Assessing the risk caused by diffuse Cd and Pb pollution: critical load modelling for forest and arable lands

Sophie Leguédois, Thomas Bur, Laure Gandois, Gaël Durbe, Jean-Luc Probst, Anne Probst

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S. Leguédois[1], T. Bur[1], L. Gandois[1], G Durbe[1], J-L Probst[1], A. Probst[1]

[1] Laboratoire d'écologie fonctionnelle (EcoLab), UMR 5245 CNRS, Université Paul Sabatier, INP-ENSAT, BP 32 607, F-31 326 Castanet-Tolosan cedex, France, anne.probst@ensat.fr

Abstract

We use critical load modelling to assess the risks caused by diffuse Cd and Pb pollution on two sites located on forest and arable lands respectively. The objectives of this work are: (i) to test the proposed critical load method on arable land and, (ii) to compare critical loads with current measured Cd and Pb fluxes. For the two sites, computed critical concentrations of Cd and Pb in soil water regarding the protection of soil organisms (2.3 and 4.9 $mg.m^{-3}$ respectively for the forest, 0.7 and 4.5 $mg.m^{-3}$ respectively for the arable site) are above current concentrations. Modelled critical loads (15.6 and 46.4 $g.ha^{-1}.a^{-1}$ for Cd and Pb respectively) are lower than current inputs for the forested site. However the arable site would be in exceedance with current inputs larger than modelled critical loads (1.3 and 7.1 $g.ha^{-1}.a^{-1}$ for Cd and Pb respectively). These results are going to be checked thanks to long-term monitoring and ecotoxicological tests.

Key words: Cd, Pb, critical load, forest land, arable land

Introduction

Within the international convention on long-range transboundary air pollution (1979, United Nations Economic Commission for Europe, Geneva), the air pollution abatement policies are supported by an effect-based approach. To assess the risk caused by air pollution on ecosystems, the critical load concept has been successfully developed and used for this convention. A critical load is defined as "*a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge*" (Spranger *et al.*, 2004 from Nilsson and Grennfelt, 1988). Critical load approaches have been first formulated for acidifying compounds and then developed for nutrient nitrogen. More recently, methods to determine critical loads for lead (Pb) and cadmium (Cd) have been proposed (Schütze *et al.*, 2004) and applied (Slootweg *et al.*, 2005) for semi-natural as well as agricultural lands.

In France, a preliminary assessment of critical load for Pb at several forest sites showed that this approach is relevant for French semi-natural ecosystems (Probst *et al.*, 2003). A nation-wide assessment and mapping for Cd and Pb in semi-natural ecosystems (mostly forest) was then performed (Probst *et al.*, 2005). However critical loads of Cd and Pb have still never been determined for French arable lands whereas these areas are subjected to higher pollution (chemical and organic fertilisers, pesticides…). Only first estimates of metal fluxes have been performed (Bur *et al.*, 2007). Moreover critical loads have not yet been compared to present loads.

Thus the objectives of this work are: (i) to test the method to determine Cd and Pb critical load for French arable lands and, (ii) to compare critical loads with current measured Cd and Pb fluxes.

Materials and Methods

Current and critical fluxes of metal were assessed for two sites on forested and arable lands respectively (see Tab. 1). The forested site belongs to the French national survey network for forest ecosystems, RENECOFOR (ONF, 1996; Ponette *et al.*, 1997). The arable site is a cultivated catchment monitored for 20 years for the impact of agricultural practices on water quality.

Tab. 1: Characteristics of the studied sites.

Site	Forested	Arable
Location	NE France	SW France
Vegetation	Norway spruce (*Picea abies*)	2-year rotation: wheat / sunflower
Soil type	Cambic podzol	Calcic cambisol
Soil pH	3.6	8.2

Ecotoxicological effects of metal on plants and soil fauna are supposed to occur via soil solution and more specifically as free metal ion (de Vries *et al.*, 2007).The stock of reactive metal S_M ($g.ha^{-1}$) in the soil surface layer (0-20 and 0-

30 cm for the forested and arable sites respectively) results from the balance of the following incoming and outgoing fluxes (g.ha^{-1}.a^{-1}) as shown in Fig. 1:

- net uptake in harvestable part of plants M_u;
- atmospheric deposition M_{dep};
- agricultural inputs (fertilisers, pesticides) M_{agr};
- rock weathering M_w, the input of reactive metal from this flux is considered negligible;
- leaching M_{le}.

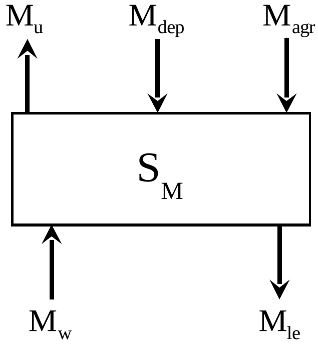

Fig. 1: Fluxes controlling the stock of metal in the soil surface layer. Variables are explained in the text.

The current fluxes were determined according to guidelines of the critical loads mapping manual (Schütze *et al.*, 2004). Metal net uptake M_u is derived from f_{Mu} the fraction of metal net uptake within the soil surface layer, Y_{ha} the yield of harvestable biomass dry weight (kg.ha^{-1}.a^{-1}) and $[M]_{ha}$ the metal content of the harvestable parts of the plants (g.kg^{-1} dw):

$$M_u = f_{Mu} \times Y_{ha} \times [M]_{ha} \quad (1).$$

As most uptake of nutrient and pollutants occurs in the topsoil, f_{Mu} was set at 1. Y_{ha} values were assessed by onsite measurements (Nys *et al.*, 1983) and farming surveys. $[M]_{ha}$ were derived from Bechtel Jacobs Company LLC (1998), Murillo *et al.* (1999) Baize *et al.* (2003) and Madejón *et al.* (2003). M_{dep} was determined with the 2005 modelled data of the European Monitoring and Evaluation Programme (EMEP). M_{agr} was estimated from farming practice surveys (amount of applied inputs) and SOGREAH (2007) for metal content in inputs. Anthropogenic inputs (M_{dep} and M_{agr}) were assumed to contain mostly reactive easily soluble metal. M_{le} is the product of the amount of water leached from the soil surface layer Q_{le} (m^3.ha^{-1}.a^{-1}) and the total concentration of metal $[M]_{sdw}$ in soil drainage water (g.m^{-3}):

$$M_{le} = Q_{le} \times [M]_{sdw} \quad (2).$$

For the forest site, Q_{le} was estimated as the difference between the mean annual precipitation and evapotranspiration measured onsite. However, for the arable land, overland flow has to be taken into account. Thus Q_{le} was determined from GR4J rainfall-runoff model (Perrin *et al.*, 2003). $[M]_{sdw}$ was measured from soil solution sampled with lysimeters.

To compute critical load soil organisms were chosen as target receptor of concern. Critical limit for soil organisms is expressed as free metal ion concentration in soil solution $[M]_{free(critic)}$ (mol.L^{-1}) below which the effects on these organisms is tolerable. $[M]_{free(critic)}$ is considered as a function of soil solution pH pH_{ss}. (de Vries *et al.*, 2007):

$$\log[Cd]_{free(critic)} = -0.32\,pH_{ss} - 6.34 \quad (3),$$

$$\log[Pb]_{free(critic)} = -0.91\,pH_{ss} - 3.80 \quad (4).$$

Corresponding critical $[M]_{sdw}$ is thus determined by applying a model of metal speciation in soil solution, WHAM6 (Tipping, 1994, 1998). At critical conditions, it is assumed that the mass balance is in a steady state and thus that the concentration of reactive metal in the soil surface does not change in time. The assumption can be considered valid at large time scales (Schütze *et al.*, 2004). Consequently, the sustainable anthropogenic load at critical condition for a given metal, i.e. the critical load $CL(M)$ (g.ha^{-1}.a^{-1}), equals:

$$CL(M) = M_{dep} + M_{agr} = M_u + M_{le(crit)} \quad (5).$$

M_u at critical condition was assumed to equal current M_u.

Results and Discussion

Current fluxes of Cd and Pb for the two sites are given in Fig. 2 and Fig. 3. Pb and Cd fluxes are larger at the forest site than at the arable site. The acidic conditions of the forested site (pH_{ss}=4.2) leads to high leaching of dissolved metals. For the arable site, Cd is mostly imported as agricultural inputs (90 % of the total incoming flux) whereas this source represents only 12 % of the total incoming flux of Pb.

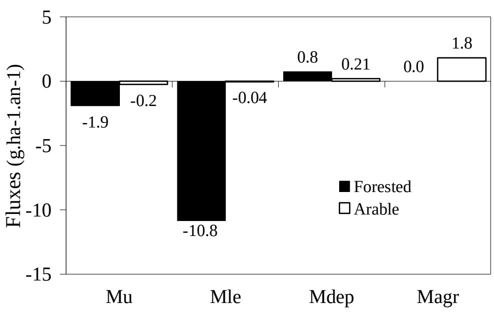

Fig. 2: Outgoing (negative values) and incoming (positive values) fluxes of Cd at the forested and the arable sites.

The current mass balances of Cd and Pb at the forested site are largely negative (see Tab. 3 and Tab. 4): the outgoing fluxes are larger than the incoming fluxes. For this site, Cd and Pb have been previously stored in the soil surface layer — 0.01 and 3.89 $g.ha^{-1}$ respectively in the 0-4-cm layer (Hernandez, 2003). Metal leaching in these acidic conditions is thus quite large. Metal leaching fluxes for this site is in the same order of magnitude than previous estimates done for other forested sites located in north-east France (Probst *et al.*, 2003). On the contrary, the mass balances are positive for the arable site (see Tab. 3 and Tab. 4): Cd and Pb are still accumulating in this high-pH, clay-rich soil.

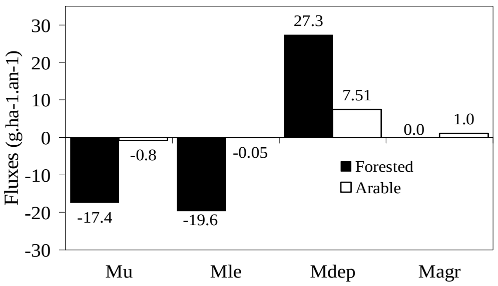

Fig. 3: Outgoing (negative values) and incoming (positive values) fluxes of Pb at the forested and the arable sites.

For the forested site current $[Cd]_{sdw}$ and $[Pb]_{sdw}$ are close to but lower than the critical concentrations (see Tab. 2). However, current inputs of Cd and Pb are far lower than *CL(M)* (see Tab. 3 and Tab. 4). The forested site is not in exceedance for these metals.

For the arable site, current $[Cd]_{sdw}$ and $[Pb]_{sdw}$ are largely lower than critical concentrations (see Tab. 2) but there is an input exceedance for the two metals (see Tab. 3 and Tab. 4). Even if the crops of this site are not generally recognised as at risk concerning metal pollution, current Cd and Pb loads seem unsustainable regarding soil organisms. Indeed metals are accumulating in this soil, increasing the ecotoxicological risk.

Tab. 2: Average current concentrations [standard deviations] and critical concentrations of Cd and Pb in the soil drainage water for the forested and the arable sites.

	$[Cd]_{sdw}$ $mg.m^{-3}$		$[Pb]_{sdw}$ $mg.m^{-3}$	
	current	critical	current	critical
Forested	1.85[0.35][1]	2.3	3.35[0.35][1]	4.9
Arable	0.028[0.017][2]	0.7	0.035[0.044][3]	4.5

Number of measurements: [1] n=2, [2] n=6, [3] n=9.

Tab. 3: Current input and output, mass balance and critical load (CL) for Cd at the forested and the arable sites.

	Input	Output	Balance	*CL(Cd)*
	$g.m^{-3}.a^{-1}$			
Forested	0.8	12.8	-12.0	15.6
Arable	2.0	0.3	+1.8	1.3

Tab. 4: Current input and output, mass balance and critical load (CL) for Pb at the forested and the arable sites.

	Input	Output	Balance	*CL(Pb)*
	$g.m^{-3}.a^{-1}$			
Forested	27.3	37.1	-9.7	46.4
Arable	8.6	0.8	+6.1	7.1

Conclusion

Our work shows that *CL(Cd)* and *CL(Pb)* can be computed for French arable lands. This computation is now possible at the country scale thanks to a recent national review on metal inputs in agricultural soils (SOGREAH, 2007). The results point out that the forested acidic site should support higher Cd and Pb loads even if the current concentrations for these metals in soil solution are close to critical concentrations. For the calcareous arable site, the current Cd and Pb inputs would already exceed critical loads and the dissolved metals would accumulate in the topsoil. To test the robustness of these modelled results, critical load should be computed for other sensitive receptors (plants, food crops and groundwater) and sensitivity analysis should be performed.

Ongoing long-term monitoring of metal stocks and fluxes in theses two ecosystems will enable us to check the results obtained with critical load model. Measurements would also be useful to test the assumptions made in critical load computation, especially the proportion of reactive metal in the anthropogenic inputs as well as the assessment of critical vegetation uptake by current value.

Cd and Pb ecotoxicological tests with soil organisms (*Folsomia candida*, Collembola) are currently performed on various soil types from French forested and arable lands (Bur *et al.*, this meeting). This study would allow to evaluate the critical limits computed for these two soils as well as to check actual ecotoxicological effects.

Finally, models taking the temporal dynamic into account should be developed to improve critical or target load assessment in these complex systems.

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References

Baize D, Mench M, Sappin-Didier V, Mocquot B, Gomez A, Proix N, Sterckeman T. Phytodisponibilité des éléments traces métalliques dans les grains de blé. Dossier Environ INRA 2003, 25:45-62

Bechtel Jacobs Company LLC. Empirical models for the uptake of inorganic chemicals from soil by plants. U.S. Dep. Energy, Office Environ Management, 1998. http://www.hsrd.ornl.gov/.

Bur T, Probst A, Gers C, Austruy A, Gandois L, Crouau Y, Leguédois S, Probst JL. Critical loads for metals in agricultural lands. Investigations in southwest France. LRTAP Conv workshop critical loads of heavy metals 2007. http://www.ceh.ac.uk/hmcritloads

Hernandez L. Dynamique des éléments traces métalliques dans les sols de différents écosystèmes forestiers français. Origine, distribution physique et chimique et facteurs de contrôle. PhD thesis Univ Toulouse III, 2003.

Madejón P, Murillo JM, Marañón T, Cabrera F, Soriano MA. Trace element and nutrient accumulation in sunflower plants two years after the Aznalcóllar mine spill. Sci Total Environ 2003, 307:239-257.

Murillo JM, Marañón T, Cabrera F, López R. Accumulation of heavy metals in sunflower and sorghum plants affected by the Guadiamar spill. Sci Total Environ 1999, 242:281-292.

Nilsson J, Grennfelt P (eds.) Critical loads for sulphur and nitrogen. Report from a workshop, Skokloster, Sweden 1988.

Nys C, Range D, Ranger J. Etude comparative de deux écosystèmes forestiers feuillus et résineux des Ardennes primaires françaises. III. Minéralomasse et cycle biologique. Ann Sci for 1983, 40(1):41-66.

ONF. Notice de présentation du réseau national de suivi à long terme des écosystèmes forestiers. 1996.

Perrin C, Michel C, Andréassian V. Improvement of a parsimonious model for streamflow simulation. J Hydrol 2003, 279(1-4) :275-289.

Ponette Q, Ulrich E, Brêthes A, Bonneau M, Lanier M. RENECOFOR — Chimie des sols dans les 102 peuplements forestiers du réseau. ONF 1997.

Probst A, Moncoulon D, Goddéris Y, Hernandez L, Party JP. Critical loads for lead in France: First results on forest soils. J Physique IV 2003, 107:1111-1114.

Probst A, Moncoulon D, Party JP. France.In Slootweg *et al.*, 2005, *opus cite*.

Schütze G, de Vries W, Tipping E, Lofts S. Chapter 5.5: Critical loads of cadmium, lead and mercury. In Spranger *et al.*, 2004, *opus cite*.

Slootweg J, Hettelingh JP, Posch M; Dutchak S, Ilyin I (eds). Critical loads of cadmium, lead and mercury in Europe, Report Working Group Effects, Conv Long-range Transboundary Air Poll, 2005.

SOGREAH. Bilan des flux de contaminants entrant sur les sols agricoles de France métropolitaine. Bilan quantitatif de la contamination par les éléments traces métalliques et les composés traces organiques et application quantitative pour les éléments traces métalliques. ADEME 2007.

Spranger T, Lorenz U, Gregor HD (eds). Manual on methodologies and criteria for modelling and mapping critical loads and levels and air pollution effects, risks and trends. Umweltbundesamt 2004. www.icpmapping.org.

Tipping E. WHAM – A chemical-equilibrium model and computer code for waters, sediments, and soils incorporating a discrete site electrostatic model of ion-binding by humic substances. Comput Geosci 1994, 20(6):973-1023.

Tipping E. Humic ion-binding model VI: An improved description of the interactions of protons and metal ions with humic substances. Aquat Geochem 1998, 4(1):3-48.

de Vries W, Lofts S, Tipping E, Meili M, Groenenberg JE, Schütze G. Impact of soil properties on critical concentrations of cadmium, lead, copper, zinc, and mercury in soil and soil solution in view of ecotoxicological effects. Rev Environ Contam Toxicol 2007, 191: 47-89.