Impact on crops, plants and soils of metal trace elements transfer and flux, after spreading of fertilizers and biosolids

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Abstract In France, the yearly production of sludge from wastewater treatment plants is 900,000 metric tons dry matter and 60% of this is reused for land application. Today, the sustainability of this pathway is open to question. Among the different arguments cited are the levels of metal trace elements and the risks of accumulation in soils. With the ultimate aim of agronomic sludge recycling, the transfer of metal trace elements has been studied using vegetation containers planted with rye-grass under controlled conditions of temperature and humidity. Samples of a domestic sludge, an industrial sludge and a fertilizer have been mixed with the soil. By monitoring the growth of the rye-grass, we have been able to observe that the addition of sludge increases production of plant matter. It appears that the roots absorb higher quantities of metal trace elements and form a barrier to their transfer to the above ground parts of the rye-grass. For the group of metal trace elements studied, no significant differences have been observed between the rye-grass grown on soil alone and that on soils amended with fertilizer or urban sludge. For the majority of the vegetation containers studied, there has been no significant modification in the soil metal distribution over time, as a result of the addition of urban sludge, and no significant difference between fertilizers and sludges.

Keywords Biosolids; flux; metal trace elements; rye-grass; soil; transfers

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Introduction

In France, the annual production of sludge from wastewater treatment plants is 900,000 tons dry matter and 60% of this is agriculturally recycled as a complement to farmers' manuring programs. This is because their organic matter, nitrogen and phosphorus content makes them good fertilizers as long as they do not also contain too many toxins such as trace elements. (Jarvis *et al*., 1976; Cataldo *et al*., 1981; Jarvis and Jones, 1978; Lindsay, 1972; Mahler *et al*., 1978, Maisonnave *et al*., 2001).

However, land application of wastewater treatment plant sludges causes concern and French regulations have been reinforced (decree of 8/12/97 and Statutory order of 8/1/98) halving maximum permitted levels of trace elements and dividing by four those for cadmium (10 mg/kg DM in 2004).

With the aim of making this pathway for the agricultural recycling of sludges from wastewater treatment plants durable, it would appear essential to study the transfer of metal trace elements from the sludges and fertilizers, to the soil and plants. An initial experiment has been carried out under controlled conditions, using vegetation containers and different amendments: a fertilizer, an urban wastewater treatment plant sludge, and an industrial sludge initially heavily loaded with metals. These amendments have been mixed with a clay soil, and some of them sown with rye-grass. The levels of metal trace elements in the soil, the mixtures, the plants and the roots as well as the growth of the vegetation have been compared to control containers.

Methodology

Sampling

A sample of about 150 kg of clay and humic soil, pH 6.6, was taken from plots of land in Poucharramet, France. The sludges chosen for this experiment came from the Toulouse (France) wastewater treatment plant (550,000 EI) and Muret-Marclan (France. 1,750 EI). From Toulouse they are urban liquid sludges, from Muret-Marclan, industrial liquid sludges. Ten 2 litre samples were taken over 1 hour and then mixed and homogenized to give a representative sample. The latter was then distributed among the vegetation containers. Apart from the above samples, a lawn fertilizer characterized by agronomic values for N, P and K of 20, 8 and 5 respectively, and a nutrient solution supplying the plant with the necessary mineral elements without recourse to absorption from the soil, have been chosen to amend the control pots.

Setting up the vegetation containers

Soil and amendment mixture. According to the French ministerial order of 8 January 1998, the maximum quantity authorized for land application of sludges is 30t DM/ha/10 yr. This dose has been chosen, added all at the same time to make up the soil–sludge mixtures in the vegetation containers. For the dose of fertilizer, agricultural practice suggests spreading 500 kg /ha/yr and so this is used for making the soil-lawn fertilizer mixtures. These amendments are repeated after the second rye-grass harvest. Eight pots are made for each amendment. Table 1 shows all the vegetation containers made.

In order to mimic and accelerate actual growing conditions, the containers filled with the soil-amendment mixtures have been put in a phytotron, an hermetically sealed enclosure with regulated temperature and humidity; day: 28°C, 75% humidity; night: 24°C, 70% humidity.

Sowing. The plant used is the rye-grass, chosen for its rapid and abundant growth and for its capacity to absorb metallic trace elements easily. In addition, a large number of individual plants can be grown (about 500) giving representative samples. In order to produce sufficient quantities of plant matter for subsequent analyses, the sowing density for the containers has been set at 630 kg per hectare, which is about 500 seeds per pot.

Physico-chemical analyses

Table 2 is a summary of the different methods used to analyse the amendments, soils and vegetation, plus the existing reference norms.

Results and interpretations

Growth of ryegrass and water efficiency

Figures 1 and 2 show the production of dry plant matter and the water efficiency for the three rye-grass harvests and for all the vegetation containers studied.

Measuring the growth of the rye-grass in the vegetation containers shows that the addition of sludge increases the production of plant matter: the mass of rye-grass produced in

Table 1 Vegetation containers

	With rye-grass	Without rye-grass
Soil only	4 pots	4 pots
Soil + nutritive solution	4 pots	
Soil + fertilizer	4 pots	4 pots
Soil + urban sludge	4 pots	4 pots
Soil + industrial sludge	4 pots	4 pots

Table 2 Analytical methods

Type of sample	Amendments	Soils and soil–sludge mixtures	Plants
Sampling	Drying, grinding	Core samples, mixture of 4	Harvests 1 and 2 months after 1st sowing, then 1 month after 2nd sowing Roots
Mineralizations	Aqua regia + microwave mineralizations Standard Methods 3030 F, K	Fusion at 1050°C + acid recovery of residue Standard Methods 3030 J	Calcination at 550°C then acid recovery of ash
Levels of Cd, Cr, Cu, Ni, Pb, Zn	Induced coupled mass spectrophotometry Standard Methods 3120 B		

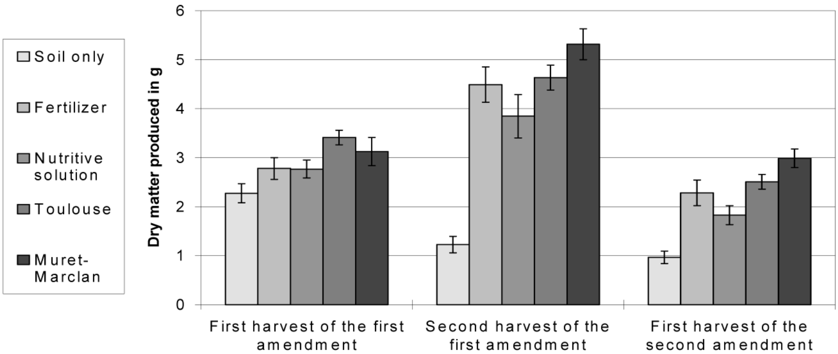

Figure 1 Production of dry plant matter

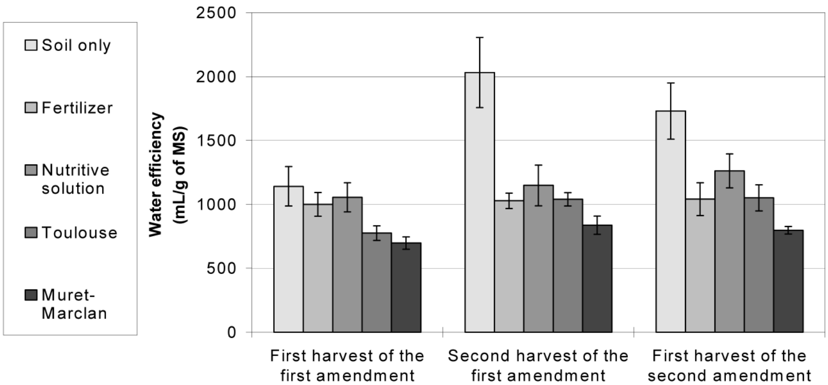

Figure 2 Water efficiency

the soil–sludge mixtures are up to five times greater than the mass produced in soil alone. It is also very interesting to note that the addition of sludge to a soil allows a reduction in water consumption for the plants growing there. Quite apart from their fertilizing qualities, wastewater treatment plant sludges can offer interesting perspectives as regards irrigation.

Levels of metal trace elements in the rye-grass

Absorption and transfer. Figures 3, 4 and 5 show the absorption of metal trace elements by the roots and their transfer to the above ground parts of the rye-grass, for all the mixtures studied.

The rye-grass roots have absorbed between 5 and 10 times more cadmium and nickel than the above ground parts. This is particularly obvious for the rye-grass which has been

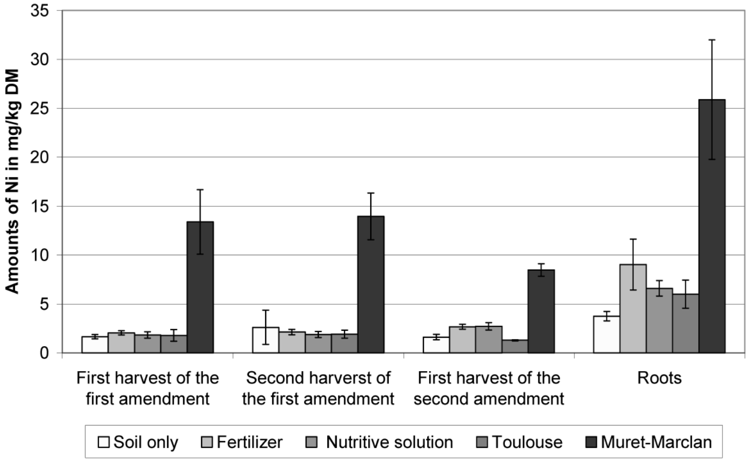

Figure 3 Amounts of cadmium or nickel in rye-grass

grown on the mixture with the sludge from Muret-Marclan, since the levels are much higher than the other samples. The rye-grass grown on soils amended with nutrient solutions of fertilizer or urban sludge, does not seem to have accumulated either cadmium or nickel in its above ground parts when harvested. On the other hand, it has absorbed a large quantity of cadmium and nickel from the Muret-Marclan industrial sludge, around seven times more than for the other amendments. Absorption of cadmium and nickel by the rye-grass roots is similar whether it was grown on the controls or the soil–sludge mixtures, excluding Muret-Marclan. Rye-grass absorbs nickel and cadmium with difficulty, but when they are present in very large amounts, they become more available and the barrier effect is less visible.

Whatever its form, the chromium is concentrated mainly in the plant's roots and very little is transferred to the above ground parts. The same is true for the lead: all that is available stays trapped in the roots. The levels of chromium and lead in the rye-grass roots are similar for all the vegetation containers studied. By comparison, the above ground parts are very different, the roots completely block the transfer of these elements to them. Thus they have very low concentrations of chromium and contain almost no lead, regardless of sample. No rye-grass sample contained a level of chromium greater than that of when it was grown in soil only.

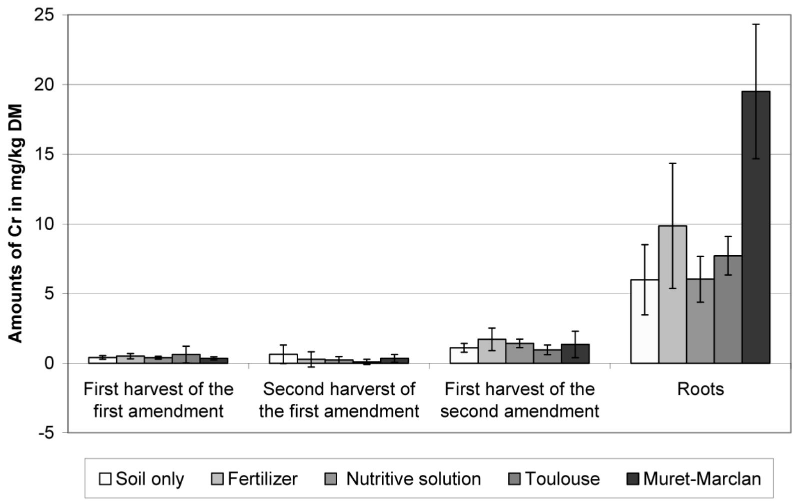

Figure 4 Amounts of chromium or lead in rye-grass

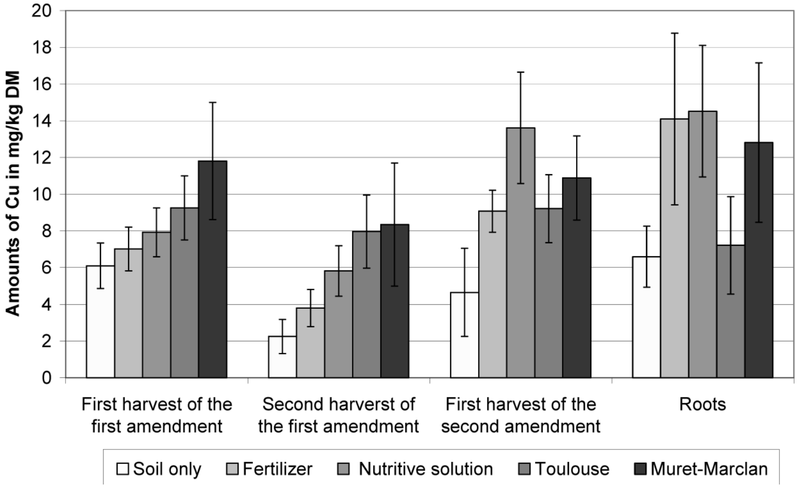

Figure 5 Amounts of copper and zinc in rye-grass

The plant does not seem to absorb chromium. The latter is strongly complexed to the organic and mineral matter and is only mobilized with difficulty in the soil. Neither is the lead available to the rye-grass plant leaves.

Absorption of copper and zinc by the rye-grass roots, is similar from one sample to another, whether it is from containers with only soil, or with a soil–sludge mixture from Muret-Marclan. In the above ground parts also, absorption is regular, there is a little more in the roots but the difference is not significant. The Poucharramet soil is lacking in copper and has only a small amount of zinc; these levels are only just sufficient for the correct development of the plants. The quantities of copper and zinc absorbed by the rye-grass on sludge enriched soil are therefore greater than those for plants grown on soil alone. Absorption is nonetheless modest and corresponds to the growth needs of the plant in essential oligo-elements. These elements are thus easily absorbed by the rye-grass ; they are bio-available.

Whatever the metal, there are no significant differences between sludges and fertilizers for the bio-availability and transfer of metal trace elements.

Regulation of the absorption. Absorption limits for metal trace elements by the rye-grass, have been observed. It is not the metals present in the largest amounts which are the most absorbed. In fact, comparison of the quantities of metal trace elements in the sludges and above ground parts of the rye-grass from Muret-Marclan, with the average quantities from the other sludges, give the following ratios:

$$R_1 = \frac{\text{Mass in Muret-Marclan sludge}}{\text{Average mass in the other sludges}} \quad (1)$$

$$R_2 = \frac{\text{Mass in rye-grass (Muret-Marclan)}}{\text{Average mass in rye-grass (other sludges)}} \quad (2)$$

The amount of chromium present in the Muret-Marclan sludge is 54 times greater, and that of nickel 41 times greater than in the other sludges, but the nickel is only absorbed 13 times more by the rye-grass grown on the Muret-Marclan sludge mixture and the chromium only twice as much (see Table 3). The rye-grass has therefore not absorbed everything that was

Table 3 Comparison of R_1 and R_2

	Cd	Cr	Cu	Ni	Pb	Zn
R1	25	54	2	41	2	1,5
R2	11	1	2	13	1	2

at its disposal in the sludge, the process stopped at the level required for correct development. For the cadmium and the lead the same phenomenon is seen but it is less obvious: the ratios are only twice as great.

Only copper and zinc are found in identical levels in the Muret-Marclan and other sludges, as they are in the rye-grass. These two metals are bio-available, they are thus easily absorbed when the plant needs them. To conclude, the plant regulates its absorption naturally.

Addition to the soil: flux assessment

Initial distribution of metal trace elements. The quantities in the soil of different particle size fractions obtained from water-sprayed sieves are given in Table 4.

The average concentration of trace metal elements per kg of soil, has been calculated using the concentrations in each particle size band and the percentage mass of each band in the soil sample. These values are well below the concentrations allowed by the French Statutory order of 8/01/98 for spreading on this type of soil.

The finest soil fraction, with a particle size of less than 20 µm, contains the greatest proportion of metal trace elements in all cases. This fraction contains the clays which exchange cations easily and particularly metallic cations, plus iron or manganese oxides. The metal trace elements from the Poucharramet soil are thus mostly adsorbed onto the clays and the iron and manganese oxides.

However, a small but important amount of certain metal trace elements is found in the largest particle size fractions of the soil; cadmium in the 20–50 µm fraction, copper in the 50–100 µm fraction and zinc in the 100–500 µm fraction.

Flux assessment. Calculating the flux over the long term is done to confirm the negligible influence of the addition of sludge to a stock of soil. During this experiment, the trace metal elements have been monitored within the sludge-soil-plant system (Guiresse *et al*., 1999). These data allow two types of flux to be measured: the flux entering with the sludge or fertilizer additions and the flux exiting with the water and the rye-grass.

Tables 5 and 6 show the flux brought in by the additions of Toulouse sludge and fertilizer to the Poucharramet soil, the flux exported by the rye-grass and the total flux as a percentage of the initial stock.

Table 4 Distribution of metal trace elements in the soil

Grain size fraction in µm	Amounts of metal trace elements in mg/kg DM						Mass
	Cd	Cr	Cu	Ni	Pb	Zn	distribution
0–20	0.5	140	48	58	61	231	45.7%
20–50	0.6	2.3	6	2.5	26	21	23.6%
50–100	0.3	35	56	7.3	31	38	10.1%
100–500	0.2	15	14	0.9	12	106	15.1%
500–2000	0.2	0.5	10	0.2	22	8.2	5.5%
Average amount in soil	0.4	70	32	28	40	131	/
Limit value, French regulation 8/01/98	2	150	100	50	100	300	/

Table 5 Flux of metal trace elements brought in soil by the fertilizer

Fertilizer	Initial stock in soil (kg/ha)	Flux brought in by amendments (g/ha/100 yr)	Flux exported by rye-grass (g/ha/100 yr)	Balance – 100 years (% initial stock)
Cd	1,2	200	51	12%
Cr	210	2,900	97	1.3%
Cu	96	3,300	1,360	2.0%
Ni	84	1,050	557	0.6%
Pb	120	600	21	0.5%
Zn	393	4,750	8,504	0.0%

Table 6 Flux of metal trace elements brought in soil by Toulouse dewatered sludge

Toulouse dewatered	Initial stock in soil (kg/ha)	Flux brought in by amendments (g/ha/100 yr)	Flux exported by rye-grass (g/ha/100 yr)	Balance – 100 years (% initial stock)
Cd	1,2	195	90	8.7%
Cr	210	1,950	101	0.9%
Cu	96	34,800	2,736	33%
Ni	84	1,350	600	0.9%
Pb	120	7,350	60	6.1%
Zn	393	46,500	13,207	8.5%

$$\text{Initial stock in soil (kg/ha)} = \text{conc. (mg/kg)} \times \text{soil mass/hectare}(10^3\ \text{t/ha}) \quad (3)$$

$$\text{Flux brought in by amendments (g/ha/100 yr)} = \text{conc. (mg/kg)} \times \text{spreading dose per hectare (t/ha)} \times 100 \quad (4)$$

$$\text{Flux exported by rye-grass (g/ha/100 yr)} = \text{mass of 2 harvests (g)/area of pot (ha)} \times 100 \quad (5)$$

$$\text{Balance-100 years (\% initial stock)} = \frac{(4)-(5)}{(3)}$$

Comparing increases in the initial stock between fertilizer and sludges, shows that the additions of cadmium, chromium and nickel are approximately the same. They are 10 times higher for lead, copper and zinc when sludge is added. The fluxes are nonetheless comparable with those produced by spreading pig slurry (e.g. 370 Cu g/ha/yr). After 100 years of spreading wastewater treatment plant sludges, the stock of cadmium, chromium, nickel, lead and zinc would not have increased by more than 10%, which corresponds to measurement errors; for copper it would increase by 33%. It is therefore interesting to see that it is only the oligo-element copper, essential for plant growth, whose flux increases significantly.

Conclusions

The transfer of metal trace elements initially contained in urban wastewater treatment plant sludges, a fertilizer and an industrial sludge, has been studied in soil–sludge mixtures and in rye-grass. With the aim of agricultural recycling of sludges, this study has been carried out in vegetation containers inside a phytotron with controlled conditions of temperature and humidity.

Each of the amendments used has encouraged growth of the rye-grass. The analyses have shown that the roots absorb greater quantities of trace metal elements and block their transfer to the above ground parts of the rye-grass. This mechanism is not so obvious for copper and, to a lesser extent, the zinc which are essential oligo-elements. For these metals, the levels are basically the same in the roots and above ground parts. The plant needs them to grow and only absorbs the necessary amounts.

As a general rule, the absorption of trace metal elements by the rye-grass is similar for soil alone, soil with added fertilizer or Toulouse sludge. Only the industrial sludge, heavily loaded with cadmium, chromium and nickel leads to higher levels in the rye-grass, mainly for cadmium and nickel and to a lesser extent, zinc.

It is not the metals which are present in the highest amounts in the sludge which are the most absorbed by the rye-grass. The plant appears to naturally regulate its absorption.

With time and under the experimental conditions, the addition of sludge has not significantly modified the distribution of metals in the soil. The fluxes of trace metal elements brought by the urban sludges remains very low. Over a year, if the conditions in the regulations are respected, their accumulation would not appear to present any risk to the natural environment. The dilution remains very high and the buffering action of the soil is considerable. The addition of 30 tons dry matter per hectare represents 1% of the mass of the soil on which the sludges are spread.

Field trials have also been made using maize and the results confirm those given here (Guiresse *et al*., 1999). Finally, a comparable study, on the transfer of organic compounds, is being made at the moment on carrot and tomato plants in soil and hydroponics cultures.

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