the experiment (1991) was mainly in the "Residual" fraction. After 4 years of spreadings metal concentrations increased in the "Organic" fraction, and slightly in the "Oxides" fraction (Figure 2).



*Figure 2.*  
*Speciation of copper in the soil surface layer (0-20 cm) in 1991 and 1995.*

*Drainage water :*

Copper total concentrations in drainage water from the experimental field were low, below  $5.0 \mu\text{g L}^{-1}$  (average of  $3.4 \pm 0.9 \mu\text{g Cu L}^{-1}$ ,  $n=178$ ), for the drainage season 1995/96. These concentrations were higher than the water from the control field (average of  $0.7 \pm 0.2 \mu\text{g Cu L}^{-1}$ ).

The total amount of copper leaving the field by lixiviation over the five-year experiment, from 1991 to 1995, was  $0.04 \pm 0.01 \text{ kg ha}^{-1}$ .

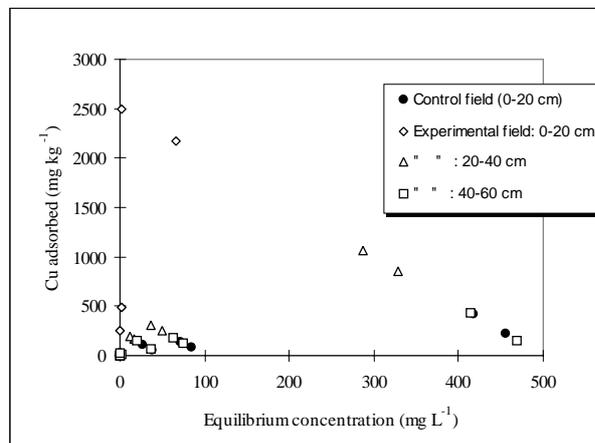
*Grass :*

Slurry inputs to the soil did not increase copper concentrations in the grass (*Lolium perenne*) in spite of slightly higher concentrations in the herbage from the experimental field than those from the control plot with concentrations, expressed in mg Cu per kg of dry matter, of respectively  $14.7 \pm 9.7$  ( $n = 8$ ) and  $2.3 \pm 2.2$  ( $n = 2$ ).

*Adsorption of copper by the soil (pH=6.0) :*

The soil surface of the experimental field adsorbed much more copper than the other layers. For an equilibrium concentration of  $100 \text{ mg L}^{-1}$ , copper adsorption was more than  $3000 \text{ mg Cu kg}^{-1}$  for the surface soil layer and respectively 450 and  $140 \text{ mg Cu kg}^{-1}$  for the intermediate (20-40 cm) and deepest (40-60 cm) layers. The adsorption by the surface layer of the control field was only  $110 \text{ mg Cu kg}^{-1}$ .

Adsorption curve of the soil surface of the control field was similar to that of the deepest layer (40-60 cm) of the experimental field.



*Figure 3.*  
*Adsorption of copper at pH=6.0 for different soils in 1995 (0-20 cm, 20-40 cm, 40-60 cm of the experimental field and 0-20 cm of the control field).*

#### **4. Discussion**

Copper brought by pig slurry appeared to be mainly in bioavailable forms, forms likely to release metal into soil solution. But the copper concentrations in drainage water remained quite low, showing a retention of metal by the soil, particularly in the upper layer. The regular ploughing of the field to a depth of 30 cm was probably responsible for the copper concentrations increase as far as 40 cm.

Metal fractions in soil were in accordance with the slurry speciation: copper input from pig slurry in the "Organic" fraction was assessed around  $92 \pm 19 \text{ kg ha}^{-1}$ , and in the same fraction of the soil speciation the input was estimated at  $90 \text{ kg ha}^{-1}$ . Copper bound to organic matter in slurry was probably "non reactive" or, as an alternative hypothesis, copper introduced by slurry additions forms strong organic complexes with organic components in the soil, mainly humic substances (Williams *et al.*, 1987; Hesterberg *et al.*, 1993). The quantity of copper brought to the field in the "Organic" fraction and the quantity of metal found in the same fraction in the soil were very close. This result reinforced the idea that copper stays in the soil bound to the organic matter of the pig slurry.

Thus the intensive slurry spreadings increased the copper retention ability of the surface soil. This retention ability decreased with depth showing that copper complexing agents stayed in the soil surface and no downward movement occurred. This conclusion does not contradict the idea that modifications of organic matter occur in this field, but these changes are too slight or the organic molecules that are formed have too low complexation properties to release a large part of copper into solution and make it bioavailable.

#### **5. Conclusion**

The high metal concentrations contained in pig slurry can introduce large amount of copper and other metals in agricultural fields where spreading is a common practice.

Copper was found in bioavailable forms in pig slurry, hence a possible effect on plants (phytotoxicity) can be anticipated. This study showed that metal from pig slurry stayed mainly in the same fraction in soil, and no downward metal movement was observed.

An important result of this study is the increase of the soil copper retention ability after intensive pig slurry spreadings. This result supports the idea that saturation of soil by copper from pig slurry is unlikely. Copper stays in the soil, associated with the organic matter brought by pig slurry.

The metal was found in the soil in bioavailable form, so further studies are necessary to find under which conditions copper could be released in the soil solution and become toxic for the crops, or could be lixiviated from the field and increase metal concentration in ground water. Actually some modifications of natural conditions, such as changes of pH, Eh or soil composition, are expected over a long time scale and a good understanding of all of these processes is necessary for predicting the fate of metals. For example waterlogging can induce reducing conditions and lead to degradation of organic matter.

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