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Critical loads for lead in France: First results on forest soils

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ABSTRACT

Within the framework of the United Nation Convention on Long Range Transboundary Air Pollution, France is part of the Working Group on Effect which aims at evaluating the impact of atmospheric deposition on ecosystems by calculating critical loads. The "critical loads" are "the highest deposition of compounds that will not cause chemical changes in soil leading to long-term harmful effects on ecosystem structure and function". A guidance manual for calculation of critical loads for heavy metals (lead and cadmium) has been proposed by the Coordination Center for Effects (executive body of the WGE). French National Focal Center (CNRS and ADEME) aims in this study at evaluating the accuracy of the european methodology for calculation of critical loads for french forest soils. It appears that critical load approach is adapted for France but need to be calibrated at least for calculation of weathering fluxes and determination of critical limits. Stand-still on the contrary is not adequate because of inherent contradictions in the method and too much uncertainties in the transfer functions.

1. INTRODUCTION

The United Nation Convention on Long-range Transboundary Air Pollution (UNECE-CLRTAP) has been ratified in 1979 by 34 governments and the European Community to deal with problems of air pollution and to set up an institutional framework, bringing together research and policy.

For this purpose, 3 working groups gathering research centers from involved countries have been created since the signature of the convention :

- the Working Group on Effect which aims at evaluating the sensibility of ecosystems to atmospheric deposition;
- the EMEP steering body which attempts to model the atmospheric transports of air pollutants;
- the Working Group on Strategies and Review which aims at considering different scenarios of pollutant emission and evaluates their financial and ecological impact.

The Working Group on Effects has developed a methodology based on a threshold, determined for a particular receptor, that atmospheric deposition should not trespass : the critical load. The definition of critical load is "the highest deposition of compounds that will not cause chemical changes in soil leading to long-term harmful effects on ecosystem structure and function" [5].

Critical loads of acidity and nitrogen have already been calculated by the european countries and submited to the WGE. Following the same approach, critical loads of lead and cadmium are now being determined by the countries involved in the project.

In this study, we attempt to evaluate the different approaches to determine critical loads of lead for french forest soils. We will focus first on the determination of dissolved lead in soil solution using transfer functions and second on the determination of weathering rates.

2. METHODOLOGY AND DATA SOURCES

2.1 Simple steady-state mass balance

The different approaches for calculation of critical loads for lead (CL_{Pb}) are derived from a simple steady-state mass balance model applied on the topsoil, which is considered as the humus layer for forest soils. The inputs are : weathering (Pb_{we}) and atmospheric deposition. The outputs are : biomass uptakes (Pb_{upt}) and leaching (Pb_{le}). Critical load (CL_{Pb}) is thus calculated as follows [4]:

$$CL_{Pb} = Pb_{le} + Pb_{upt} - Pb_{we} \quad (1)$$

Although other inputs and outputs of lead actually occur in the upper soil horizon, like biomass return, surface runoff, bypass flow and foliar uptake, their determination are difficult due to the lack of data. Hence, they will be neglected in the mass balance.

2.2 Determination of mass balance parameters

The lead weathering rate (Pb_{we}) in the mineral topsoil is derived from the base cation weathering release (BC_{we}), and the ratio between lead (X_Pb) and base cation (X_Bc) contents in the parent material. F_{rt} is a factor that scales down the weathering rate from 1m to the considered depth [4] :

$$Pb_{we} = 5 \cdot 10^{4} \times F_{rt} \times BC_{we} \times \left(\frac{X\_Pb}{X\_bc} \right) \quad (2)$$

Base cation weathering rate has been determined using the PROFILE model [10] on representative french soil samples [6]. The content of lead and base cations in the parent material have been measured [3] on selected french soil samples or taken from the RIVM[1] guidance [4].

The biomass uptake of lead (Pb_{upt}) is derived from the average annual biomass growth (Y) and from the lead content in biomass (X_{hpp}) with an uptake factor (F_{ru}) scaled down to the considered depth.

$$Pb_{upt} = F_{ru} \times Y \times X_{hpp} \quad (3)$$

Y is determined using the IFN (National Forestry Inventory) data for french forest area and corresponding wood productivity. The average lead content in biomass is from Hettelingh et al. [4].

The leaching of lead from topsoil is calculated using runoff data and dissolved lead concentration in soil solution [6,8].

2.3 Effect-based critical loads and stand-still loads

"Effect-based critical loads" and "stand-still loads" are 2 different approaches for calculation of a treshold for atmospheric deposition, both based on the same steady-state mass balance (eq.1).

2.3.1 Effect-based critical loads

In the "effect-based" principle, the steady state mass balance is used with a critical lead concentration above which the chosen receptor will be damaged. Different approaches for the determination of a receptor and its critical limit for lead are currently discussed in the Working Group on Effects. However, in order to test the effect-based approach, a preliminary critical limit for microbiota has been settled to 8 $mg.m^{-3}$ of dissolved [Pb] in soil solution.

2.3.2 Stand-still loads

In the "stand-still" principle, the steady state mass balance is used with the current lead concentration in topsoils. It allows an atmospheric deposition that just maintains the heavy metal concentration at its present level. Because of the lack of measured total [Pb], we chose to apply this approach only on 7 soil samples [7] where total lead concentration is known [3]. To calculate the actual leaching of lead from the topsoil, a dissolved [Pb] in soil solution must be determined from the total [Pb] in soil. For that purpose, a sequence of 3 transfer functions [4] is used (eq. 4, 5, 6, 7).

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[1] RIVM : National Institute of Public Health and the Environment (Netherlands)

Transfer function to derive "so-called" lead (Aqua Regia) from total lead[2] [4]

$$\log10(Pb_{so-called}) = a0 + a1 \times \log10(Pb_{total}) \qquad (4)$$

Coefficients values : a0=-0,54;a1=1,31 for sandy soils (depend on parent material)

Transfer function to derive reactive lead from "so-called" lead [4]

$$\log10(Pb_{reactive}) = b0 + b1 \times \log10(Pb_{so-called}) + b2 \times \log10(\%MO) + b3 \times \log10(\%clay) \qquad (5)$$

Coefficients values : b0=0,063;b1=1,042 ;b2=0,024 ;b3=-0,122

Transfer function to derive dissolved lead from reactive lead [4] (Freundlich coefficient)

$$\log10(Kf) = c0 + c1 \times \log10(\%OM) + c2 \times \log10(\%clay) + c3 \times pH \qquad (6)$$

$$Pb_{soilsolution} = \left(\frac{Pb_{reactive}}{Kf}\right)^{1/n} \qquad (7)$$

Coefficients values :c0=-3,06;c1=0,85;c2=0,02 ;c3=0,26 ; n=0,67

3. RESULTS AND DISCUSSION

Preliminary values for critical loads were determined for french forest ecosystems. Effect-based critical loads values range between 4,9 $g.ha^{-1}.an^{-1}$ and 133 $g.ha^{-1}.an^{-1}$. Stand-still loads values range between 19 $g.ha^{-1}.an^{-1}$ and more than 150 $g.ha^{-1}.an^{-1}$. For one particular soil, not included in the range, stand-still load is very high (450 $g.ha^{-1}.an^{-1}$) because of a high lead concentration in the upper horizon (134,4 $mg.kg^{-1}$).

In tab.1, we present critical load and stand-still load calculations on 3 french forest sites [7].

Table 1. Results for the calculation of critical loads and stand-still loads for 3 french forest sites

Site [7]	**PM 40**	**EPC 63**	**SP 57**
Region of France	Landes	Massif Central	Vosges
Parent material	Sand	Basalt	Sandstone
Soil type [1]	Ferric podzol	Mollic Andosol	Dystric cambisol
Pb biomass uptake ($g.ha^{-1}.an^{-1}$)	18,8	16,8	17,2
Pb weathering ($g.ha^{-1}.an^{-1}$)	0,024	0,20	0,032
Net runoff ($m.an^{-1}$)	0,4	0,6	0,4
Critical limit of dissolved lead ($mg.m^{-3}$)[4]	8	8	8
Critical Pb leaching ($g.ha^{-1}.an^{-1}$)	**32**	**48**	**32**
Effect-based critical load ($g.ha^{-1}.an^{-1}$)	50,77	64,6	49,16
Current total lead in topsoil ($mg.kg^{-1}$) [3]	**3,4**	**51,8**	**26,3**
"So-called" lead ($mg.kg^{-1}$)	1,4	50,8	20,9
Reactive lead ($mg.kg^{-1}$)	0,9	30,7	13,6
Dissolved lead ($mg.m^{-3}$)	0,06	6,07	3,35
Current Pb leaching ($g.ha^{-1}.an^{-1}$)	0,24	36,5	13,4
Stand-still load ($g.ha^{-1}.an^{-1}$)	19	53,1	30,56

Effect-based critical loads are mainly controlled by leaching. The soils where runoff is high (EPC 63) can tolerate a higher atmospheric deposition. This imply important leaching in some coarse soils and damage on draining surface water. For both effect-based and stand-still loads, weathering rates seem neglectables in comparison with leaching and biomass uptakes.

Stand-still approach allows important atmospheric inputs where Pb concentrations are high (EPC 63). This means that stand-still cannot be applied where present concentrations are higher than critical limits.

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[2] *Coefficient values [a0, a1, b0, b1, b2, b3, c0, c1, c2 and c3] are taken from RIVM guidance [4].*

3.1 Discussion on transfer functions

Transfer functions are used in the stand-still approach to derive [Pb] in soil solution from total [Pb] in soil. We compared transfer function results to measured dissolved [Pb] in two granitic sites (PP and HP) in the Strengbach catchment (Vosges, France) where total [Pb] is also known. Soil solutions were collected using zero-tension lysimeter plates. Dissolved lead was measured with ICP-MS on dissolved phase [2].

Transfer functions applied on two granitic soils overestimate the dissolved [Pb] in soil solution (fig. 1). Stand-still load is thus overestimated. Transfer functions must thus be calibrated for french soils.

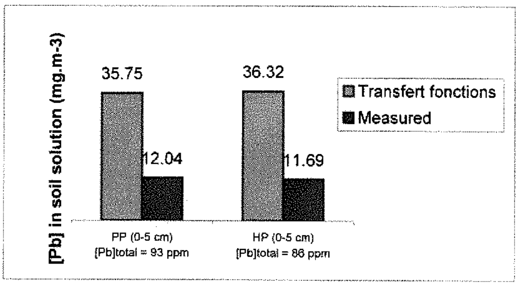

Fig 1. Comparison between measured and calculated [Pb] in soil solution

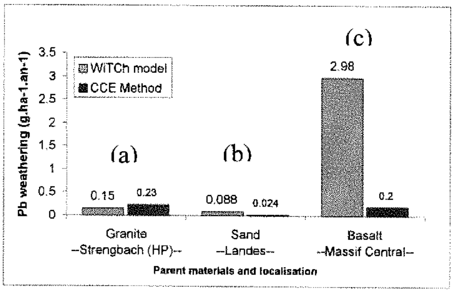

Fig 2. Comparison between WiTCh model and CCE recommandations for lead weathering

3.2 Discussion on weathering fluxes

Two different approaches for the determination of lead weathering rate were compared. The first approach refers to equation (2). The second one uses the WiTCh model [9]. WiTCh is a dynamic model of weathering which determines weathering rates using kinetic mineral dissolution. Three soils from very different lithology were chosen to compare the two approaches : a granitic site in the Vosges (HP), a sandy site in the Landes (PM 40) and a basaltic site in the Massif Central (EPC 63) (fig. 2).

The weathering rates determined according to equation (2,a ; 2,b) seems in agreement with the WiTCh model outputs. Exception occurs when the chemical rock composition is different from the proposed standard bedrock composition (equ. 2,c).

Our goal in this study was to evaluate the accuracy of the european methodology for calculation of critical loads for the french forest soils. It appears that critical load approach is adapted for french soils but need to be calibrated at least for calculation of weathering fluxes and determination of critical limits. On the contrary, Stand-still is not adequate se because of inherent contradictions in the method and too much uncertainties in the transfer functions.

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