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# Quantification of Trace Elements fluxes (As, Cd, Cu, Pb, Zn) into agricultural fields amended with pig slurry

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## Abstract

The accumulation of trace elements in agricultural soils may have long-term implications for quality of crops. Pig slurry is known as a major source of copper or zinc, because these elements are supplemented in pig feed. But the inputs in arsenic, cadmium or lead are not well quantified. The aims of our study were to quantify the trace elements inputs by pig slurry spreading, to compare them to other sources and to estimate the balances. This analysis was performed on 24 fields located in the South-West of France. Copper and zinc fluxes from pig slurry corresponded to 90 % of the total input fluxes. Soils accumulated these elements with an annual increase of the metal stock equal to 0.5 % for copper and 0.3 % for zinc. For cadmium, the major source was the phosphate fertilizers (60 % of the total inputs). Accumulation of As and Cd in soils was low (2,6 g/year/ha and 1,2 g/year/ha respectively). The major contamination source for lead was the atmospheric inputs.

## Introduction

Inorganic fertilizers lime and manure or sludge are potential sources of trace elements [1, 2]. It is well known that the pig manure is an important source of copper or zinc, because these trace elements are added to pig feed. More than 40% of the total copper or zinc inputs could be due to livestock manure [3]. But the inputs of arsenic, cadmium or lead are not well quantified in pig manure.

Soils accumulate trace element and this accumulation in agricultural soils can have long-term consequences on the quality of crops [4]. In a context of limitation of trace elements contents in feed and food, it is essential to correctly quantify the inputs and the balance of trace elements at the field scale.

The aim of our study was (1) to quantify the inputs of trace elements by the application of pig slurry, (2) to compare them to other sources of trace elements (fertilization, atmospheric inputs) and (3) to estimate the input-output balances.

## Materials and Methods

### *Sampling*

In the southwest of France, 24 fields were sampled: 13 sunflower fields including 7 with spreading pig slurry, 11 corn fields including 10 with regular application of pig slurry. Surface horizons of soil (0-30 cm), pig manures and crops were collected and analyzed for trace elements contents.

### *Analytical methods*

After sampling, soil samples were dried at 50°C and 2 mm sieved. Soil chemical analyses were carried out by a soil testing laboratory (Laboratoire d'Analyses des Sols, INRA Arras, France) according to standardized French procedures. Before analysis of total major and trace elements, soil samples were digested by HF, HClO<sub>4</sub>, and HCl. Pig manures were freeze-dried and digested at 90°C using Digiprep system.

Maize and sunflower samples were dried at 50°C and dissolved in 70% HNO<sub>3</sub> (7 mL) and H<sub>2</sub>O<sub>2</sub> (1ml) heated in a microwave oven. The concentrations in the digests of soils, pig manure or plants were determined by ICP-AES for copper and zinc and by ICP-MS for arsenic, cadmium and lead at the LCABIE laboratory. The validity and accuracy of digestion of samples were checked by using controls and certified references.

### *Balance calculation*

Inputs due to manure application were calculated using these data and information provided by farmers. An investigation allowed to identify and to quantify the contributions of other sources of trace

elements in the field. The atmospheric inputs were estimated using Ademe data (Sogreah, 2007). The inputs by fertilizers were calculated from an estimation of the mean annual volume provided by the farmers and Ademe data (Sogreah, 2007).

The outputs are maize grains or sunflower seeds exportations. The lixiviation fluxes were neglected, according to the AROMIS results.

## Results and discussion

### *Trace elements concentrations*

**Table 1 : Trace elements concentrations in soils, pig slurry, maize and sunflower**

	Number of samples	Median concentration in mg/kg of dry matter ( <i>minimum-maximum</i> )				
		Cd	Pb	As	Cu	Zn
Soil	24	0,24 (0,09-0,75)	21,9 (8,99-60,0)	11,6 (0,69-36,9)	16,6 (6,5-80,2)	67,8 (13,4-127,7)
Pig slurry	17	0,33 (0,17-0,42)	1,13 (0,53-2,06)	1,32 (0,76-2,08)	355 (172-502)	969 (623-1926)
Maize seeds	11	0,013 (0,009-0,026)	0,070 (0,036-0,41)	0,007 (0,004-0,014)	1,2 (1,1-2,2)	21,1 (9,4-24,6)
Sunflower seeds	13	0,245 (0,051-0,385)	0,267 (0,045-2,996)	0,005 (0,002-0,012)	18,2 (9-21,2)	47,8 (29,6-60,2)

As seen in table 1, the studied soils show no obvious anomalies and correspond to a diffuse contamination of Cu, Zn, Pb, Cd and As. The contents follow this order: Zn>Cu>Pb>Cd>>As. There was no significant difference with the results of RMQS, French soil quality monitoring network (Jolivet, 2006) on agricultural soils in the same region. In pig slurries, the median concentrations of copper are 355 mg/kg DM and 969 mg zinc/kg DM, which in the case of copper is higher than the values of the European study AROMIS (AROMIS, 2005), 237 mg Cu/kg DM and 926 mg Zn/kg DM. On the other hand, the median concentrations of cadmium and lead in pig slurry (0.331 and 1.13 mg / kg DM) were lower than those of the European study (0.5 mg Cd/kg and 3.6 mg Pb/kg DM). We found 1.32 mg/kg DM of median arsenic content in pig slurry in our survey, which is the same as the few values available in the literature. Finally, in plants, the concentrations of cadmium, copper, lead and zinc are much higher in the sunflower seeds than in maize. Trace elements contents measured in all fields were clearly below regulatory thresholds for animal feed (regulatory thresholds: 2 mg/kg for As, 1 mg/kg for Cd, 10 mg/kg for Pb).

### *Trace elements in agricultural soils*

The copper contents in soils were mainly explained by the historical land use. Some fields were vineyards in the past. As copper is used as a fungicide of the vine, it has accumulated in these soils. This past land use had a greater effect than the spreading of pig slurry. But on soils that have only been cultivated in cereals or oilseeds, the copper content of soils was explained by the volume of manure applied to soils. For other trace elements, concentrations in soil were systematically related to concentrations of Fe or Mn. These elements coming from the pedogeochemical background, we thought that As, Cd, Pb and Zn came from the parent rock material rather than a source of accurate contamination.

### *Trace elements in maize and sunflower*

The concentrations of trace elements in maize were not related to a parameter of soil or to an indicator of bioavailability. For sunflower, we highlighted a trend depending on the pH of the soil and manure use: As, Cu and Cd concentrations in sunflower seeds were higher in acidic soils not receiving manure. But it was the opposite for Pb.

### *Quantification of trace elements inputs and input-output balances*

In sunflower fields, applying pig slurry increased Cu and Zn inputs, while it allowed lower inputs of Cd (figure 1). We found that inputs of copper and zinc from pig manure accounted for more than 90% of the total inputs to soils (figure 2). The copper and zinc balance was positive and the soil accumulated these elements with an annual increase of metal stock equal to 0.5% for copper and 0.3% for zinc. For cadmium, the main source was the phosphate fertilizer (60% of total inputs). As and Cd

accumulation in soils was low (2.6 g/year/ha and 1.2 g/year/ha respectively on both crops together). Important source of contamination for lead was atmospheric inputs.

### Conclusion and perspectives

As, Cd and Pb concentrations are low in pig slurry. The accumulation of trace elements in agricultural soils is low, except for copper in the case of a massive use of manure. The past use of soil as vineyards implied an increase of the concentration of copper in soil. But the effects on crops are not clear, probably due to the presence of different varieties of maize and sunflower between fields, which could hide soil variability.

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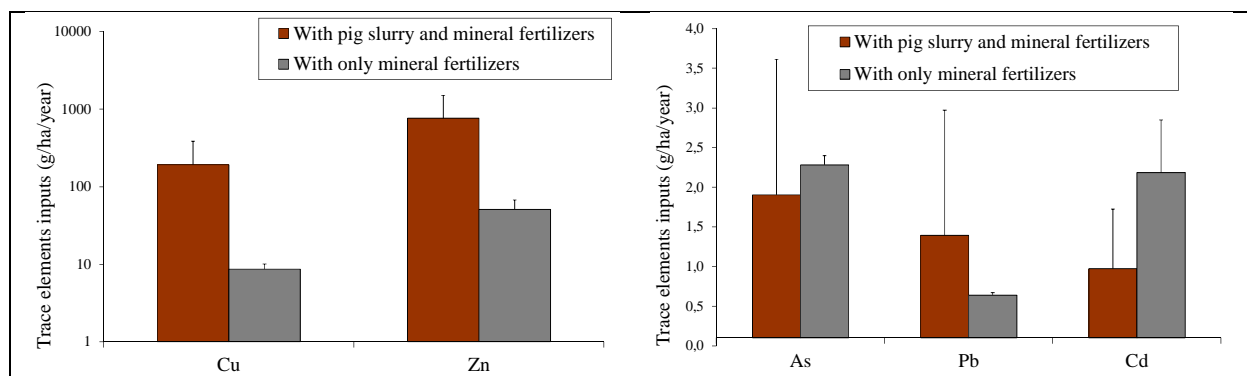


Figure 1: Trace elements inputs on soils from organic and mineral fertilizers in sunflower fields (vertical bar: standard deviation)

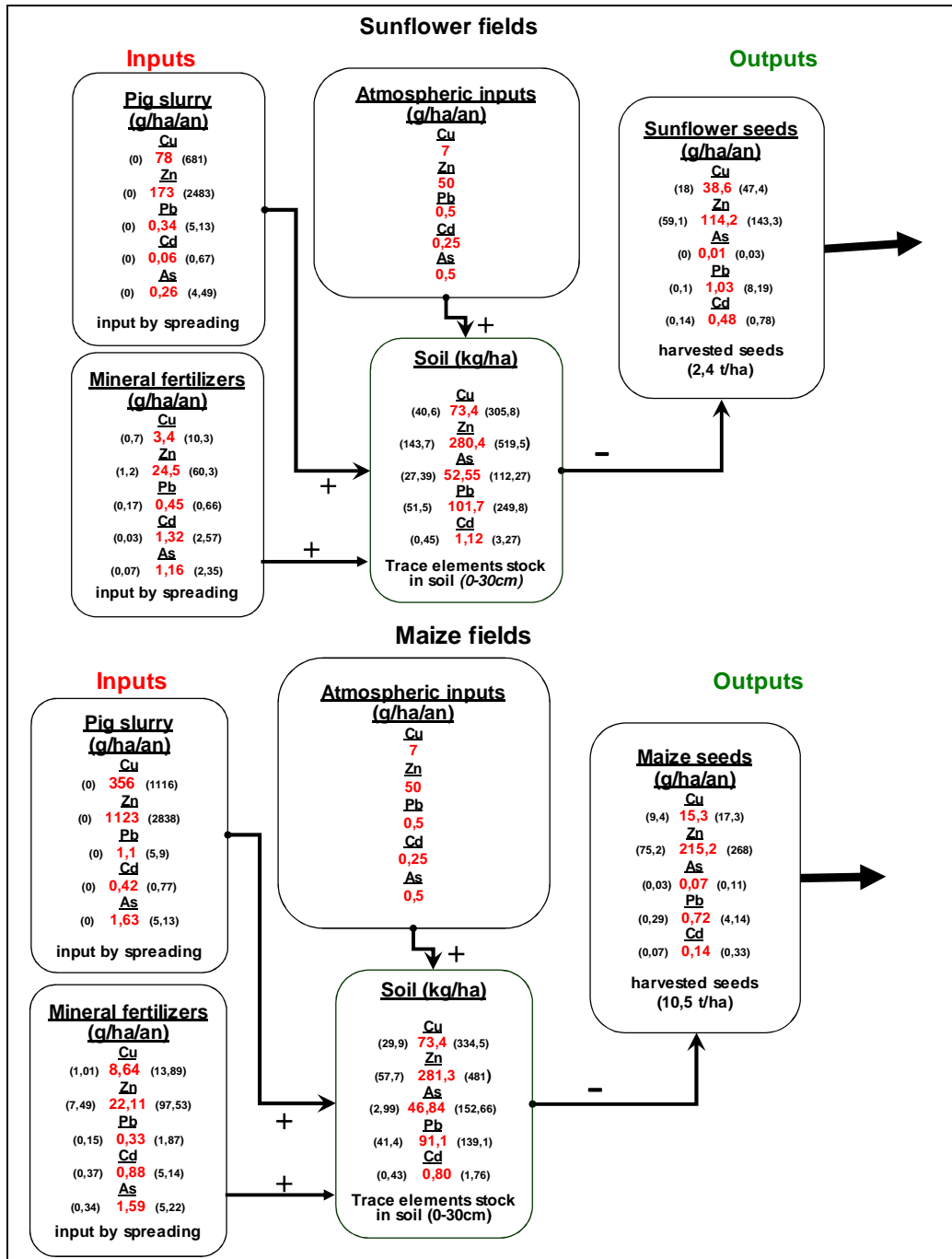


Figure 2: Trace elements flow diagram in studied fields [(min) median (max)]