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HEAVY METAL DETERMINATION IN ATMOSPHERIC DEPOSITION AND OTHER FLUXES IN NORTHERN FRANCE AGROSYSTEMS

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Abstract. The aim of this study is to assess the annual balance of the fluxes of Cd, Cu, Ni, Pb and Zn within different cropping systems, in an experimental site located near Versailles, France. Four fluxes through the cultivated horizon were considered to assess the annual heavy metal balance in these systems: 1) atmospheric depositions, 2) fertilisers as inputs, 3) crops and 4) leaching water as outputs. The water mass flow was estimated with a model (CERES) while the other parameters were actually measured through field sampling. Some large uncertainties are related to analytical detection limits, specially for Pb which presents very low concentrations in nitrogen fertilisers, in crops and in soil solution. Cd was also close to the detection limits in atmospheric deposition and in soil water, and Zn could not be analysed in soil solution. Nevertheless, the following trends clearly appeared: firstly, atmospheric deposition is the major input way of Cu, Ni, Pb and Zn in the soil, whatever the cropping system, whereas Cd is introduced mainly by fertilisers. Secondly, the uptake of heavy metal by wheat is generally larger than by a pea culture, except for Ni. Finally, the global pattern shows an accumulation of Cd, Ni and Pb in the cultivated horizon while Cu decreased. The annual balances, during the cropping year 2001–2002, represented about 0.33, –0.024, 0.014 and 0.014% of the actual stocks in the cultivated horizon, of Cd, Cu, Ni, and Pb, respectively.

Keywords: accumulation, balance, Cd, crop uptake, Cu, cultivated horizon, fertilisers, Ni, Pb, trace elements, Zn

1. Introduction

The contamination of soil and agrosystems by heavy metals affects the health of soil–plant ecosystems. Such pollution also affects the human being through the contamination of the food chain. At a local-scale, many areas in Europe have been severely contaminated by industrial emissions or by hazardous applications of wastes on fields. At a large scale, atmospheric pollution has been recognised as an important heavy metal source for soils, with historical maximum loads around the 1970–1980s in the case of lead (Lobinski, 1995; Weiss *et al.*, 1999). Another source of large-scale contamination of cultivated soils is the use of common amendments and fertilisers. Indeed, some phosphate fertilisers and organic manures have



been well established as sources of heavy metals (Jones *et al.*, 1987; Jones *et al.*, 1987; Juste and Robert, 2000; Juste and Tauzin, 1986; Mench, 1998). These potential sources, both from large and local scales, associated with natural outputs (leaching water, run-off) and crop uptake contribute to the heavy metal balance in cultivated soils (Hovmand, 1984). Nevertheless, the atmospheric depositions were decreased during the last decade (Azimi *et al.*, 2003; Lawlor and Tipping, 2003). Therefore, the balance of heavy metals in agrosystems remains a debated issue, related to the determination of critical loads from atmospheric pollution (Brus *et al.*, 2002; De Vries and Bakker, 1996) or to the recycling of urban waste (Bartl *et al.*, 2002).

However, the data needed for the determination of all fluxes and balances in agrosystems are not easily measurable. Indeed, Brus *et al.* (2002) compared the Cd concentrations in soils expected from different reported fluxes and the estimated critical Cd concentration by modelling soil-water-plant transfers. Moolenaar and Lexmond (1998) directly measured most of the fluxes of Cd, Cu, Pb, and Zn in agrosystems of the Netherlands at the 'farm-gate' scale and at field scale but used a model and laboratory adsorption experiments to evaluate the outputs by leaching. Keller *et al.* (2001) also used several models to estimate heavy metal fluxes from agricultural statistics at a regional scale. Moolenaar and Lexmond (1998) as well as Keller *et al.* (2001) pointed out 1) the relative importance of atmospheric deposition for Pb inputs in arable-land systems and 2) the importance of fertilisers and farming systems for the balances of Cd, Cu and Zn. Both studies differentiated arable-land, animal husbandry and mixed-farm systems, the latter appearing more sustainable with respect to heavy metal accumulation (Moolenaar and Lexmond, 1998).

The aim of the present study is to provide a detailed analysis of the fluxes of heavy metals (Cd, Cu, Pb, Ni and Zn) through a site representative of Northern France agrosystems, and compare the different cropping systems which are used on it. To reach this goal, element fluxes coming from diffuse sources, i.e., agricultural inputs and long-range atmospheric pollution as well as output fluxes, i.e., crops and leaching water, were measured on an experimental site devoted to develop and compare cultivation systems.

2. Materials and Methods

2.1. EXPERIMENTAL SITE

Samples were taken from the site 'La Cage', an experimental field of 12 ha which has been used for several decades by the French national institute of agronomic research (INRA), in a representative way of intensive cereal production. This site is located near Versailles, 15 km west from Paris (France) on a typical silt loam soil of Northern France. Table I resumes the characteristics of the cultivated horizon from samples collected in 1998, when a new long-term experimentation started, to develop, test

TABLE I

Main soil characteristics in 1998 at the beginning of the Sustainable and Integrated Cultivation System (SICS) experimentation (mean \pm standard deviations of 12 samples at 0–25 cm depth)

Clay content	Silt	Sand	C orga.	C/N	pH in water
16.7 \pm 0.7%	58.4 \pm 6.6%	24.9 \pm 7.2%	0.96 \pm 0.12%	9.94 \pm 0.16	7.33 \pm 0.21
CEC	[Fe] _{total}	[Mn]	[Cd]	[Pb]	[Zn]
111 \pm 7	16 855 \pm 1435	511 \pm 64	0.233 \pm 0.020	44.3 \pm 10.0	55.0 \pm 6.0

CEC = Cation Exchange Capacity in mmol . kg⁻¹; metal concentrations are given in mg . kg⁻¹ dry weight.

and compare alternative cultivation systems (Sustainable and Integrated Cultivation Systems program, SICS). These systems are not defined by constant procedures but by different sets of decision rules. They are: 1) a productive system (PRO), aiming to get the maximum potential yield, which is used as a reference; 2) an integrated system (IN), aiming both to preserve the economic profitability and to limit the environmental impacts and 3) an organic system (ORG), following the French charter for organic agriculture, and a system with no soil tillage which will not be considered in the present study. These cultivation systems were applied on plots of 11200 m² each, divided in two parts for a rotation. Every year, one part is used for wheat and the other part is used for another culture (Figure 1). A buffer zone with fallow or a reference culture surrounds each cultivation system in order to avoid treatment drifts and border effects.

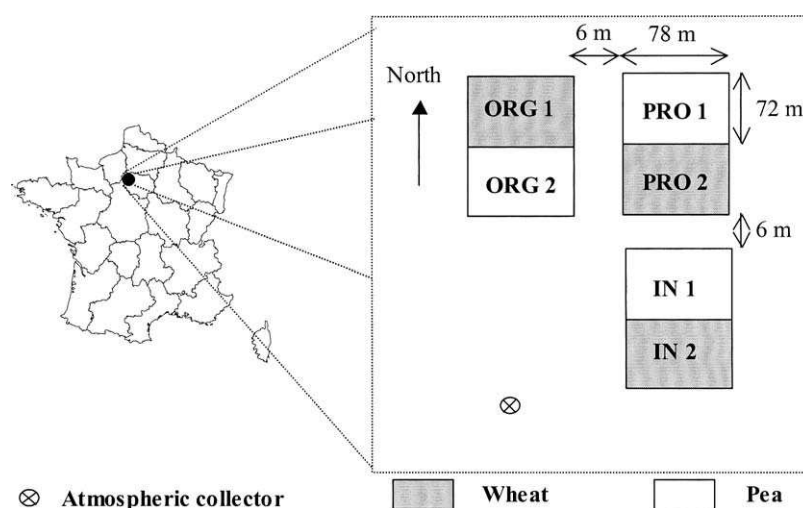


Figure 1. Place of wheat and pea following each cultivation systems: productive (PRO), integrated (IN) and organic (ORG) of the experimental site of Versailles (France).

2.2. INPUT/OUTPUT FLUXES CONSIDERED

The fluxes which are considered are those passing through the limits of the cultivated horizon (0–30 cm) at an annual time scale. The input fluxes concern the atmospheric depositions, the seeds, the fertilisers and the pesticides. The output fluxes are due to crops and leaching water. Other fluxes can be identified: lateral fluxes caused by lateral leaching, surface run-off, and earth displacement (Juste and Mench, 1992). They were all neglected in the present work because studied plots were large and uniformly flat. Another flux corresponds to the uptake of elements by deep roots (deeper than 30 cm) from soil sub-layers towards other roots or plant shoots. But the density of roots in the cultivated horizon is generally much higher than in deeper layers (Barber, 1995). Gaseous fluxes could be of concern for elements like mercury or selenium. These three types of fluxes were neglected in the present study dealing with Cd, Cu, Ni, Pb and Zn.

Except for the leaching water, all the considered fluxes were measured at the 'La Cage' site. Indeed, the water mass flow corresponding to leaching has been calculated using the model (CERES). This model simulates the growth of cultivated plants and water, N and C cycles in various soil–crop systems (Gabrielle *et al.*, 1995; Jones and Kiniry, 1986). The input data used by the model were of three kinds:

- Daily meteorological data (temperature, radiation, precipitation, potential evapotranspiration);
- Soil characteristics given by layers at a decimetric scale, down to 120 cm (texture, organic matter, bulk density, hydraulic conductivity, field retention capacity);
- Agronomic and physiologic data: date and seeding density, plant characteristics, nitrogen inputs, mass and C/N ratio of plant residues after harvesting, etc.

The hydraulic part of the model, which takes into account only vertical flows, has been validated on a soil similar to the one investigated in this study (Gabrielle *et al.*, 1995).

2.3. SAMPLING

Atmospheric deposition. The total atmospheric deposition (TD) collection integrating both dry and wet deposition was performed using a system made with a high density polyethylene (HDPE) bottle (5 L) connected to a Teflon funnel of 113 cm² collection area. All this equipment was placed inside a PVC pipe with PVC needles on top to avoid bird nesting. Collector heights reached 190 cm to avoid the collection of re-suspended soil particles (Azimi *et al.*, 2003). The sampling period of TD was 7 days from 1 October 2001 to 22 November 2002.

Seeds. They were stored in their commercial bags for the purpose of the SICS research program. Samples of a few hundred grams were randomly grabbed from one bag corresponding to each kind of seed and kept in new plastic containers for

TABLE II

Annual fertiliser loads (kg ha^{-1} per year) from 1999 to 2002. Horizontal arrows display the cultivation period

	1999	2000	2001	2001		2002				Total annual flow ($\text{kg}\cdot\text{ha}^{-1}$)		
				Sept	Oct	Feb	Mar	Apr	May		Jun	Jul
IN – 1	wheat	colza	wheat								IN pea	
N	465	520	600								0	
MgS		100							←	pea	→	0
PK				200								200
IN – 2	colza	wheat	pea									IN wheat
N	600	590					270		120			390
MgS	100					←		wheat		→		0
PK		300		200								200
PRO – 1	wheat	colza	wheat									PRO pea
N	655	600	745									0
MgS		100							←	pea	→	0
PK				300								300
PRO – 2	colza	wheat	pea									PRO wheat
N	660	538					200	300		120		620
MgS	100					←		wheat		→		0
PK		300		300								300
ORG – 1	colza	wheat	pea									ORG wheat
Org am.	260							←	400	wheat	→	400
ORG – 2	wheat	lupin	wheat									ORG pea
Org am.	260		650						←	pea	→	0

For cultivation systems: IN = Integrated; PRO = Productive; ORG = Organic. See Figure 1 for their place on the site. For fertilisers: (N) ammonitrate 33.5 %: NH_4NO_3 ; (MgS) kieserit: $\text{MgSO}_4\cdot\text{H}_2\text{O}$; (PK) NPK 0-25-25: CaHPO_4 , $\text{KCl}\cdot 2\text{H}_2\text{O}$.

further analyses. Six different wheat varieties (Charger, Somme, Malacca, Virtuose, Apache, Renan) and blends of them have been used for the SICS program. One variety of pea (Athos) has been cultivated. Other plants cultivated before 2000 will not be considered in the present study (Table II).

Fertilisers and amendments. Products applied in significant quantities during the last 4 years (Table II) were also randomly sampled from their commercial containers. The feather flour used in the ORG system was sampled from two different bags.

Pesticides. Pesticides were also considered as potential trace element inputs. Thirty-eight different products were used on the site during the period 1998–2002. According to commercial specifications, their active molecules are only organic and they do not contain any heavy metal (ACTA, 2001). However their exact chemical

composition is confidential and some unmentioned additive could contain one of the studied elements. Therefore, two of them were chosen and analysed: the levels of the studied element were under the detection limit or very low (about 2 mg kg⁻¹ for Zn). Considering the low mass input of pesticides, their applications were assumed to bring no significant amount of heavy metal into the soil.

Crops. For the purpose of SICS and other research programs, crop yields were measured. The weights of grains harvested from three or four passages of the reaping-machine on accurately measured areas of each plot provided average and standard deviations for the yields. Samples of a few kilograms of each crop were collected at the same time. Then, sub-samples were taken for the need of the present study, exactly like for seeds.

Leaching water. Humid soil (1 kg) was sampled at 30 cm depth in three locations around the centre of each plot, a few hours after a rain period. The retained procedure of soil solution extraction (centrifugation of 0.7 kg at 1700g during 20 min) brought the soil samples to a water content of 22%, corresponding to a suction of about 10 kPa (pF 2) by comparison with water retention curves obtained for the same soil horizon (D. Tessier, personal communication). So the supernatant water was assumed to be like the soil solution leaching downwards in the fields. It was then filtered (Minisart, pore diameter 0.2 µm) before analysis. Centrifugations and filtrations were done at 20 °C but humid samples were kept in outdoor conditions until they were treated, i.e., no more than 2 h after field sampling.

2.4. SAMPLE TREATMENT

2.4.1. Atmospheric Deposition Samples

The collection bottle was filled before each sampling period with 50 mL of a 10% acidified (HNO₃ 65% Suprapur, Merck) Milli-Q water (18.2 MΩ Milli-Q water, Millipore S.A.). This water layer allowed to dissolve particles during the sampling period. For similar reasons, at the end of each sampling period the funnel was rinsed with 100 mL of a 1% acidified Milli-Q water in order to collect particles deposited or adsorbed on funnel walls (Azimi *et al.*, 2003). All this equipment was replaced by a clean one at the end of each collection period. As soon as the material was brought back to the laboratory, a 50 mL sub-sample of atmospheric deposition collected in the bottle and a 50 mL sub-sample of the rinsing water were filtered through 0.45 µm porosity membranes (Sartorius, cellulose nitrate) previously washed in a 5% HNO₃ bath. Samples were stored in a dark room at 4 °C waiting for analysis. The washing procedure of all the material necessary for samples collection and treatment is described in detail elsewhere (Azimi *et al.*, 2003).

2.4.2. Plant and Fertiliser Digestion

Dry weights of crop samples were determined by heating two aliquots of them in an oven at 105 °C during 48 h while fertilisers were air-dried. Without any preliminary grinding, 0.5 g samples was put in a Teflon vessel with 2 mL HNO₃ 65% (Prolabo

Normapur for analysis). After 1 h at room temperature and pressure, 8 mL of ultrapure water was added, and the closed vessel was heated in a microwave-oven (MARS type, CEM corp., Matthews, NC, USA). The heating program consisted in increasing temperature up to 200 °C during 15 min, then keeping this temperature for 10 min. The pressure reached about 2 MPa. The resulting solution was filtered and adjusted up to 50 mL. Filters were rinsed with HNO₃ 1%, and all vessels were soaked overnight in HNO₃ 10%, and rinsed with pure and ultrapure water before use. Reference vegetal samples were also digested in order to validate the digestion method and the trace metal analysis. Crop and fertiliser samples were digested in replicates (3 and 5, respectively) and mean results were used for the flux determination.

2.5. TRACE ELEMENT ANALYSIS

The atmospheric depositions were analysed by Inducted Coupled Plasma (ICP-AES Perkin Elmer Optima 3000) with an ultrasonic nebuliser and an axial slit. These two devices combined together enhance the sensitivity and the detection limits for trace element analysis. Solutions obtained from crop and fertiliser sample digestions, and centrifuged soil solutions were analysed using a flame (Zn) and furnace (Cd, Cu, Ni and Pb) atomic absorption spectrometer (AAS Varian SpectrAA 220).

2.6. QUALITY CONTROL

2.6.1. Atmospheric Sample Analysis

A quality control has been performed using following test samples which were treated like the field samples: 1) acidified water blanks for checking the contamination during sample treatment in the laboratory; 2) acidified water blanks for checking the contamination during field collection; 3) two certified samples in trace metals presenting similar concentration and matrices as atmospheric fallout: (a) NIST 1643d: "Trace elements in water", U.S. Department of Commerce; (b) SPS-SW1 batch 105: "surface water", Spectra pure standards.

2.6.2. Vegetal Sample Analysis

The validation step has been performed by the analysis (after digestion when solids) of three certified samples: (a) NIST SRM 1640: "Trace Elements in Natural Water" standard reference material of National Institute of Standards and Technology (USA); (b) "Maize powder" and (c) "ground oak leaves", both certified samples of the "Unité de Service et de Recherches en Analyses Végétales et Environnementales" (USRAVE, Bordeaux, France).

2.6.3. Analysis Validation

Table III shows the detection limit (DL) values obtained by both ICP-AES and AAS as well as the measured values of certified samples. The DL has been deduced

TABLE III

Detection limits (DL, $\mu\text{g} \cdot \text{L}^{-1}$) obtained with both ICP-AES and AAS equipment and validation of analytical procedures on reference samples (mean \pm SD)

		Cd	Cu	Ni	Pb	Zn
ICP DL		0.06	1.07	1.69	0.96	7.50
AAS DL		0.03	1.40	3.20	0.3	13
SPS – SW1 (105) ^(a) (Aqueous)	CV	0.50 \pm 0.01	20.00 \pm 1.00	10.00 \pm 0.10	5.00 \pm 0.10	20.00 \pm 1.00
	MV ($n = 7$)	0.48 \pm 0.11	17.02 \pm 0.94	9.99 \pm 0.49	4.83 \pm 0.36	24.45 \pm 7.67
SRM 1643d ^(a) (Aqueous)	CV	6.47 \pm 0.37	20.50 \pm 3.80	58.10 \pm 2.70	18.15 \pm 0.64	72.48 \pm 0.55
	MV ($n = 7$)	7.11 \pm 0.72	29.53 \pm 1.48	69.25 \pm 4.78	20.45 \pm 2.00	82.23 \pm 6.52
SRM 1640 ^(b) (Aqueous)	CV	22.79 \pm 0.96	85.20 \pm 1.20	27.40 \pm 0.80	27.89 \pm 0.14	–
	MV ($n = 5$)	23.63 \pm 1.10	92.10 \pm 21.00	25.60 \pm 1.00	38.46 \pm 16.17	–
Maize ^(b) (Solid)	RV	1.68 \pm 0.26	4.72 \pm 0.54	3.37 \pm 0.18	–	61.19 \pm 1.39
	MV ($n = 5$)	1.50 \pm 0.11	4.45 \pm 0.10	–	7.82 \pm 0.99	58.10 \pm 3.40
Oak leave ^(b) (Solid)	RV	0.130 \pm 0.068	6.78 \pm 1.36	3.65 \pm 0.48	2.68 \pm 0.36	26.9 \pm 2.2
	MV ($n = 14$)	0.10 \pm 0.03	5.25 \pm 0.79	3.00 \pm 0.46	1.34 \pm 0.40	28.5 \pm 1.73

CV = certified values ($\mu\text{g} \cdot \text{L}^{-1}$); MV = mean measured values for aqueous ($\mu\text{g} \cdot \text{L}^{-1}$) and solid ($\mu\text{g} \cdot \text{g}^{-1}$) samples; RV = reference values ($\mu\text{g} \cdot \text{g}^{-1}$); mean measured values with either ICP-AES (a) or AAS (b).

from the analyses of 10 blanks (acidified water), by summing the mean value and three times the standard deviation of the results obtained. The relative deviations between certified or reference values and the mean measured values were below 20% in most cases. The main difference was observed for Pb in the NIST 1640 and oak leaf samples which may be induced probably by (1) a sample pollution and (2) a matrix effect. Figure 2 shows on its left column the concentration of heavy metals ($\mu\text{g.L}^{-1}$) in each TD sample. The corresponding DL was represented by an horizontal dotted line. There were only few concentration values under this limit for Cu, Pb and Zn. Concerning Cd and Ni, some concentration values were in the same order of magnitude as the DL and some of them are even lower. However, we have used all these values for the calculation of the total deposition, even those below the detection limits.

3. Results and Discussions

3.1. ATMOSPHERIC DEPOSITION

Figure 2 presents on its right column the temporal evolution of Cd, Cu, Ni, Pb, and Zn ($\mu\text{g m}^{-2}$ per week) in bulk deposition (i.e. both dry and wet atmospheric depositions) from 1 October 2001 to 22 November 2002 at Versailles. It has to be noticed that Ni deposition measured for week 5 was discarded because of its very high level ($330 \mu\text{g m}^{-2}$ were collected during this week) which may most probably be induced by a sample contamination. Nevertheless, there is a tendency for deposition to be low when precipitation volumes were high while high deposition occurred during dry periods. These deposition peaks were mainly noticed four times in the Ni case (week 13, 26, 37 and 45), three times for Cd, Cu and Zn (weeks 24, 25 and 44; week 37, 41 and 44 and week 24, 26 and 44, respectively) and twice for Pb (week 24 and 43). It is also noteworthy that the deposition of none of the five elements appeared to be correlated with the amount of precipitation. Indeed, atmospheric deposition processes occurring during dry weather periods are an important and even prevalent contribution to total atmospheric deposition (Azimi *et al.*, 2003; Sweet *et al.*, 1998). Consequently, low metal concentrations with high volume precipitation samples arise from the dilution of dry deposition during rain events. The total annual depositions (g km^{-2} per year) were calculated aggregating weekly depositions for each element (Table IV). Uncertainties were estimated taking into account the uncertainty on weekly values, mostly resulting from standard deviation of triplicate analyses. Results showed the predominance of Zn which was more than four times higher than the other elements in atmospheric depositions which were ranked as $\text{Cu} > \text{Pb} > \text{Ni} > \text{Cd}$. Such a global pattern was already observed at a similar urban site in the east side of the Paris area. Indeed, a previous research program (Azimi *et al.*, 2003) measured depositions of 335, 9700, 9450 and $15\,000 \text{ g km}^{-2}$ per year for Cd, Cu, Pb and Zn, respectively, during the year 2001. Nevertheless, heavy metal depositions seem to be lower at the Versailles

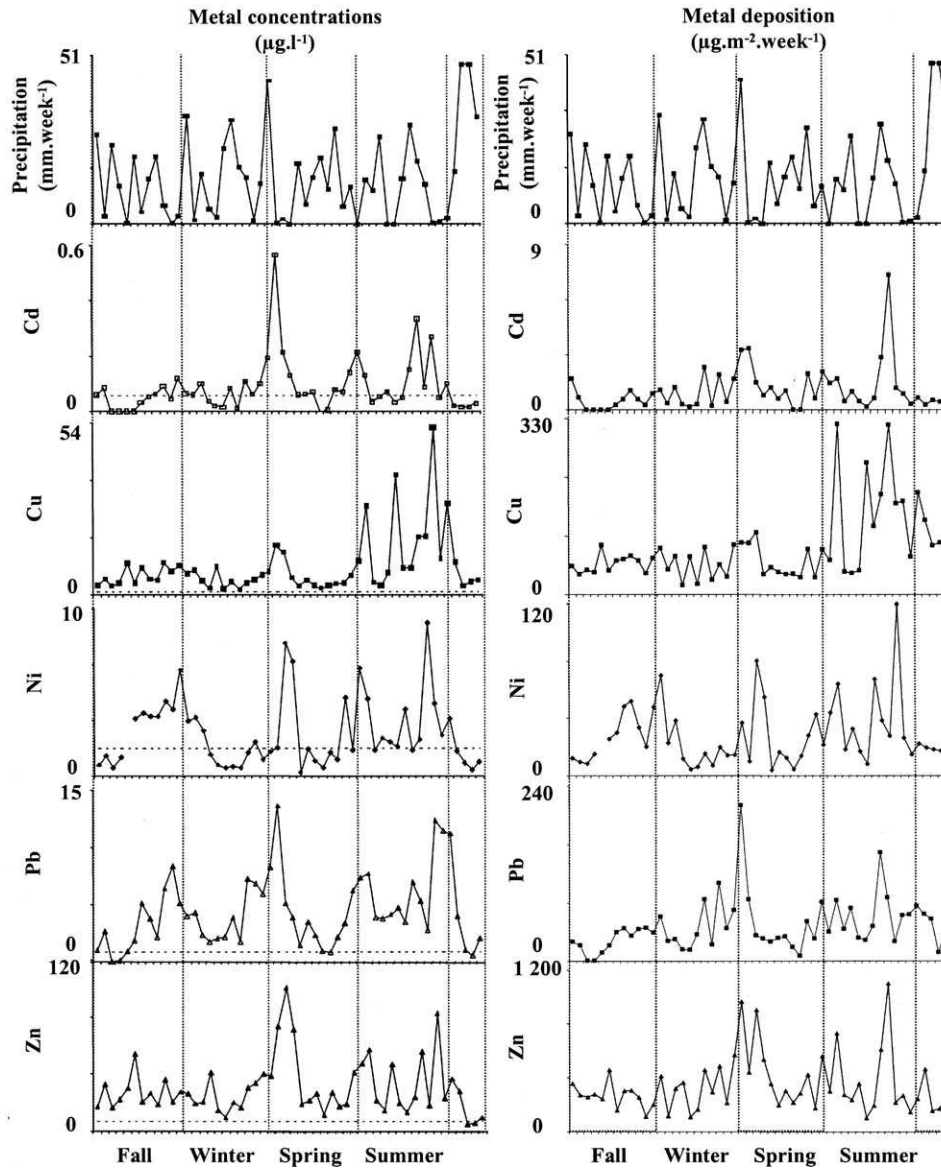


Figure 2. Weekly evolution in heavy metal concentrations ($\mu\text{g L}^{-1}$, left column) and total atmospheric depositions ($\mu\text{g m}^{-2}$ per week, right column) from October 2001 to November 2002 at Versailles. The dotted horizontal line on the left column indicates the detection limit for each metal. Upper graphs on both columns represent weekly evolution of precipitation (mm per week).

site which is located at the west side of Paris. Such decrease may probably be induced by the lower impact of the Paris area since the global air mass flow of this region is mainly from the west to the east (Garban *et al.*, 2002). The Ni deposition was also in the same order of magnitude as measured by other studies performed in

TABLE IV

Annual atmospheric deposition of heavy metal (g km^{-2} per year) aggregating weekly deposition values. The uncertainty is assessed by aggregating the uncertainty of each week determination step

Cd	Cu	Ni	Pb	Zn
47 ± 5	3900 ± 415	1500 ± 140	2200 ± 230	15600 ± 1600

urbanised locations. Indeed Lawlor and Tipping (2003) found values ranging from 300 to 1200 g km^{-2} per year for Ni in Northern England and Kim *et al.* (2000) found 800 and 1100 g km^{-2} per year at Chesapeake and Delaware Bay, USA.

3.2. OTHER FLUXES OF HEAVY METALS THROUGH THE EXPERIMENTAL PLOTS

3.2.1. Fertilisers and Amendments

Mass flows. Table II presents a summary of operations during 4 years, with more details on application periods along the crop year 2002, i.e., from September 2001 to July 2002. Since the different cultivation systems are defined by different sets of decision rules rather than by a definite experience procedure, applications of fertilisers and crops vary with time. The only stated option is to cultivate wheat every two years in all systems. In order to present the influence of cultivation systems and crops on heavy metal fluxes, annual mass flows of the different fertilisers were considered for each association system/crop (wheat or pea) under definite pedoclimatic conditions, i.e., on a definite plot during 2002. The sum of two annual fluxes in the same field allowed us to compare the different systems without referring to a particular crop.

Heavy metal contents of fertilisers and corresponding input fluxes. Table V presents results of chemical analyses of all agricultural products applied on experimental plots during the period 1998–2002, except the organic amendment used up in 1999. From these contents and from mass flows given in Table II, the input fluxes of Cd, Cu, Ni, Pb, and Zn in plots cultivated could be deduced following the three systems with wheat or pea. Contrary to crops, no attempt was made to assess the uncertainty on the rates of applied fertilisers. So the uncertainty on inputs from fertilisers was estimated only from analytical results reported in Table V and the following formula (Frontier *et al.*, 2001). Knowing that the input of each metal is calculated with:

$$F = aX + bY, \quad (1)$$

where X and Y are the metal contents of different fertilisers, and a and b are the rates of their application, the variance of (1) is given by:

$$V(F) = a^2V(X) + b^2V(Y), \quad (2)$$

TABLE V
Concentrations (mg kg⁻¹) and annual loads (g km⁻² per year) of heavy metals in agricultural inputs (fertilisers)

	Cd	Cu	Ni	Pb	Zn
Heavy metal contents					
N (<i>n</i> = 1)	0.03	3.6	<1	<2	7.2
MgSO ₄ (<i>n</i> = 5)	0.15 ± 0.03	0.95 ± 0.16	40.6 ± 0.8	0.9 ± 0.2	6.9 ± 1.3
PK (<i>n</i> = 5)	10.3 ± 1.2	18.3 ± 0.7	9.8 ± 0.3	5.9 ± 0.2	87 ± 1.7
Feather flour (<i>n</i> = 3)	1.02 ± 0.16	1.95 ± 0.05	2.3 ± 0.2	1.79 ± 0.35	120 ± 4
Wheat					
PRO	311 ± 36	772 ± 37	325 ± 32	239 ± 62	3056 ± 106
IN	207 ± 24	506 ± 24	216 ± 20	157 ± 39	2020 ± 68
ORG	41 ± 6	78 ± 2	92 ± 8	72 ± 14	4800 ± 160
Pea					
PRO	309 ± 36	549 ± 21	294 ± 9	177 ± 6	2610 ± 51
IN	206 ± 24	366 ± 14	196 ± 6	118 ± 4	1740 ± 34
ORG	0	0	0	0	0

Uncertainty for heavy metal content corresponds to standard deviation of analysis. For cultivation systems: IN = Integrated; PRO = Productive; ORG = Organic. See Figure 1 for their place on the site. For fertilisers: (N) ammonitrate 33.5%: NH₄NO₃; (MgS) kieserit: MgSO₄ · H₂O; (PK) NPK 0-25-25: CaHPO₄ · KCl · 2H₂O.

and the uncertainty on annual inputs is calculated as:

$$\sigma(F) = \sqrt{(a^2\sigma^2(X) + b^2\sigma^2(Y))}, \quad (3)$$

where $V(X)$ and $V(Y)$ represent the variances of X and Y , and σ the standard deviation.

The contents of Ni and Pb in the N fertiliser are low in a range close to the blank values. But the high application load of N on wheat in PRO and IN systems may induce a significant contribution of this fertiliser. Indeed differences between inputs of metal on wheat and pea (Table V) are due to this application. In the Pb case, it may represent about 40% of the metal input on wheat, considering the upper plausible limit of the 'ammonitrate' Pb content (Table V). The N fertiliser also carries about 30% of the input of Cu in PRO and IN systems on wheat. Its contribution to Ni and Zn input loads lies between 10% and 20% and it is negligible for Cd. For this latter element, inputs are mainly due to the PK-fertiliser, applied on both crops in PRO and IN systems. However, PK fertilisation also induces significant input fluxes of Cu, Ni, Pb, and Zn.

The organic amendment carried significant amounts of Ni, Pb, and mostly Zn, into the ORG system on wheat. The inputs of heavy metals in organic agriculture

from the authorized amendments and fertilisers may clearly vary with their origin and quality. MgSO_4 fertiliser was not used on fields in 2002, but it can be seen from Tables II and V that it induced a major input of Ni in fields cultivated with colza in PRO and IN systems.

Finally, among agricultural inputs, seeds have been analysed for their heavy metal contents. The calculated input fluxes were very low, so they were neglected in the rest of the study.

3.2.2. Crops

All crop varieties of wheat and pea from the different systems were analysed with three replicates. Concerning wheat, no significant differences were observed between varieties (two values for Cd and two values for Pb were considered as non significant and rejected). The statistical tests only showed that the average content of Zn in ORG wheat samples was significantly different from the corresponding overall average. Therefore, results are distinguished for ORG and other wheat grains. Means and standard deviations were obtained from 20 results for the wheat grown in PRO and IN systems, from six analyses for ORG wheat, and from 12 analyses for pea (Table VI). Table VI also presents crop yields obtained in 2001. The cultivated plots were homogeneous for pea, whereas up to six different varieties of wheat were cultivated in IN and ORG systems. However, since no significant variations of heavy metal contents were observed within each system, calculations were done

TABLE VI
Heavy metal contents ($\mu\text{g g}^{-1}$), yield (kg m^{-2} per year) and output fluxes (g km^{-2} per year) in crops

	Yield	Cd	Cu	Ni	Pb	Zn
Crop						
Wheat (no ORG) ($n = 20$)		0.036 ± 0.016	3.25 ± 0.88	<0.3	<0.03	19.6 ± 2.0
Wheat (ORG) ($n = 6$)		0.046 ± 0.013	5.16 ± 1.02	<0.3	<0.03	33.1 ± 2.4
Pea ($n = 12$)		0.007 ± 0.0001	6.66 ± 0.63	1.09 ± 0.17	<0.03	30.6 ± 2.5
Wheat						
PRO	1.01 ± 0.01	36.0 ± 16.0	3279 ± 904	<303	<30	19776 ± 2116
IN	0.61 ± 0.07	22.0 ± 12.0	1966 ± 747	<181	<18	11858 ± 2504
ORG	0.13 ± 0.04	6.1 ± 3.8	681 ± 367	<40	<4	4369 ± 1806
Pea						
PRO	0.32 ± 0.08	2.2 ± 0.8	2131 ± 680	349 ± 130	<9.6	9790 ± 3000
IN	0.22 ± 0.04	1.6 ± 0.5	1492 ± 390	244 ± 80	<6.7	6854 ± 1723
ORG	0.27 ± 0.02	1.9 ± 0.4	1792 ± 275	293 ± 61	<8.1	8230 ± 1160

For cultivation systems: IN = Integrated; PRO = Productive; ORG = Organic. See Figure 1 for their place on the site.

with the yield mean values, and the standard deviations were considered to assess the uncertainties on yields. Consequently, the output fluxes of heavy metals induced by harvesting were calculated (Table VI) and the uncertainties were calculated taking into account both uncertainties, from the chemical analyses and from the yields. Ni and Pb contents in grains were generally under DL values, thus outputs of Pb due to crops are very low. The fluxes are low for Cd and Ni, and rather high for Cu and Zn. Except for Cd, output fluxes from the ORG system were higher with pea cultures than with wheat. Considering wheat, large variations between the different systems also occurred, which are due, above all, to large differences in yields.

3.2.3. Leaching

Samples of leaching water were collected from March to May 2002. In April and May, volumes of soil solution samples obtained by centrifugation were less than a few millilitres, and actually, the water flow estimated by the CERES model was nil during this period. Therefore, analytical results were obtained only for samples collected in March, which were used to calculate the heavy metal fluxes for the whole year. Whatever plot considered, the calculated annual amount of leached water was about the same, despite the different crop yields. Indeed, no or little drainage was found from April to October, when crops covered fields. The calculated annual drainage was 240 ± 5 mm for all plots.

Differences between concentrations for one element in the different systems were generally lower than the variations observed within a particular plot (three replicates). Therefore, a mean value ($n = 24$), or an overvalue (when concentration was below DL), was adopted for each element in all plots and the corresponding fluxes have been calculated (Table VII). No value could be obtained for zinc because water sample volumes were not sufficient for flame AAS analysis. The flow of water leached from the 0–30 cm layer has been considered known with more accuracy than its composition. So uncertainties on heavy metal fluxes were estimated from chemical data only. The relatively high uncertainties for Cd and Pb compared to the DL values, are mainly due to the dispersion of analytical results for waters extracted from soil samples, and partly to the levels of blanks. Results found for Ni were significantly above blank values, although they were close to the DL values.

TABLE VII

Heavy metal concentrations ($\mu\text{g L}^{-1}$) in soil water (mean \pm SD) and estimated annual drainage fluxes (g km^{-2} per year) at 30 cm depth

	Cd	Cu	Ni	Pb	Zn
	$n = 9$	$n = 23$	$n = 23$	$n = 23$	–
Concentrations	0.2 ± 0.2	13.7 ± 2.0	2.4 ± 0.7	<5	n.a.
Fluxes	48 ± 48	3288 ± 480	576 ± 160	<1200	n.a.

n.a.: not available.

The leaching of Cu has been quantified with more accuracy, and seemed to be relatively important (see below).

3.3. HEAVY METAL FLUXES AND BALANCES IN THE DIFFERENT PLOTS AND CULTIVATION SYSTEMS

Figures 3 and 4 present the inputs (grey arrows), the outputs (white arrows) and the balance of Cd, Cu, Ni and Pb for each system and each crop. Atmospheric depositions were the main inputs of Cu, Ni and Pb, whatever the system and the crop considered. Indeed, except for Cd and for pea in the ORG system, the atmospheric inputs were 5 to 50 times higher than the agricultural ones. On the contrary, agricultural inputs of Cd were higher than atmospheric inputs by a factor 6 and 4 in PRO and IN systems, respectively. In the ORG system, wheat fields received the same inputs of Cd from fertilisation and atmospheric deposition, while pea received no agricultural inputs at all.

The outputs were lower than inputs in most cases. Indeed, whatever the system and the crop considered, an accumulation of Ni and Pb appeared in the cultivated soil, with a balance comprised between 630 and 1200 g km⁻² per year. However, the high uncertainty on Pb leaching has to be pointed out, and it could allow for a net balance of more than 2000 g km⁻² per year of Pb. The accumulations of Cd present larger variations with cropping systems, lying between 39 and 279 g km⁻² per year for wheat, and between 2 and 311 for pea. In the case of Cu, an essential nutriment, the crop uptake and the leaching were high, so the balance was negative, ranging from -512 to -1900 g km⁻² per year, except for wheat in the ORG system where the fluxes were practically balanced.

To assess the significance of these fluxes, the annual balance determined for each element must be compared to the stock of the same element in the cultivated horizon. This stock was calculated from the heavy metal contents shown in Table I or, for Cu and Ni, obtained by Juste and Tauzin (1986) in neighbouring plots, and from the rough estimation of 4×10^8 kg km⁻² of soil in the cultivated horizon. The annual balances of Cd, Cu, Ni, and Pb, reached 0.33, -0.024, 0.014 and 0.014%, respectively, of their total amounts in this horizon. Therefore, the present accumulation rate of Cd may significantly change the Cd content of a surface horizon at the time scale of a century (mainly in the PRO system). The other elements should accumulate, or deplete in the case of Cu, much more slowly. However, only a fraction of these heavy metals is available for plants and organisms. Then, for a better assessment, the determination of the annual variation of the total stock should be completed by an estimation of the variation of the available fraction for each studied element (Coïc and Coppenet, 1989; Juste and Mench, 1992).

The comparison of the different cultivation systems allowed a better understanding of heavy metal accumulation in the cultivated horizon. Knowing that the ORG systems do not receive any PK fertiliser, the heavy metal accumulation is weaker than in other systems for Cd, and to a lesser extent for Ni and Pb. Concerning Cu,

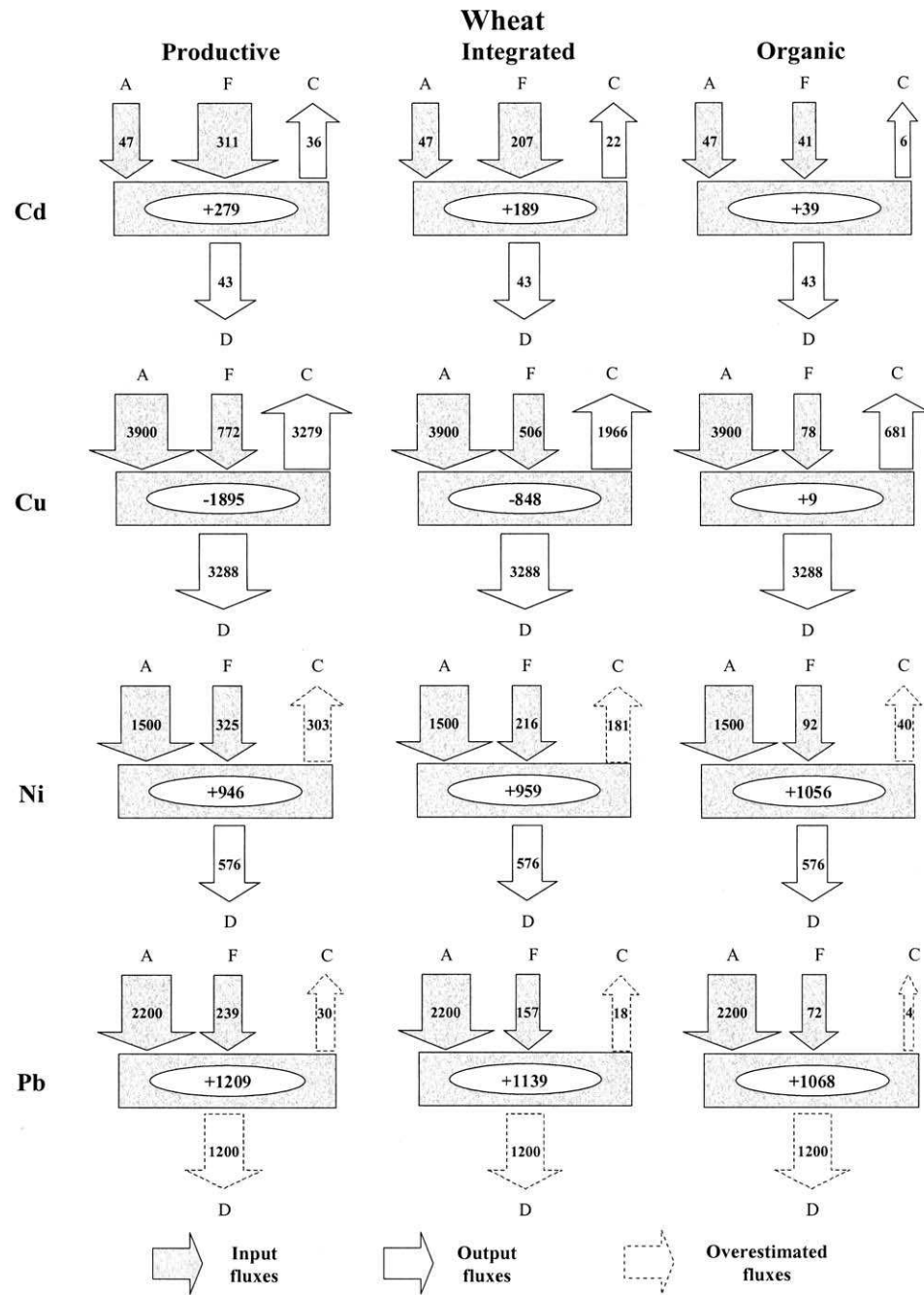


Figure 3. Annual balance (g km^{-2} per year) of heavy metal fluxes in soil in the case of wheat culture under the three cultivation systems (A: atmospheric depositions, F: fertilisers, C: crops, D: drainage water).

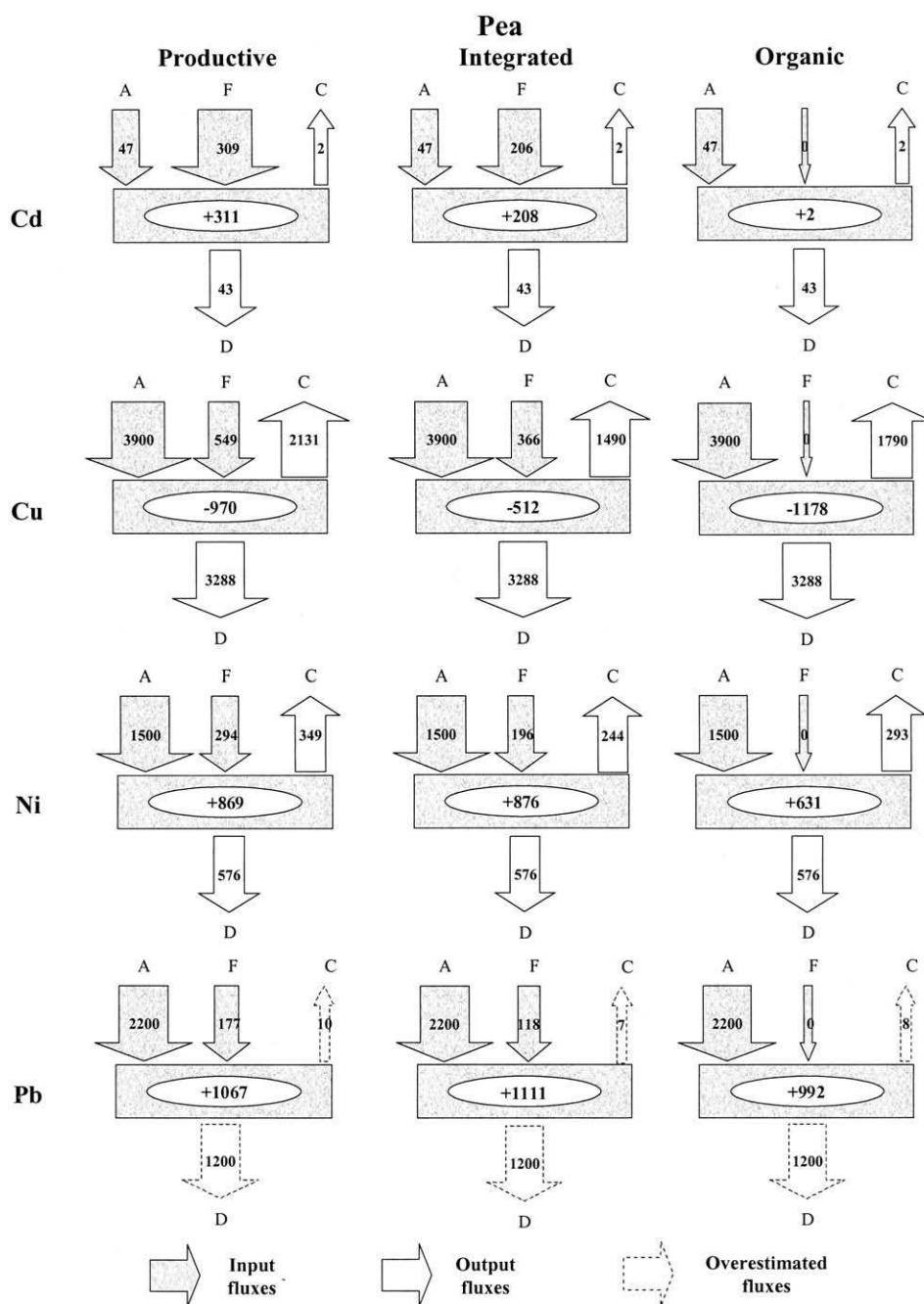


Figure 4. Annual balance (g km^{-2} per year) of heavy metal fluxes in soil in the case of pea culture under the three cultivation systems (A: atmospheric depositions, F: fertilisers, C: crops, D: drainage water).

the high yield for both wheat and pea productive system induces high output fluxes for copper, which may lead to a copper depletion in the soil.

4. Conclusions

The present work assessed the annual balance and fluxes of Cd, Cu, Ni, Pb and Zn, in agrosystems of Northern France. Although the studied area was experimental fields not far from urban areas inducing an anthropogenic influence, the large surfaces and the cultivation history make them representative for wheat-pea rotations on soils which are little or not contaminated. To estimate the balances throughout the soil, two input and two output fluxes were determined.

Both input fluxes were determined with enough accuracy, the main difficulty arising from the large load of nitrogen fertiliser in productive system with Pb and Ni contents close to the analytical detection limit. The determination of output fluxes also faced low contents of Cd, Pb and Ni in crop grains and in soil water. The comparison of different cultivation systems, with organic farming avoiding PK mineral fertiliser, pointed out the effect of this product on Cd accumulation in soils. For the other elements, atmospheric depositions remain the main source of heavy metals to these fields in 2002. All the studied element trends are to accumulate in the cultivated horizons, except Cu which is depleted by intensive crops. On the other hand, the annual net balances are much lower than the present stocks of elements.

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