HEAVY METALS TRANSFER FROM SOIL TO RAPESEED OIL

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ABSTRACT

Transfer coefficients of heavy metals (brought in non toxical doses for rape crop) study showed that chromium, mercury and lead are very little transferred while cadmium, copper, zinc and nickel are much more transferred in rapeseed. Cadmium and copper, often found in urban sludges, involve health (Cd) and technological (Cu) risks. So a rape crop has been conducted in field on an acidic silty soil previously treated with either a Cd-rich urban sludge, or a Cu-rich urban sludge, or Cu salt. Higher treatments for copper and cadmium corresponded to the maximal level of metal inputs authorized for ten years by French regulations on sludge uses in agriculture (1998). High inputs didn't increased seed Cu-content while Cd-rich urban sludge leaded to higher seed Cd-content. Seeds have been crushed and refined in quasi-industrial pilots. Trace metals observed in seeds are almost exclusively transferred to meals after seed crushing. After the refining step, no risk for human health could be identified regarding the rapeseed oil in these conditions of cropping and industrial process. The rapeseed oil characteristics fitted with the hardest industrial specifications and even meals Cu and Cd-contents fitted with feed regulations.
Keywords: *heavy metals, industrial process, rapeseed, urban sludge.*

INTRODUCTION

Using urban sludge (850 000 tonnes of dry matter each in France) in agriculture has many advantages, mainly because it allows recycling organic matter and it is less expensive than incineration for the community. But some toxic metal trace elements from sludge can be stored in plants and contaminate the food chain (Juste et al.,1995). Some works show that rapeseed crops (*Brassica napus*) are able to store heavy metals, so that they are proposed for phytoremediation. Rapeseed is an important crop in France (1 million hectares) and, after seed crushing and refining, the products obtained are meal for animal feeding and oil for human consumption.

The first step of this study is to work out the transfer coefficient for different metal trace elements, brought on soil at non toxic dose for plants, in controlled conditions. Then, rapeseed is cultivated in a field, in real conditions, with two heavy metals chosen in the first part for their risk (toxicity, transfer coefficient, frequency in sludge), cadmium and copper. The third step consists in crushing seed at a pilot scale and refining crude oils.

The objective is a better understanding, for rapeseed oil and meal, of the influence of industrial process on pollutants and of the heavy metals distribution in the food chain.

MATERIALS AND METHODS

a) <u>Study of trace metal element transfer coefficient under controlled conditions</u>

Rapeseed (*Brassica napus*, var. Capitole) was grown on acidic loamy soil in controlled conditions during three months, with trace metal elements in non toxic concentrations. Each pot receive the same fertilization N,P,K,S. The brought heavy metals were at doses (mg/kg of soil): Cd 5 (toxic dose > 8 ppm), Cr 10 (t.d.=50 ppm), Cu 25 (t.d.=40 ppm), Hg 50 (t.d.>50 ppm), Ni 5 (t.d.=20 ppm), Pb 400 (t.d.>400 ppm), Zn 150 (t.d.=400 ppm). These doses corresponded to the maximal level of metal inputs authorized by French regulations on sludge uses in agriculture (1998) : for 10 000 years (Hg), 1000 years (Cd), 800 years (Pb), 100 years (Zn), 50 years (Cu, Ni), 20 years (Cr). They were brought as sulphates for Cd, Cu and Zn, dichromates of potassium, chlorides of Hg, nitrates for Ni and Pb. The analytical methods for soils : mineralization with fluorhydrate acid and determination by plasma optical spectrometry (Cr, Cu, Ni, Pb, Zn) and electrothermal atomization atomic absorption spectrometry (Cd). For seeds : mineralization by dry way calcination, ashes in hydrochloric and fluorhydrate acids, then determination by electrothermal atomization atomic absorption spectrometry (Cd, Cr, Cu, Ni, Pb, Zn). For Hg: combustion under oxygen, trapping on gold amalgam and determination by atomic absorption spectrometry. Two coefficients were calculated : transfer to seeds coefficient (CT), which is the percentage of initial quantity (endogenous and exogenous) stored in seeds, and the apparent bioaccumulation coefficient (CAB), which is the ratio of the difference between accumulation in seeds produced on soil treated and non treated, to the brought quantity of heavy metals (expresses the exogenous metal transfer).

b) Study of Cd and Cu transfer in field

Trial with six treatments on four repetitions, on an acidic silty soil, harvested in normal conditions. **T1** : No sludge, with an equivalent inorganic fertilization for main elements. **T2** : treatment with a Cu-rich sludge (8.94 kg/ha of Cu). **T3** : treatment without sludge, equivalent inorganic fertilization for main elements and Cu. **T4** : treatment with a Cd-rich sludge (310 g/ha Cd). **T5** : treatment without sludge, equivalent inorganic fertilization for main elements and Cd. **T6**: treatment without sludge, equivalent inorganic fertilization for main elements, and 30 kg/ha Cu.

c) Becoming of Cu and Cd during rapeseed crushing

Seeds, issued from the previous field trial, have been crushed in a pilot-scale plant with two steps : partial deoiling by expelling after flaking and cooking, and then hexane extraction of residual oil from press cake.

d) Effects of refining

Refining of rapeseed crude oil issued from the previous crushing was performed at a pilot-scale

RESULTS AND DISCUSSION

a) Study of trace metal element transfer coefficient under controlled conditions

The results in table 1 show that transfer toward seeds depends on the exogenous or endogenous heavy metal source. For bioavaibility for seeds of exogenous heavy metals (comparing CAB) : Cr, Hg and Pb are very little transferred (CAB<0.01) ; Cd and Cu relatively transferred (0.01<CAB<0.05) ; Zn and Ni are the most easily transferred (CAB>0.05). From CT comparison (non treated soil, endogenous source), it appears that Cr, Ni, and Pb are very little transferred (CT<0.005) and Cd, Cu, Hg, and Zn are much more easily transferred (0.01<CT<0.05).

According to their risk (technological or toxicological) and their transfer ability, Cd and Cu are chosen for the field trial and industrial trial (Boudene, 1986).

b) Study of Cd and Cu transfer in field

The results in table 2 show that sludge treatments do not affect yield. No difference could be statistically proved for Cd and Cu-concentrations in seeds. Nevertheless, it appears that the more important is the Cu-provision to soil, the lower is the Cu-concentration in seeds. An hypothesis, no checked, to explain is that copper has a negative effect on rapeseed roots development. Cadmium provision to soil leads to an increase of seeds Cd-content, and the increase is bigger for inorganic Cd-source.

***Table 1**. Results regulatory limits (f = feed ; ca = Codex Alimentarius for oils).*

Element	Exogenous source / total quantity (%)	Bioavailable source	Mean CT on non treated pot (%)	Mean CAB (%)	Max CAB (%)	Maximum concentration in seeds (ppm)	Limits (ppm)
Cd	95 %	=	0.019	0.009	0.013	0.97	1 [f]
Cr	10 %	Endogenous ?	0.0013	< 0	< 0	4.5 *	-
Cu	50 %	=	0.016	0.012	0.028	13.7	0.1 [ca]
Hg	99.9 %	Endogenous	0.046	< 0	0.000001	0.11	0.1 [f]
Ni	10 %	Exogenous	0.0043	0.048	0.062	7.7	-
Pb	90 %	=	0.0034	0.0029	0.007	26.6	0.1 [ca]
Zn	60 %	=	0.041	0.023	0.051	187	-

***Table 2**. Results on rape seeds*

	Yield 9% H_2O (kg/ha)	Cu concentration (ppm)	Cd concentration (ppm)
T1	4206	3.55	0.077
T2	3731	2.95	
T3	4227	3.09	
T4	4412		0.087
T5	4459		0.128
T6	3917	2.45	

c) <u>Becoming of Cu and Cd during rapeseed crushing</u>

Results in table 3 show that almost all of the heavy metals are going in meal during crushing. So, oils do not present any risk concerning food chain contamination. On the other hand, meals, which are used for animal feeding, can insert heavy metals into the food chain. In this study the maximum concentrations found are under the regulatory limits.

***Table 3**. Cu and Cd-content during rapeseed crushing (mg/kg)*

	Seeds		Press cake before extraction		Meal after extraction		Oil after expelling		Oil after extraction	
	Cu	Cd	Cu	Cd	Cu	Cd	Cu (ppb)	Cd (ppb)	Cu (ppb)	Cd (ppb)
T1	3.55	0.077	5.10	0.085	6.39	0.11	8	<2	36	<2
T2	2.95		5.16		8.34		7	<2	30	2
T3	3.09		5.53		6.13		<5	<2	18	<2
T4		0.087		0.078		0.17	<5	<2	24	<2
T5		0.128		0.14		0.097	5	<2	17	<2
T6	2.45		5.61		6.49		35	<2	32	2.8

d) <u>Effects of refining</u>

Refined oils comply with the industrial specifications for copper (10 to 20 ppb) and for cadmium (20 ppb) : all the Cd and Cu-concentrations are under the detection limit (Lacoste et al., 1993). But crude oils could not fit with these specifications for copper which can lead to technological difficulties (no health concern). The normal refining conditions are suitable for eliminating Cu-residues.

***Table 4**. Cu and Cd-content of crude oil (oil after expelling + oil after extraction) and refined oil*

	Crude oil		Refined oil	
	Cu (ppb)	Cd (ppb)	Cu (ppb)	Cd (ppb)
T1	18	<2	11.4	<2
T2	16	<2	<5	<2
T3	10	<2	<5	<2
T4	9	<2	<5	<2
T5	12	<2	<5	<2
T6	29	<2	<5	<2

CONCLUSIONS

In these cropping conditions, we can conclude that the rules in force concerning sludge, industrials processing and rapeseed plant metabolism for copper guarantee safe oils and meals for consumers. But our trial was performed on a soil with low initial Cd and Cu-concentrations. It could be interesting to study the accumulation of these heavy metal in seeds from crop on rich soils (naturally or after a pollution), with the same rapeseed variety.

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