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Dynamic modeling of the long term behavior of cadmium, lead and mercury in Swiss forest soils using CHUM-AM

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Abstract

The applicability of the dynamic soil model CHUM-AM was tested to simulate concentrations of Cd, Pb and Hg in five Swiss forest soils. Soil cores of up to 50 cm depth were sampled and separated into two defined soil layers. Soil leachates were collected below the litter by zero-tension lysimeters and at 15 and 50 cm soil depth by tension lysimeters over two years. The concentrations of Cd, Pb and Hg in the solid phase and soil solution were measured by ICP-MS (Cd, Pb) or CV-AFS (Hg). Measured metal concentrations were compared with modeled concentrations using CHUM-AM. Additionally we ran the model with three different deposition scenarios (current deposition; maximum acceptable deposition according to the Swiss ordinance on Air Pollution Control; critical loads according to CLRTAP) to predict metal concentrations in the soils for the next 1000 years. Assuming current loads concentrations of Cd and Pb showed varying trends (increasing/decreasing) between the soils. Soils rich in organic carbon or with a high pH value showed increasing trends in Cd and Pb concentrations whereas the concentrations in the other soils decreased. In contrast Hg concentrations are predicted to further increase in all soils. Critical limits for Pb and Hg will partly be exceeded by current loads or by the critical loads proposed by the CLRTAP but the critical limits for Cd will rarely be reached within the next 1000 years. In contrast, maximal acceptable deposition will partly lead to concentrations above the critical limits for Pb in soils within the next 400 years, whereas the acceptable deposition of Cd will not lead to concentrations above the proposed critical limits. In conclusion the CHUM-AM model is able to accurately simulate heavy metal (Cd, Pb and Hg) concentrations in Swiss forest soils of various soil properties.

1. Introduction

Contamination of terrestrial ecosystems with heavy metals (HM) has increased in the last century as a consequence of human activities. Research regarding emission, deposition and the behavior of HMs in soil has been intensified due to negative impacts of HMs on biota and human health. The pollutants emitted into the atmosphere can be transported over large distances before being deposited on the ground. The rising awareness of problems related to transboundary pollution with HMs led to the *Protocol on Heavy Metals* agreed in 1998 in the frame of the convention on Long-Range Transboundary Air Pollution (LRTAP) of the United Nations Economic Commission for Europe (UNECE). The Working Group on Effects (WGE) coordinates the international co-operative research and compiles information on major pollutant effects and geographical extent of pollutions. The WGE considers three harmful HMs: cadmium (Cd), lead (Pb) and mercury (Hg). The involved parties decided to monitor the HM pollution, to encourage research on relevant effects on human health and the environment and whenever necessary to reduce the emission of these three HMs.

To predict future concentration of pollutants in ecosystems, the past, present and future inputs of HM have to be considered. The past atmospheric emission and deposition of HM in Europe have been investigated with peat cores (Ross-Barraclough and Shotyk, 2003; Weiss et al., 1999), lake sediments (Farmer et al., 1996; Petit et al., 1984), alpine ice cores (Barbante et al., 2004; Schwikowski et al., 2004), and tree rings (Watmough and Hutchinson, 2002). Atmospheric deposition of Cd increased since industrialization and was in 1970 about 36 times higher than before industrialization (Barbante et al., 2004). The deposition increased especially since 1930 and was almost doubled by 2000 (Barbante et al., 2004). The annual Cd deposition at sites far away from any emission source in Switzerland was about 90 µg Cd m^{-2} in the year 2007 (FOEN, 2008). Cadmium is important in the industrial sector and is used e.g. in steel and iron manufacturing or in Ni-Cd batteries. Emissions of Pb in Europe increased since the beginning of the 20th century mainly due to the introduction of leaded gasoline around 1950, drastically decreased since 1980 through the drop of use of leaded gasoline and its interdiction at all European gasoline stations in the year 2000 (Schwikowski et al., 2004). The annual Pb deposition at sites far away from any emission source in Switzerland was about 5 mg Pb m^{-2} in the year 2007 (FOEN, 2008). During the last century, the Hg concentrations in the atmosphere have increased by about a factor of three (Mason et al., 1994). It is assumed that half of the emitted Hg enters the global atmospheric cycle whereas the other half is

deposited near the emission source (Mason et al., 1994). In 1880, the anthropogenic Hg emissions in Switzerland increased due to the introduction of steam railways with Hg-containing coal as fuel for the locomotive until the electrification of the railways started at the beginning of the 20th century. After the Second World War, the emissions of Hg in Switzerland increased again due to post war industrialization followed by a decrease since about 1970 (Ross-Barraclough and Shotyk, 2003). The current annual Hg deposition in rural sites without any nearby Hg source is about 20 µg Hg m^{-2} (Ross-Barraclough and Shotyk, 2003). In the frame of the LRTAP convention, the concept of critical loads (CL) has been introduced and defined as the maximum atmospheric depositions below which no concentrations of pollutants in soil and water will ever be reached leading to adverse effects on the soil biota according to current knowledge (De Vries and Groenenberg, 2009). These concentrations are called critical limits and are based on ecotoxicological studies. The standard model for calculation of CL is a steady state model named Simple Mass Balance (SMB) model (Posch et al., 1997; Sverdrup and De Vries, 1994; UBA, 2004). To be able to predict when the steady state will be reached, dynamic models must be used (Alveteg et al., 1998). Dynamic models were developed more than 20 years ago mainly to predict soil acidification and surface waters acidification. A simple dynamic model to predict metal concentrations in soils was developed by Posch and De Vries (2009). Tipping (1996) developed a more complex dynamic soil model – CHUM (CHemistry of the Uplands Model) – which can be used to predict metal concentrations in soil and in soil water. Tipping further adapted CHUM to CHUM-AM (CHemistry of the Uplands Model - Annual, Metals).

In Switzerland, maximal deposition values have been defined by Swiss Federal Council (OAPC, 1985, Annex 7). Swiss ‘critical limits’ for HMs in the solid phase of the soil have been introduced in 1998 (OIS, 1998) based on an assessment of health risks related with all major pathways (e.g. food chains) and the relevant known toxicological uptake rates (Hämmann and Gupta, 1997). Jauslin et al. (2004) suggested a refinement of the risk assessment procedure. However, the effect of deposition of Cd, Pb and Hg on the future accumulation of these HMs in the soils of Switzerland has never been tested with a comprehensive dynamic model such as CHUM-AM. CHUM-AM (and also CHUM) has only been used for soils rich in organic matter in the UK so far. The model considers the organic matter content as the main factor controlling HM mobility in soils. In contrast, European and in particular Swiss forest soils usually do not contain large amounts of organic matter and the HM mobility is suggested to be largely controlled by other

factors such as the soil type and clay content. Therefore it would be highly relevant to assess if CHUM-AM is also able to simulate HM concentrations in forest soils with different soil properties.

In this study, we tested the applicability of CHUM-AM to model Cd, Pb and Hg concentrations in five Swiss forest soils varying in physicochemical properties. Additionally we ran the model with three different deposition scenarios (I. current deposition; II. maximum acceptable deposition according to the *Swiss ordinance on Air Pollution Control*; III. site specific CL according to the WGE of the convention on LRTAP) and compared the simulated concentrations to critical limits proposed in the literature and the Swiss legislation on soil protection.

2. Material and Methods

2.1 Sites description:

This study was carried out on five well characterized forest soils (Beatenberg, Lausanne, Novaggio, Schänis, Vordemwald) of the *Swiss long-term forest ecosystem research programme* (LWF) that were selected due to their geographical location, soil properties and available data sets (Graf-Pannatier et al., 2011; Heim and Frey, 2004; Thimonier et al., 2005; Walthert, 2003). All soils were from natural forest sites distributed over the different geographical regions in Switzerland. Soils have been characterized as Podzol, dystric and eutric Cambisol and dystric Planosol (Table1).

2.2 Model description:

CHUM-AM (CHemistry of the Uplands Model - Annual, Metals) was developed by Tipping et al. (2006a) and is an improvement from CHUM (Tipping, 1996). In contrast to CHUM, CHUM-AM runs on annual and not on daily time steps. Furthermore the water movements in CHUM-AM are simplified and biogeochemical processes are included. Originally, CHUM-AM considers a soil column composed of three homogenous layers. In our more simplified approach we only used the first two layers (L1, L2) up to 50 cm varying in their soil properties (e.g. organic matter content). Highest microbial activity, bioturbation, root growth and organic matter turnover are suggested to be in the first 50 cm of soil depth. Furthermore, heavy metals strongly accumulate in the topsoils. The two soil layers are described in Table 1 for each soil site. In this study the simulation of stream water was neglected and only the soil and soil solution are considered in contrast to studies in UK (Tipping et al., 2006a; Tipping et al., 2006b).

The model uses mean annual precipitation and deposition values and provides mean annual concentrations of elements in the solid phase of the soil and in the soil water. CHUM-AM assumes that the soils were in steady state with respect to atmospheric metal deposition before industrialization. Therefore, CHUM-AM calculates 50 times the years between 1400 and 1600 (data for 10 000 calculating years) to reach steady state, which is necessary for the initial conditions of the model. The carbon content in the solid phase and in the soil solution is specified in the input file because CHUM-AM does not include a carbon cycling model. CHUM-AM aims to consider the main processes to calculate soil acidity and solution chemistry and the metal behaviour in ecosystems. How mentioned before, CHUM-AM considers the organic matter content (especially content of humic and fulvic acids) as the key factor controlling HM mobility in soils. The competitive interactions of cations (including H^+) with organic matter in the solid phase and in soil solution and also with mineral cation exchanger mainly determine the fate of metals in soils. Thus the simultaneously prediction of soil solution chemistry and especially soil acidity are mandatory to predict the fate of metals in soils. CHUM-AM calculates the reactive HM pools in soil. Therefore the calculated HM concentrations are assumed to be lower than the total HM concentrations in the soils.

The species on which the chemical reactions are based are the major cations H^+, Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+}, Fe^{3+}, NH_4^+; the trace cations Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}; the anions OH^-, Cl^-, NO_3^-, SO_4^{2-}, F^-, CO_3^{2-} and the neutral species $Si(OH)_4$. The solutes may bind to minerals and organic matter (humic and fulvic acids) whereby the organic matter can be in solid phase, dissolved in soil water, or in suspension. The chemical interactions were calculated by the soil version of WHAM/Model VI (Tipping et al., 1998; Tipping et al., 2003) which has been implemented in CHUM-AM. Cycling in vegetation, seasonal variability of soil properties, flow pathways and depositions and also bioturbation were not considered in CHUM-AM.

2.3 Input data:

The data used for modelling were measured in the field (LWF data; time frame of measurements 1997 – 2011) or estimated from models or literature (Table 2). Soil properties were previously determined (Blaser et al., 2005; Graf-Pannatier et al., 2011; Lazzaro et al., 2006a; Lazzaro et al., 2006b; Walthert, 2003; Walthert et al., 2004; Zimmermann et al., 2006) except for the HM concentrations in the solid phase and in the solution. The soil profiles were divided into different soil layers due to changing soil properties (e.g.

organic matter content). In this study we only considered two soil layers (L1 and L2) for which mean soil properties were calculated (Table 1). The soil depths and main properties of L1 and L2 are given for each soil site in Table 1. Annual average precipitation data, data of total and wet deposition (for cations, N and S) have been determined on these five LWF sites with continuous sampling of bulk (1 to 3 samplers in a nearby open field) and throughfall deposition (4 to 16 samplers below forest canopy) in bi-weekly to monthly intervals since 1997 (Thimonier et al., 2010; Thimonier et al., 2005). In the few cases with overflow of the samplers, precipitation has been reconstructed using data of unheated tipping buckets or of the nearest meteorological station of the Swiss meteorological institute MeteoSwiss.

There were several assumptions made for the input variables. Depositions of Cd were not measured at the LWF sites. The current depositions in Switzerland were obtained from the Swiss country report 2007/2008 of EMEP *(European Monitoring and Evaluation Programme;* http://www.emep.int*)* documenting Cd, Pb and Hg depositions derived from modelling with a spatial resolution of 50 x 50 km. In addition, data from the Swiss National Air Pollution Network (NABEL, 2011) and from moss analyses were used (FOEN, 2008). Depositions were derived from concentrations of several elements (including Cd, Pb) in mosses by FOEN (2008) by transforming the elemental concentrations in mosses with measured depositions (Bergerhoff analyses) data according to Thöni (1996). Historical Cd depositions were estimated from peat bog record data according to Shotyk et al. (2002) and from ice cores (Barbante et al., 2004). The historical deposition of HM was estimated for each site separately by using the current deposition values which were than back calculated with the historical trends in HM depositions.

Similar as for Cd, no date was available for Pb depositions at the selected LWF forest sites. Current Pb depositions (between 1990 and 2008) were obtained from EMEP modeled data, from deposition analyses in Switzerland (NABEL, 2011), and from moss analyses (FOEN, 2008). Historical Pb deposition data were obtained from five peat profiles (Weiss et al., 1999). These studies calculated depositions of Pb in time steps between 2 and 10 years back to at least 1871. Between the particular time points, we assumed a linear change of the deposition. We have chosen the peat profiles from Weiss et al. (1999) located closest to our forest sites [profile SwM for Beatenberg, Vordemwald and Schänis; profile PRd for Lausanne; profile GdL for Novaggio, profile abbreviations according to Weiss et al. (1999)].

Hg depositions were also not available for the selected LWF forest sites. Current Hg depositions were estimated by EMEP modeled data. Historical Hg depositions (since 1400) were obtained from analyses of

peat cores of two bogs from the Swiss Jura Mountains (Ross-Barraclough and Shotyk, 2003). Hg depositions modeled by EMEP (2008) for this region were, with values between 16 – 18 µg Hg m^{-2} $year^{-1}$, similar to the Hg depositions of 10 – 25 µg Hg m^{-2} $year^{-1}$ estimated by Ross-Barraclough and Shotyk (2003) for 1990. Historical Hg depositions were calculated by approximating the peat core analyses to the current depositions. In contrast to Cd and Pb, Hg is not only lost from soil by leaching, Hg is also lost by reduction of Hg^{2+} to the volatile Hg species Hg^0 followed by evasion (Schluter, 2000; Zhang and Lindberg, 1999). Evasion is dependent on numerous abiotic and biotic factors such as temperature, soil moisture or microbial activity (Bahlmann et al., 2006; Choi and Holsen, 2009; Fritsche et al., 2008; Johnson et al., 2003; Zhang and Lindberg, 1999). During calibration we tested various evasion rates [between 0.03 and 0.1% of total Hg; selected from Tipping et al. (2011)], and have applied a rate of 0.03% in the model runs presented here.

The deposition rates derived from EMEP, from moss analyses, NABO data and peat and ice cores studies intend to cover all land use types and we thus assumed that deposition at selected LWF sites are higher due to the filtering effects of the forests canopy depending on e.g. the dominant tree species (De Vries and Bakker, 1998; Driscoll et al., 1994; Gandois et al., 2010; Lindberg et al., 2007; Perez-Suarez et al., 2008; St Louis et al., 2001). Therefore, we increased depositions values from literature by a factor of 2 (deciduous forests) and 2.5 (conifer forest) for Cd and Hg, and 2 (deciduous forests) and 3 (conifer forest) for Pb. The increasing factors were defined by literature values and fine adjustment during the calibrations of the model.

The N depositions were measured in each forest site. The model simulates the acidifying effect on N deposition, i.e. pH changes but not the uptake of N into vegetation and soil. However, the measurement of total deposition also includes amounts of N that are directly taken up by vegetation or washed out as surface runoff without having an acidifying effect. Therefore we estimated the remaining acidifying N depositions out of the N concentrations in the soil solution. We assumed that the current NO_3 and NH_4 concentrations in the soil solution influence the soil pH. All deposited N compounds which were immediately washed out or taken up by plants and thus not influencing soil pH were neglected. We calculated the current depositions for $N_{dep.}$ according to equation (1).

$$N_{dep.} = [N] \times (\text{precipitation} - \text{evapotranspiration}) / \text{precipitation} \quad (1)$$

where N is the concentration of NO_3 or NH_4 in soil solution (mean concentration of the soil solution collected in 15 and 50 cm depth). The historical NO_3 and NH_4 emissions were calculated relative to the year 2000 ($N_{emission\ 2000}$=1) and their depositions were estimated by multiplying the $N_{dep.}$ value for NO_3 and NH_4 with the relative N emission values in Switzerland (FOEN, 1995).

The current SO_2 and SO_4 depositions were measured in all sites whereas the historical depositions were estimated from the emission of SO_2 (FOEN, 1995). Therefore the normalized historical SO_2 emissions were calculated relative to the year 2000 ($S_{emission\ 2000}$=1) and the historical deposition of SO_2 was estimated by multiplying the normalized emission value with the current SO_2 emission value (FOEN, 1995). The SO_4 deposition was calculated by multiplying the SO_2 depositions with a site specific relation factor of SO_2 to SO_4, calculated from a 10 years deposition observation in each forest site.

The weathering inputs of major and trace metals through chemical weathering of the mineral soil fraction were calculated according to equation (2) (Schnoor and Stumm, 1986).

$$\text{weathering rate} = kw\ a_{H+}^{nw} \qquad (2)$$

where the kw value was estimated from weathering rates calculated by using the model SAFE (Alveteg et al., 1998) and was adjusted to match observations (calibration parameter). The a_{H+} was the activity of protons in soil solution and the exponent *nw* was set to 0.7 for Al and Fe and 0 for Si, Mg and Ca (Stidson et al., 2002).

2.4 Soil sampling and determination of metal concentrations:

To calibrate the model, measured concentrations of Cd, Pb and Hg throughout the soil profile were needed. To measure the total contents of HMs in the soils three soil cores were taken around the soil profiles described in Walthert (2003). The soil cores were sampled with a soil auger (5 cm in diameter) up to about 60 cm soil depth whenever possible (bedrock) within a radius of 2 m from each of the soil profiles described by Walthert (2003). Thereafter the soil cores were separated in two clear defined soil layers (L1, L2) according to previous studies (Walthert, 2003; Walthert et al., 2004; Zimmermann et al., 2006). The soil samples were then sieved (2 mm) to remove stones and litter, air-dried at 15° C in a forced draught

oven for 5 days and homogenized by crushing in an acid-washed porcelain pestle and mortar. For determining the residual moisture contents, aliquots of the soils were dried at 105° C for 3 days. The contents of Cd and Pb of each soil horizon were determined by extracting 2.5 g of the dried soil sample in 25 ml of 2 M HNO_3 for 2 h at 95°C (100 rpm) (Ernst et al., 2008). All soil extracts were filtered through filter paper (No. 790 1⁄2; Schleicher & Schuell). The concentrations of Cd and Pb in the extracts were measured by inductively coupled plasma-mass spectrometry [ICP-MS: ELAN 6000, Perkin–Elmer; detection limits: 0.01 mg Cd kg^{-1} dw; 0.02 mg Pb kg^{-1} dw; Ernst et al. (2008)]. The Hg contents in the soils were determined by a direct mercury analyzer [(DMA), AMA 254 Mercury Analyzer, LECO Corporation; detection limit: 0.001 mg Hg kg^{-1} dw]. Mean concentrations of HMs were calculated for both soil layers (L1, L2).

Soil solutions were collected at a soil depth of 15 cm and 50 cm between 2007 and 2009 (n=8 per site and depth). The soil solution was sampled by tension lysimeters using ceramic suction cups (Graf-Pannatier et al., 2011) and collected bi-weekly in 1 L glass bottles. Elemental concentrations of Cd and Pb in soil solution were determined by ICP-MS (Perkin Elmer, OPTIMA 3000; detection limits: Cd < 0.02 µg L^{-1}; Pb < 0.05 µg L^{-1}). For Hg analyses, aliquots of the soil leachates were filled in 125 mL PTFE Teflon bottles (acid washed) and the Hg concentrations were determined by cold vapour atomic fluorescence spectroscopy (CV-AFS; detection limit < 0.0003 µg L^{-1}) according to Akerblom et al. (2008).

2.5 Model Calibration:

Firstly, we calibrated the pH and the concentrations of Al, Ca, K, Mg and Na in the soil solution for both soil layers (L1, L2). Therefore, we adjusted the initial weathering rates of each soil cation, until the measured and calculated concentrations were in good accordance, which means r<5 according to equation (3). The initial weathering rates were calculated by using the model SAFE (Alveteg et al., 1998).

$$r= \sum[([M]_{measured}-[M]_{calculated})/[M]_{measured}]^{\wedge 2} \quad (3)$$

where [M] is the concentration of element M (H^+, Al, Ca, K, Mg, Na) in soil solution. We further adjusted the input parameter within the range of analyses (e.g. HM deposition, precipitation, DOC concentration), modelled values [evapotranspiration according to Jansson and Karlberg (2004)] and evasion rates for Hg

according to determined rates for deciduous forest soils (Tipping et al., 2011) to improve the accordance of modelled and measured concentrations.

2.6 Scenarios:

After calibration we ran the model with different deposition scenarios for the next 1000 years starting at the year 2010. The three scenarios were as follows:

1) Current deposition (2010 deposition)
2) Maximum acceptable deposition of Cd and Pb according to the Swiss ordinance on Air Pollution Control [OAPC (1985), Annex 7]
3) Critical loads (CL) according to the Working Group on Effects (WGE) of the convention on LRTAP (Slootweg et al., 2005) as deposition input parameters (carried out with the lowest site specific values)

When modelling the different scenarios, we manipulated only the deposition of the studied HM and maintained all other deposition parameters at their current level. The different deposition scenarios are shown in Table 3. We compared the measured and modelled HM concentrations with several critical limit concentrations based on total contents of HM g^{-1} soil (OAPC, 1985; Tipping et al., 2010a); on total HM per g^{-1} SOM (Lofts et al., 2004; Meili et al., 2003; Tipping et al., 2010a); or on HM concentrations per L^{-1} soil solution (De Vries et al., 2007; Lazzaro et al., 2006a; Lazzaro et al., 2006b; WHO, 2004) (Table 4). The critical limits were calculated per site and per soil layer as they depend on soil properties.

3. Results:

3.1 Cd, Pb and Hg concentrations in forest soils:

Contents of Pb and Hg in the solid phase were highest in the top layer (L1) of the soils (Table 5). Similarly, the contents of Cd were highest in the top layer (L1) but varied largely. At two sites the total Cd contents were below the detection limit (0.01 mg kg^{-1}). No top layer (L1) reached the critical limit for Cd set by the OIS (0.8 mg Cd kg^{-1} soil or 0.32 mg Cd kg^{-1} soil for Beatenberg). Soils in Beatenberg and Novaggio exceeded the critical limit set by OIS for Pb (20 and 50 mg kg^{-1}, respectively) and all top layers (L1)

exceeded the critical limit for Pb proposed by Lofts et al. (2004). Contents of Hg in the top layer of Beatenberg exceeded the critical limit set by OIS (0.2 mg kg^{-1}). The Hg contents in the top layer (L1) of Beatenberg, Schänis and Vordemwald exceeded the critical limit (0.13 mg kg^{-1}) proposed by Tipping et al. (2010a) but only in Schänis also the SOM based limit (0.17 mg Hg kg^{-1}) is exceeded. Proposed critical limits by Meili et al. (2003), also based on SOM, are exceeded in the top layers (L1) of Lausanne, Schänis and Vordemwald.

The concentrations of Cd in the soil solution showed a large variation and tended to increase with soil depth (Table 5). The concentrations of Pb in the soil solution tended to increase with soil depth. The concentrations of Hg in the soil solution strongly decreased with increasing depth (Table 5). Concentrations of Cd, Pb and Hg in the soil solution were below the WHO guideline for drinking water protection and the Hg concentrations in Vordemwald exceeded the ecotoxicological value (0.035 µg L^{-1}) given by De Vries et al. (2005).

3.2 Model applicability for Swiss forest soils and calibration:

The calculated pH values in the soil solution were in good accordance with the measured pH values. In Lausanne, Vordemwald and Novaggio, the measured and calculated pH values were similar (±0.2 pH units), in Beatenberg the calculated pH values were too high (+0.5) and in Schänis too low (-1.2), whereby in Schänis, the pH measurements varied widely (5.0 and 7.6; data not shown).

In general, the modeled Cd, Pb and Hg concentrations in the soil matrix and the soil solution were in line with the measured concentrations (Figure 1). In the top layer (L1), the measured total HM contents were somewhat higher than the calculated contents, whereas the opposite is true for the concentrations in soil solutions (Figure 1 a, b). In the second soil layer (L2), the modeled HM contents were less accurate (Figure 1 c) whereas the modeled concentrations in soil solution were in line with the measured concentrations (Figure 1 d).

3.3 Scenarios:

3.3.1 Current deposition:

Cadmium: The total contents of Cd will still increase in the top soil layers up to 70% or decrease up to 80% during the next 1000 years depending on the forest site (Figure 2; Table 6). Concentrations of Cd will

never exceed the Swiss guide value for soil protection (OIS; 0.8 or 0.32 mg Cd kg^{-1}) nor the critical limit estimated by Lofts et al. (2004) for both soil horizons (L1, L2).

The Cd concentrations in soil solution will also increase or decrease (up to 70%) in the topsoils (Figure 2; Table 6). The concentration of Cd in soil solution will never reach the critical limit.

Lead: The total contents of Pb will further increase in two soils (Beatenberg, Schänis) and decrease in the other soils (Figure 3; Table 6). The OIS guide value (0.5 resp. 0.2 mg Pb kg^{-1} soil) has already been exceeded in the top layer (L1) of Beatenberg and Novaggio but in Novaggio the Pb contents will decrease. In Schänis the OIS guideline value of Pb will be exceeded in the next 1000 years.

The Pb concentration in soil solution will further increase (Figure 3; Table 6). The calculated Pb concentrations are overestimated but based on measured values and the slope in future Pb concentrations in soil solution, we assume that the WHO guideline for groundwater protection (10 µg Pb L^{-1}) and the critical limit proposed by Lazzaro et al. (2006b) (1.8 µg L^{-1}) will never be reached at each site.

Mercury: Total Hg contents will further increase in all studied forest soils (Figure 4; Table 6). In 1000 years, the Hg contents in the top layer (L1) are about twice as high as the present-day contents (Table 6). The Swiss guide value for soil protection (OIS; 0.5 mg Hg kg^{-1} soil and 0.2 mg Hg kg^{-1}) in top layers (L1) will never be reached in each soil except for Beatenberg where this value has already been exceeded (Table 5). The critical limit for total Hg contents (0.13 mg kg^{-1} soil) proposed by Tipping et al. (2010) has already been exceeded or will be reached in Beatenberg, Lausanne Novaggio and Schänis in the next 1000 years. The critical limit based on SOM by Tipping et al. (2010) is already exceeded in Schänis and will be reached in Lausanne and Vordemwald in the current millennium. The critical limit proposed by Meili et al. (2003) is already exceeded or will be exceeded in the top layers (L1) of all soils in the current millennium.

The Hg concentrations in soil water will further increase at all forest sites (Figure 4). In 1000 years, the Hg concentrations in soil solution will be about three times higher than the present-day Hg concentrations (Table 6). The WHO guideline for drinking water protection (1 µg Hg L^{-1}) (WHO, 2004) will never be reached whereas the ecotoxicological default value (0.035 µg Hg L^{-1}) proposed by De Vries et al. (2005) will be exceeded in the top layer (L1) of three soils during the next 1000 years.

3.3.2 OAPC deposition:

Cadmium: The maximum acceptable Cd deposition in Switzerland (OAPC, 1985) is about eight times higher than the current deposition at our forest sites. Such a deposition would substantially increase the Cd content in the soil matrix and also in the soil solution at all forest sites (Figure 2; Table 6). In the top layer (L1) of soils in Beatenberg and Schänis the contents of Cd in the solid phase will exceed the OIS guide value (0.32 or 0.8 mg Cd kg^{-1} soil) in less than 300 years but the proposed critical limit by Lofts et al. (2004) for total HM concentration will never be reached in neither of the two soil. In 1000 years the contents of Cd will be about 10 times higher than the current concentrations in Beatenberg and Schänis but only somewhat higher in the other soils (Table 6).

In soil solution the WHO guideline for drinking water (3 µg L^{-1}) for Cd will never be reached in any soil but the critical limit proposed by Lazzaro et al. (2006a) (1.2 µg L^{-1}) will be reached in Lausanne and Vordemwald within the next hundred years.

Lead: Similarly to Cd the maximum acceptable Pb deposition in Switzerland (OAPC, 1985) is much higher (about ten times) than the current deposition at our forest sites and would lead to a dramatic increase in the Pb contents in the solid phase except for Lausanne and Novaggio (Figure 3; Table 6). The OIS guide value (0.5 resp. 0.2 mg Pb kg^{-1} soil) will be exceeded in the top layers (L1) of Beatenberg and Schänis in less than 400 years and shortly in Novaggio.

In soil solution the Pb concentrations will increase in all soils in particular in the second soil layers (Figure 3; Table 6). The WHO guideline (10 µg Pb L^{-1}) will be exceeded in Beatenberg, Lausanne, Novaggio and Vordemwald within the next 100 years.

3.3.3 Critical Loads (CL) deposition:

Cadmium: The CL for Cd were between 8 and 16 times higher than the current Cd depositions. By depositions according to the CL, the Cd contents in the solid phase will largely increase in all soils and in the soil water of four out of five soils (Figure 2; Table 6). The OIS guide value (0.8 resp. 0.32 mg Cd kg^{-1} soil) will partly be exceeded in the next 1000 years. The Cd contents in the upper layer (L1) will rise up to 19 times and in the lower layer (L2) up to almost 40 times the present-day contents. The critical limit for Cd in soil solution proposed by Lazzaro et al. (2006a) (1.2 µg L^{-1}) will be exceeded in four soils within the next 1000 years.

Lead: The CL for Pb are smaller than the current depositions in Lausanne, Novaggio and Vordemwald. In Beatenberg and Schänis the current loads are similar than the CL (Figure 2 a-e; grey dots). The CL scenario usually will lead to similar or lower Pb concentrations in the soil matrix and in soil water compared to the current deposition.

Mercury: Mercury concentrations in the soil matrix and in the soil solution will further increase in all forest soils (Figure 4; Table 6). The Swiss guideline of the OIS (1998) (0.5 mg Hg kg^{-1} resp. 0.2 mg Hg kg^{-1} soil) will never be reached except for Beatenberg (Table 5). The critical limit (0.13 mg Hg kg^{-1} soil) proposed by Tipping et al. (2010a) is already exceeded (Beatenberg, Schänis, Vordemwald) or will be reached within the next 1000 years (Lausanne, Novaggio) (Table 5, Figure 4). The SOM based critical limit proposed by Tipping et al. (2010) is already exceeded or will be reached during the next 1000 years in Lausanne, Schänis and Vordemwald. In top layers (L1), the critical limit proposed by Meili et al. (2003) is already exceeded (Lausanne, Schänis, Vordemwald), will be exceeded in Novaggio during the next 1000 years but will never be reached in Beatenberg. The Hg concentration in soil solution will never exceed the WHO guideline (1 µg Hg L^{-1}) for drinking water (WHO, 2004), and the critical limit (0.035 µg Hg L^{-1}) proposed by De Vries et al. (2007) in any of the studied soils.

4. Discussion:

4.1 Exceedances of critical metal concentrations:

The concentrations of Cd in the soil solution (<0.02 – 0.18 µg Cd L^{-1}), based on the current findings, are ecotoxicologically not critical. Soluble Cd concentrations in all soils were below the WHO guidelines for drinking water (3 µg Cd L^{-1}) (WHO, 2004) and the critical limit (1.2 µg Cd L^{-1}) proposed by Lazzaro et al. (2006a). A similar result was observed for Pb in the soil solution (<0.05 – 6.5 µg Pb L^{-1}). We did not find any concentration exceeding the WHO guidelines for Pb in drinking water (10 µg L^{-1}) but at three sites (Beatenberg, Lausanne, Novaggio) the critical limit (1.8 µg Pb L^{-1}) concentrations estimated by Lazzaro et al. (2006b) were exceeded in at least one soil layer. The Hg concentrations in the soil solution (<0.001 – 0.037 µg Hg L^{-1}), as far as we know, were also ecotoxicologically not critical (0.035 – 1 µg Hg L^{-1}).

The current depositions will not lead to ecotoxicologically critical concentrations of Cd and Pb in soils [according to the OIS (1998) guidelines, the WHO guidelines (WHO, 2004) and the critical limits proposed by Lazzaro et al. (2006a); Lazzaro et al. (2006b)]. In contrast, the concentrations of Hg will increase in all

soils and will exceed the critical limits for Hg (De Vries et al., 2007; OIS, 1998; Tipping et al., 2010a) but the concentrations will never exceed the WHO guideline (1 µg Hg L^{-1}) for Hg in drinking water (WHO, 2004). The critical limit proposed by the WHO was mainly based on studies conducted in organic rich soils in Northern Europe and only considers Hg concentrations in the humus layer (O horizon). Forest soils in Switzerland often contain a very small humus layer. If we estimate critical concentrations for soluble Hg in surface soils (L1) according to the Mapping Manual (LRTAP, 2004) and De Vries and Bakker (1998) and taking into account the low DOC concentrations of Swiss forest soils (A-horizons), the critical limits for Hg were substantially lower (between 0.004 and 0.008 µg Hg L^{-1}) than the WHO guideline (1 µg Hg L^{-1}) and the critical limit (0.035 µg Hg L^{-1}) proposed by De Vries et al. (2007). In three out of four soils (Beatenberg not considered because of the large organic layer), this critical limit would be below the estimated preindustrial Hg concentrations in the soil solution (data not shown). As a consequence we assume that the estimation of critical limits for Hg according to others [Mapping Manual of the convention on LRTAP (2004), De Vries and Bakker (1998); De Vries et al. (2005)] is not appropriate for forest soils in Switzerland and needs to be re-evaluated.

4.2 Uncertainties of input data and model:

The modeled HM concentrations are highly dependent on the input data. Large uncertainties exist about the HM depositions. Historical HM inputs were assessed by peat and ice core studies conducted in Switzerland (Barbante et al., 2004; Ross-Barraclough and Shotyk, 2003; Shotyk et al., 2002; Weiss et al., 1999). In addition, the tree species also influences the HM inputs (Perez-Suarez et al., 2008; St Louis et al., 2001) which has been taken into account in our estimations with different corrections factors for conifer and deciduous forests. Uncertainties are also related to the sampling of the soil matrix and the soil solution at the same spot. To avoid any disturbance of the lysimeters, the soil samples had to be collected several meters from the lysimeters. Depending on the soil heterogeneity, it might lead to discrepancies between the soil and the soil solution properties. This was the case in Schänis where the soil solutions were collected in more alkaline soils than the soil cores. The ceramic cups used for the soil solution sampling might also have adsorbed metals, in particular Pb in acidic and alkaline conditions and Cd at alkaline pH (Rais et al., 2006). This might explain the higher calculated concentrations of heavy metals in the soil solution (Figure 1b). There are also uncertainties related to the model itself. CHUM-AM calculates

concentrations on an annual timescale and neglects seasonal variations. Furthermore, CHUM-AM neglects erosion, bioturbation or changes in the vegetation (Tipping et al., 2010b). In general, the calculated HM contents in the solid phase of the topsoils were lower than the measured concentrations. These calculated values are comparable to the reactive HM pools in soils (Tipping et al., 2003) which could be estimated in soil samples using a diluted (0.43 M) HNO_3 extraction followed by ICP-MS or CV-AAS detection (Tipping et al., 2003). In our study, we measured the HM concentrations in the soil matrix using a 2 M HNO_3 extraction (Cd, Pb) or by DMA (Hg) resulting in higher measured than calculated concentrations. The measured Hg concentrations using DMA were also in a good accordance to a 2M HNO_3 extraction followed by CV-AAS detection (Rieder et al., 2011).

Nevertheless, the modeled Cd, Pb and Hg concentrations in the soil matrix and the soil solution were in line with the measured concentrations. Therefore CHUM-AM can be used to model HM in for wide range of soils over Europe and not only for organic soils in UK.

4.3 Long term trends in HM concentration:

The long-term behavior of HM in Swiss forest soils is site (soil)-specific. Assuming a current deposition, the Cd and Pb concentrations will increase in two soils whereas in the other soils the concentrations will decrease or remain constant. Soils rich in organic carbon or with a high pH will increase in Cd and Pb concentrations whereas the concentrations in the other soils decrease. In contrast, the Hg concentrations will increase in all soils. The deposition of Cd largely decreased during the last 50 years (Shotyk et al., 2002). At that time, the Cd deposition was about twice as high as in 1990 and since then the Cd deposition further decreased (FOEN, 2008). A similar trend was observed for Pb deposition. We assume that in Lausanne and Novaggio the former Pb deposition was much higher for many years as in the other soils according to the peat profiles reported in Weiss et al. (1999) and that at these sites the Pb deposition in the last decades decreased more as in the other sites. In Novaggio, the deposition of Pb is still about three times higher than in the other sites (FOEN, 2008). The strong decrease in Pb depositions in Lausanne and Novaggio and their soil properties leads to the trend of decreasing Pb concentrations in soils. In contrast to Cd and Pb, the Hg depositions decreased only a little during the last decades. Therefore and because of Hg is highly immobile in soils, the Hg concentrations in the soils will further increase in all soils. In our calculations we used an Hg evasion rate of 0.3% per year. Higher evasion rates

will decrease the Hg concentrations in soils but they hardly will affect the long-term trends (data not shown). Tipping et al. (2011) modeled the long term behavior of Hg in three UK soils. Two of these soils were located near a former Hg source. In these two soils, the highest Hg depositions were about nine times higher as the current depositions. Tipping et al. (2011) estimated that the concentrations of Hg in these soils will decrease whereas in the third soil no decrease was estimated, indicating that the historical Hg deposition strongly influences the Hg dynamics in future.

The maximum tolerable deposition in Switzerland [according to the OAPC (1985)] will substantially increase the Cd and Pb contents in soils and will exceed the critical limit concentrations (Lazzaro et al., 2006a; Lazzaro et al., 2006b; OIS, 1998; WHO, 2004). With the OAPC (1985) the Swiss regulations aim to protect human, animals, plants and the soil biota from air pollutants. Maximal acceptable deposition values are determined for Cd and Pb but not for Hg (OAPC, supplement 7, Art. 2 Abs. 5). These maximal acceptable depositions in Switzerland were comparable to the CL of the UNECE. The OAPC (OAPC, 1985) deposition values, for both Cd and Pb, should be reduced to maintain soil fertility with an unconfined microbial activity. The CL will lead to concentrations rarely exceeding the critical limits, except for the critical limit for Hg as proposed by Tipping et al. (2010a). In contrast, critical limits for Cd are exceeded in most soils by a deposition according to the CL (Lazzaro et al., 2006a; OIS, 1998).

5. Conclusion:

In conclusion we found that the CHUM-AM model was able to accurately simulate HM (Cd, Pb and Hg) concentrations in Swiss forest soils. Thus, it was shown that CHUM-AS, which has only been applied in UK before current study, may be applicable for a wider range of soils throughout Europe. Long-term trends of Cd and Pb in soils differ between the sites whereas Hg tends to increase in all soils by the current HM depositions. The concentrations of Cd and Pb in soils rich in organic carbon or with a high pH value will further increase whereas the concentrations in the other soils will decrease. The maximal acceptable depositions for Cd and Pb in Switzerland according to the OAPC (OAPC, 1985) are too high and we suggest that they should be reduced in order to maintain long-term soil fertility with an unconfined microbial activity. The critical loads (CL) will lead to concentrations rarely exceeding the critical limits for Pb and Hg. In contrast, critical limits for Cd are exceeded in most of the soils by a deposition according to the CL. Critical limits for Cd and Pb are based on ecotoxicological studies whereas little is known with

respect to Hg. Furthermore, the CL for Cd defined in the frame of the LRTAP convention are also too high according to the current findings whereas the CL for Pb seem to be fairly accurate. More research is needed to validate the CL of Hg to better understand the ecotoxicity of Hg in temperate forest soils.

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Figure captions:

Figure 1: Model calibration: measured (mean value per site) versus modeled HM concentrations (Cd, Pb and Hg) in the solid phase (a, c) or in the soil solution (b, d) in L1 (a, b) or L2 (c, d). In samples below the detection limit, the value of the detection limit was used.

Figure 2: Long-term total Cd concentrations in the solid phase (left) and the soil solutions (right) for L1 (line) or L2 (dashed line) simulated with three deposition scenarios: 1) Current: current (2010) deposition represented by bold black lines; 2) OAPC: maximal acceptable deposition according to OAPC (1985) represented by thin black lines 3) CL: critical loads (CL) according to the Working Group on Effects (WGE) of the convention on LRTAP (Slootweg et al., 2005) represented by grey thin lines.

Figure 3: Long-term total Pb concentrations in the solid phase (left) and the soil solutions (right) for L1 (line) or L2 (dashed line) simulated with three deposition scenarios: 1) Current: current (2010) deposition represented by bold black lines; 2) OAPC: maximal acceptable deposition according to OAPC (1985) represented by thin black lines 3) CL: critical loads (CL) according to the Working Group on Effects (WGE) of the convention on LRTAP (Slootweg et al., 2005) represented by grey thin lines.

Figure 4: Long-term total Hg concentrations in the solid phase (left) and the soil solutions (right) for L1 (line) or L2 (dashed line) simulated with two deposition scenarios: 1) Current: current (2010) deposition represented by bold black lines; 2) CL: critical loads (CL) according to the Working Group on Effects (WGE) of the convention on LRTAP (Slootweg et al., 2005) represented by grey thin lines.

Table 1: Site characteristics and soil properties of the two surface soil layers (L1 and L2) of studied forest sites and collection depth of soil water for both soil layers (Graf-Pannatier et al., 2011; Thimonier et al., 2005; Walthert et al. 2003).

	Beatenberg		Lausanne		Novaggio		Schänis		Vordemwald	
Altitude (m a.s.l.)	1510		807		950		733		480m	
Mean annual temperature (C°)	4.6		7.6		9.7		7.9		8.4	
Mean annual precipitation (mm)	1305		1210		2022		1801		1106	
Soil type (FAO, 1997)	Podzol		Dystric Cambisol		Dystric Cambisol		Eutric Cambisol		Dystric Planosol	
Humus form	Raw Humus		Mull		Moder		Mull		Moder	
Dominant trees	Picea abies		Fagus sylvatica		Quercus cerris		Fagus sylvatica		Abies alba	
Horizons	L1	L2	L1	L2	L1	L2	L1	L2	L1	L2
Thickness [cm]	17	27	10	40	9	31	10	10	11	42
Organic C [%]	41	0.5	2.8	1.0	9.6	6.5	2.6	1.5	4.8	0.8
Dissolved organic C [mg l^{-1}]	31	29	3.9	1.0	8.0	3.1	6.2	4.2	4.6	1.1
Clay content [%]	0.1	4.6	13	17	12	9	24	20	16	20
Bulk density [g cm^{-3}]	1.6	1.8	1.3	1.4	0.7	0.8	1.0	1.1	0.8	1.2
pH (H_2O)	3.8	4.1	4.5	4.8	4.6	4.9	7.6	7.6	4.7	4.7
Suction cups buried [cm]	15	50	15	50	15	50	15	15	15	50

Table 2: Input parameters of the model

Input parameter	Remarks
Annual wet deposition of: Na, Mg, K, Ca, Cl, F	Measured for 10 years; mean precipitation used as historic inputs -> charge balancing calculated
Annual total deposition of: Al, Si, Fe, Ni, Cu, Zn	Measured for 10 years; mean precipitation used as historic inputs
NH_4, NO_3	Estimated from soil concentrations, deposition measurements and historical emission data
SO_4, SO_2	Estimated from deposition measurements and historical emission data
Total annual deposition of Cd	Modeled values from EMEP 2008; moss monitoring (FOEN, 2008); peat core (Shotyk et al., 2002) and ice cores drilling values (Barbante et al., 2004) for historical data
Total annual deposition of Pb	Modeled values from EMEP 2008; moss monitoring (FOEN, 2008); peat core values (Weiss et al., 1999) for historical data
Total annual deposition of Hg	Modeled values from EMEP 2008; peat core values (Ross-Barraclough and Shotyk, 2003) for historical data
Annual mean precipitation	Measured for 10 years; mean precipitation was used as historic annual inputs
Annual mean evapotranspiration	Modeled for each site by using the one dimensional CoupModel (Jansson and Karlberg 2004); mean evapotranspiration was used as ancient annual evapotranspiration
Occult deposition factor	Estimated
Fraction covered by grass, heather, trees	Estimated
Soil temperature	Mean annual value; measured
Density of soil solids	Measured
Fine earth bulk density	Measured
Fraction of volume is rock	Measured
% water saturation of soil	Estimated a mean annual saturation
OC content of soil	Measured
Humic and fulfic acid fraction of OM	Default values by Tipping et al. (2006a, 2006b)
Clay content of soil	Measured
Weathering inputs: Na, Mg, Al, K, Ca, Fe, Ni, Cu, Zn, Cd, Pb, Hg, Si,	Modeled by SAFE and adjusted during calibration; input of Metals due to mineral weathering
Dissolved organic carbon (DOC)	Measured

Table 3: Deposition scenarios for Cd, Pb and Hg

	2010 deposition [mg m^{-2} a][1]			Swiss OAPC[2] [mg m^{-2} a]			CL[3] [mg m^{-2} a]		
	Cd	Pb	Hg	Cd	Pb	Hg[4]	Cd	Pb	Hg
Beatenberg	0.09	4.5	0.04	0.73	36.5	-	1.1	5.1	0.02
Lausanne	0.09	3.0	0.04	0.73	36.5	-	1.1	2.1	0.03
Novaggio	0.28	5.6	0.05	0.73	36.5	-	2.1	2.1	0.04
Schänis	0.07	1.5	0.04	0.73	36.5	-	1.1	2.1	0.03
Vordemwald	0.07	3.0	0.04	0.73	36.5	-	0.6	2.1	0.03

[1] Estimated current deposition in the **forests** (wet deposition + throughfall + litterfall)
[2] Maximal acceptable HM depositions in Switzerland according the OAPC (ordinance on Air Pollution Control, 1985)
[3] Critical loads (CL) were obtained from the WGE report 2005 (Slootweg et al., 2005). The WGE report presents a range for deposition for 277 forest soils in Switzerland. We chose the lowest CL of this range as deposition value.
[4] No maximal deposition values for Hg are defined in the Swiss OAPC

Table 4: Critical limits for Cd, Pb and Hg

Critical limits for soil water			
	Cd [µg L^{-1}]	Pb [µg L^{-1}]	Hg [µg L^{-1}]
WHO guideline for drinking water	3	10	1
Lazzaro et al. (2006a, b)	1.2	1.8	-
De Vries et al. (2007)	-	-	0.035

Critical limits for soil solid phase		
	Lofts et al. (2004)[1]	
Cd [mg kg^{-1}]	L1	L2
Beatenberg*	21.0	0.3
Lausanne	1.9	0.7
Novaggio	6.6	5.0
Schänis	5.4	3.1
Vordemwald	3.4	0.6

	Lofts et al. (2004)[1]	
Pb [mg kg^{-1}]	L1	L2
Beatenberg*	30.5	1.9
Lausanne	7.2	4.2
Novaggio	17.0	15.1
Schänis	28.6	20.0
Vordemwald	11.3	3.5

	Tipping et al. (2010)			Meili et al. (2003)[3]	
Hg [mg kg^{-1}]	L1, L2[2]	L1[3]	L2[3]	L1	L2
Beatenberg*	0.13	2.7	0.03	0.41	0.01
Lausanne	0.13	0.2	0.07	0.03	0.01
Novaggio	0.13	0.6	0.43	0.10	0.07
Schänis	0.13	0.2	0.10	0.03	0.02
Vordemwald	0.13	0.3	0.05	0.05	0.01

*critical limits for soil protection according to Swiss Ordinance relating to impacts on the soil (OIS, 1998):
-for Beatenberg: Cd: 0.32 mg kg^{-1}, Pb: 20 mg kg^{-1}, Hg: 0.2 mg kg^{-1},
-for all others: Cd: 0.8 mg kg^{-1}, Pb: 50 mg kg^{-1}, Hg: 0.5 mg kg^{-1}

[1] based on organic carbon content and pH conditions.
[2] based on total Hg content in the soils
[3] based on the SOM content in the soils

Table 5: Measured Cd, Pb and Hg concentrations (mean ± std.dev.) in the two soil layers (L1 and L2) in the solid phase (n=3) and in the soil solution (n=8).

Metal concentration in the solid phase*						
	Cd [mg kg^{-1}]		Pb [mg kg^{-1}]		Hg [mg kg^{-1}]	
	L1	L2	L1	L2	L1	L2
Beatenberg	<d.l.[1]	<d.l.	60 ± 1	<d.l.	0.27 ± 0.07	0.03 ± 0
Lausanne	0.08 ± 0.09	<d.l.	23 ± 3	12 ± 1	0.12 ± 0.03	0.05 ± 0
Novaggio	0.39 ± 0.06	<d.l.	51 ± 17	21 ± 0	0.07 ± 0.01	0.05 ± 0.01
Schänis	0.25 ± 0.35	<d.l.	34 ± 3	23 ± 1	0.18 ± 0.13	0.08 ± 0.01
Vordemwald	<d.l.	<d.l.	29 ± 1	13 ± 1	0.25 ± 0.08	0.06 ± 0

Metal concentration in soil solution**						
	Cd [µg L^{-1}]		Pb [µg L^{-1}]		Hg [µg L^{-1}]	
	L1	L2	L1	L2	L1	L2
Beatenberg	0.02 ± 0	0.07 ± 0.02	2.3[2]	4.0 ± 1	0.03 ± 0.01	0.02 ± 0
Lausanne	0.06 ± 0.03	0.18 ± 0.07	0.3 ± 0.1	1.8 ± 2	0.03 ± 0.01	0.004 ± 0.001
Novaggio	0.09 ± 0.07	0.02 ± 0.01	0.7 ± 0.3	4.0 ± 3	0.02 ± 0.01	0.001 ± 0
Schänis	<d.l.	<d.l.	0.1 ± 0.0	0.1 ± 0	0.004 ± 0	0.004 ± 0.004
Vordemwald	0.07 ± 0.05	0.32 ± 0.25	0.2 ± 0.1	1.0 ± 1	0.04 ± 0.02	0.005 ± 0.002

[1] <d.l.=below detection limit
[2] Only one measurement available
*Detection limits per kg^{-1} soil: Cd: 0.01 mg; Pb 0.02 mg; Hg: 0.001 mg
**Detection limits per L^{-1}: Cd: 0.02 µg; Pb 0.05 µg; Hg: 0.0003 µg

Table 6: Ratio ([M_{3000}]/[M_{2010}]; M= Cd, Pb or Hg) between the concentrations in the year 3000 and the current (measured) concentrations in the solid phase and in the soil solution. The ratios are shown for both modeled soil layer (L1, L2) and for all three deposition scenarios [1) Current: current (2010) deposition; 2) OAPC: maximal acceptable deposition according to OAPC (1985); 3) CL: critical loads (CL) according to the Working Group on Effects (WGE) of the convention on LRTAP (Slootweg et al., 2005)]

		solid phase			**soil solution**		
1) Current		Cd	Hg	Pb	Cd	Hg	Pb
Beatenberg	L1	1.7	2.0	1.8	1.7	3.3	1.7
	L2	1.8	1.9	2.1	1.8	2.5	2.1
Lausanne	L1	0.2	2.0	0.1	0.3	2.6	0.1
	L2	0.1	1.2	0.3	0.7	1.3	8.4
Novaggio	L1	0.8	2.0	0.1	1.1	3.7	0.1
	L2	0.3	1.5	1.3	1.2	2.4	4.6
Schänis	L1	1.6	1.4	2.0	1.7	1.8	2.0
	L2	3.5	2.2	1.4	5.2	2.9	1.6
Vordemwald	L1	0.2	1.9	0.6	0.3	3.1	1.1
	L2	0.1	1.3	2.1	0.8	1.6	15.2
2) OAPC		Cd	Hg*	Pb	Cd	Hg*	Pb
Beatenberg	L1	11.6	-	11.8	11.9	-	11.9
	L2	12.3	-	13.3	12.3	-	14.0
Lausanne	L1	1.3	-	0.8	2.3	-	1.5
	L2	0.4	-	3.6	6.0	-	93.5
Novaggio	L1	2.2	-	0.6	2.9	-	0.7
	L2	0.9	-	4.3	3.2	-	15.7
Schänis	L1	12.6	-	20.2	14.1	-	41.7
	L2	25.6	-	5.6	39.0	-	7.1
Vordemwald	L1	1.8	-	6.5	3.4	-	12.2
	L2	1.4	-	17.8	7.5	-	127.8
3) CL		Cd	Hg	Pb	Cd	Hg	Pb
Beatenberg	L1	17.4	1.1	2.0	17.8	1.1	1.9
	L2	18.3	1.2	2.3	18.5	1.2	2.3
Lausanne	L1	1.9	1.6	0.1	3.5	2.1	0.1
	L2	0.6	1.1	0.2	9.1	1.2	6.1
Novaggio	L1	6.4	1.6	0.04	8.4	2.7	0.1
	L2	2.6	1.4	0.9	9.2	2.0	3.4
Schänis	L1	18.7	1.1	2.2	21.3	1.3	2.4
	L2	38.1	1.6	1.4	58.9	2.2	1.6
Vordemwald	L1	1.5	1.5	0.4	2.8	2.5	0.8
	L2	1.1	1.2	1.7	6.2	1.4	12.2

*No maximal deposition values according to the OAPC exists for Hg

Figure 1

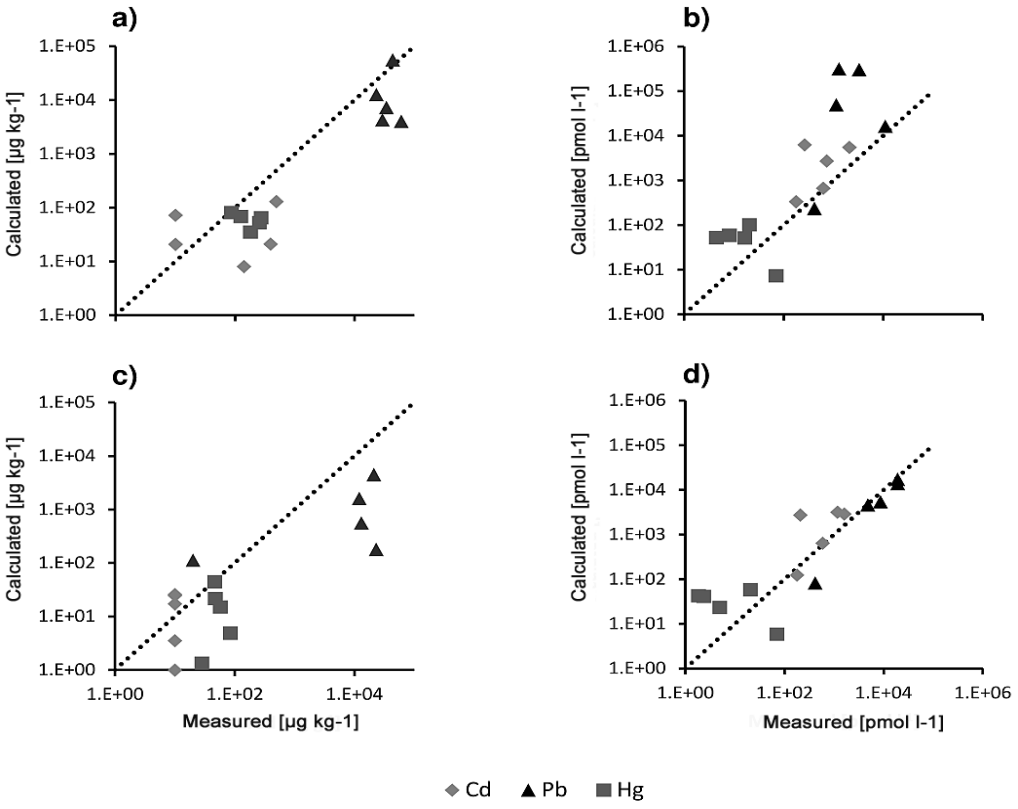

a)
b)
c)
d)
Calculated [µg kg-1]
Calculated [pmol l-1]
Measured [µg kg-1]
Measured [pmol l-1]
1.E+00
1.E+01
1.E+02
1.E+03
1.E+04
1.E+05
1.E+06
Cd
Pb
Hg

Figure 2

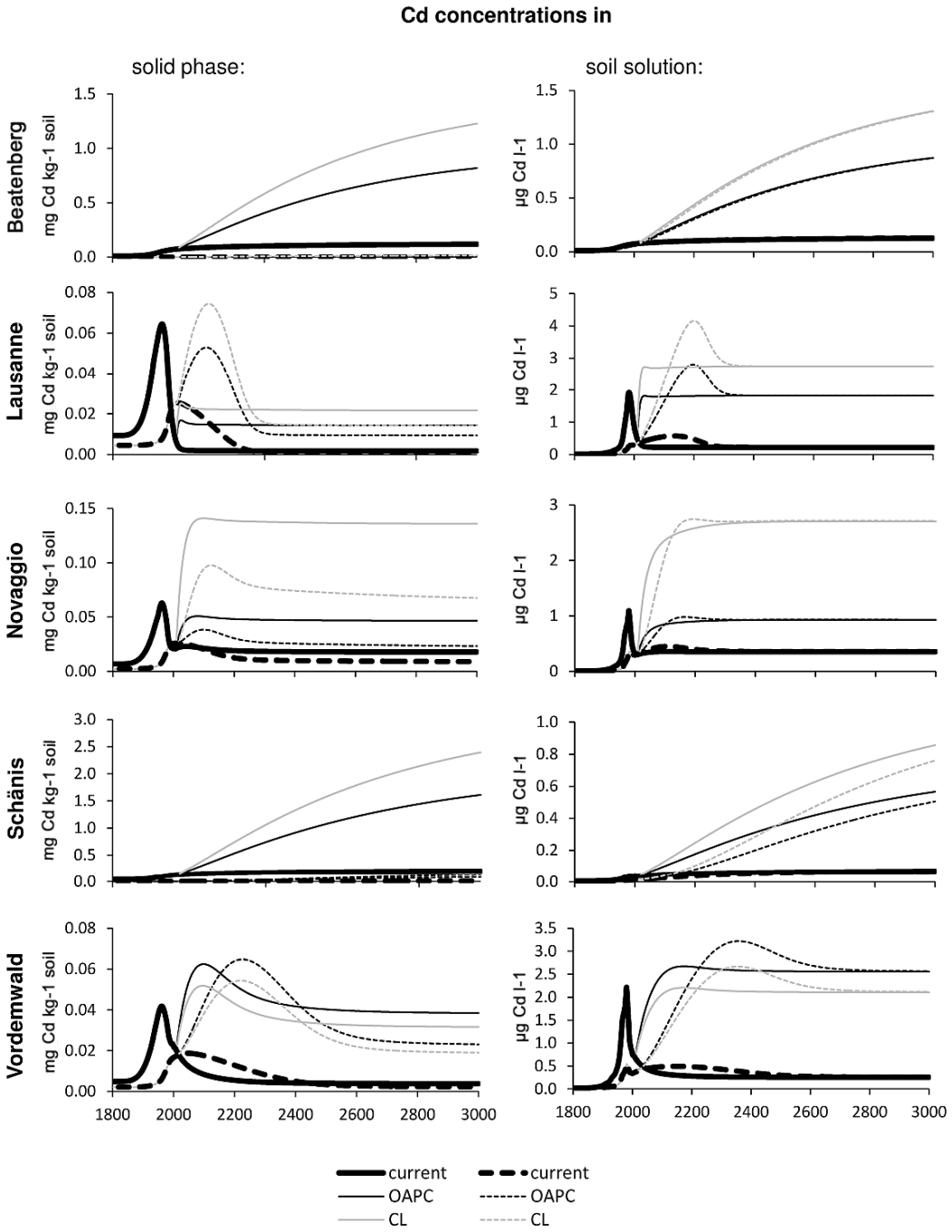

Cd concentrations in
solid phase:
soil solution:
Beatenberg
Lausanne
Novaggio
Schänis
Vordemwald
mg Cd kg-1 soil
µg Cd l-1
1800
2000
2200
2400
2600
2800
3000
current
OAPC
CL
current
OAPC
CL

Figure 3

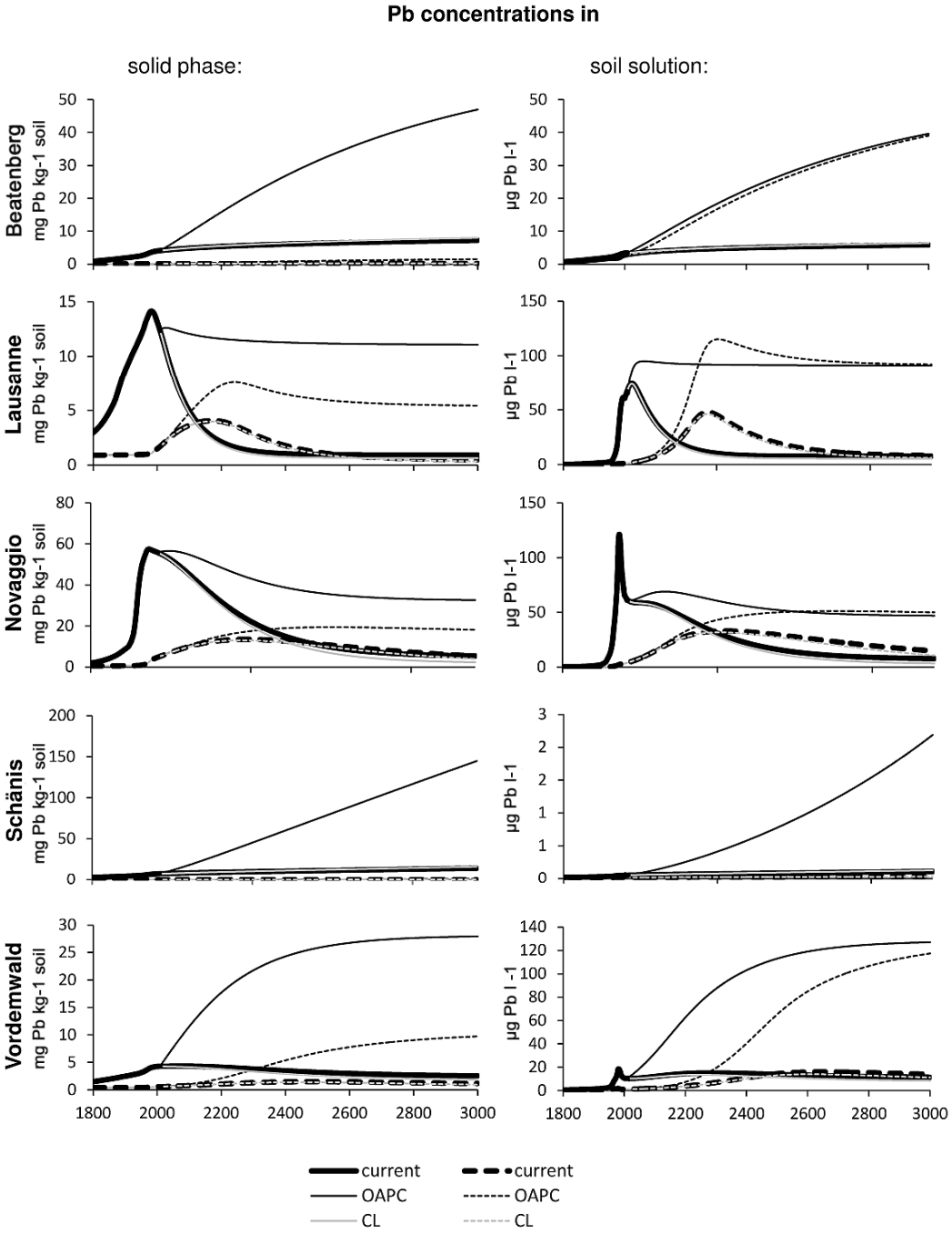
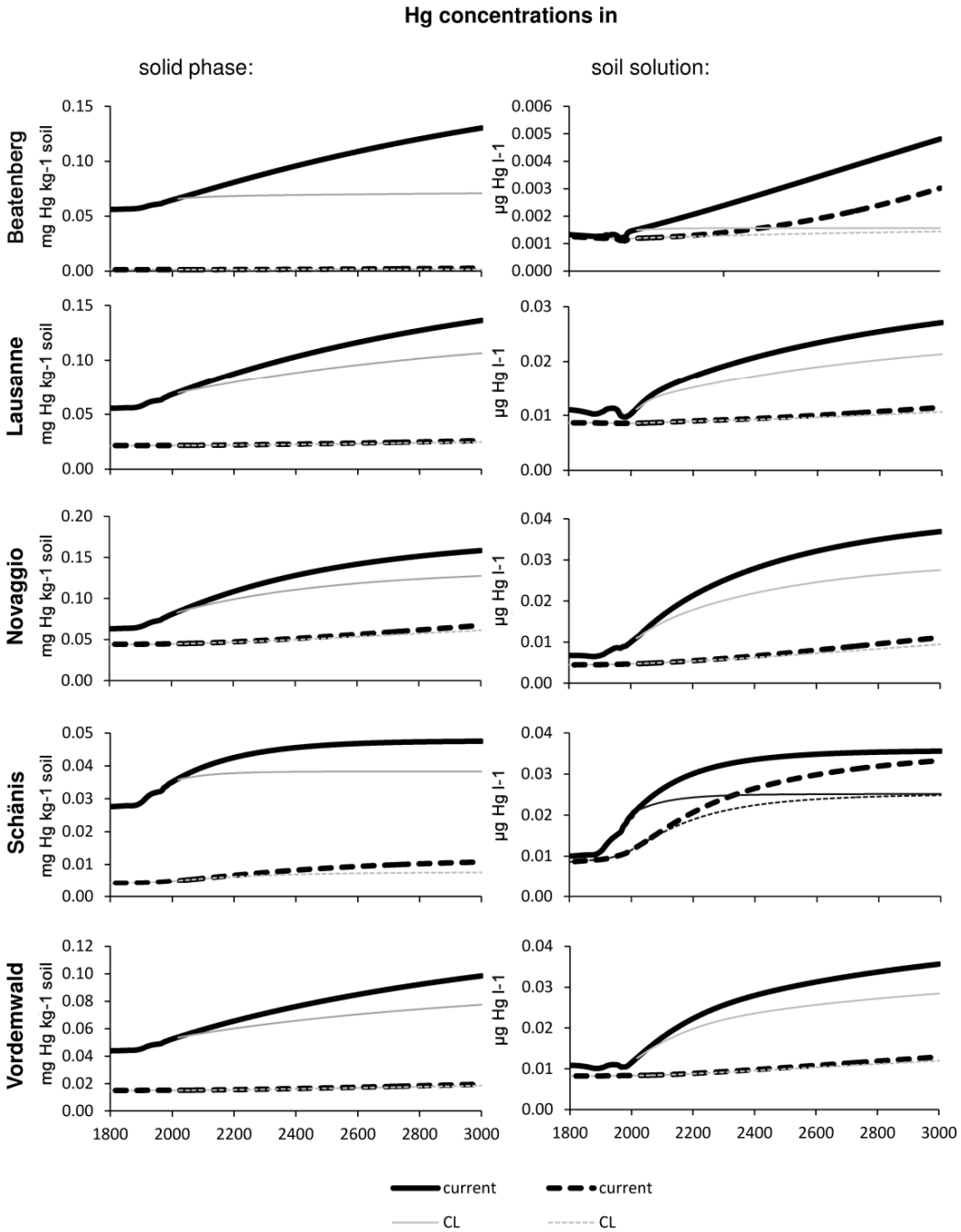

Pb concentrations in
solid phase:
soil solution:
Beatenberg
Lausanne
Novaggio
Schänis
Vordemwald
mg Pb kg-1 soil
µg Pb l-1
1800
2000
2200
2400
2600
2800
3000
current
OAPC
CL
current
OAPC
CL

Figure 4


Hg concentrations in
solid phase:
soil solution:
Beatenberg
Lausanne
Novaggio
Schänis
Vordemwald
mg Hg kg-1 soil
µg Hg l-1
0.15
0.10
0.05
0.00
0.006
0.005
0.004
0.003
0.002
0.001
0.000
0.03
0.02
0.01
0.20
0.04
0.12
0.08
0.06
1800
2000
2200
2400
2600
2800
3000
current
current
CL
CL