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**Deliverable 3.3:
Metals transfer from soil to water, models and theory**

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1 ABSTRACT

Metals are often associated with contaminated sites, and one part of the MuSA project was to focus on the modelling of impacts of metals on ecosystems, and initially, the focus was put on the use of the HSAB concept (Hard and Soft Acid and Bases) to model the impact of metals, as what was done for terrestrial ecosystems. Nevertheless, as presented by Helen Beauchamp in the Deliverable 3.1, the MuSA Project considers first substances of concern in the Ronde Venen case study, and the metals that are present in high concentration in this case study are border line metals which can not necessarily be well covered by this concept. Therefore, the focus was put in the review of available models to identify the intermedia transfer and to quantify the mobility of metals in soils especially considering their ability to be applied in LCA. After comparing three models comparing the mobility of Cd, Cu, Pb and Zn, the results are coherent, highlighting the high mobility of Cadmium and Zinc afterward, while Cu and Pb appears to be more sensitive to the media conditions. Four key parameters are identified such as fraction of metals in soil, fraction of organic matter, Redox-potential and pH. This is currently feasible because the four metals here mentioned are very well studied and easy to model. Impact assessment of anions are not feasible using these approaches and it will require further investigations.

2 INTRODUCTION

2.1 Context

Metals are often associated with contaminated sites, and one part of the MuSA project was to focus on the modelling of impacts of metals on ecosystems, and initially, the focus was put on the use of the HSAB concept (Hard and Soft Acid and Bases) to model the impact of metals, as what was done for terrestrial ecosystems by Haye et al (2006). Nevertheless, as presented by Helen Beauchamp in the Deliverable 3.1, the MuSA Project considers first substances of concern in the Ronde Venen case study, and the metals that are present in high concentration in this case study are border line metals which can not necessarily be well covered by this concept. Therefore, the focus was put in the review of available models to identify the intermedia transfer and to quantify the mobility of metals in soils especially considering their ability to be applied in LCA.

The first part of the deliverable below is describing the framework the model has to fit in. It especially concerns the time and space scale issue and the units and methods that we have to take into account. In a second part, the work compares three models that can be used for assessing mobility of metals and intermedia transfer from soil to water. In a third part, the key aspects needed in building up the models are presented, especially with the description of the main soil parameters influencing the mobility of metals.

2.2 Time and space scale in LCA

Assessing the impact of substances involves assessing both their behaviour and interactions in the environment, as well as their evolution in space and during time. Transfer of pollutants in the different environmental compartments (air, water, soil) is a fundamental problem in LCA.

In LCA, the spatial dimension in IMPACT2002+ is represented by a one-box model for all Europe, inserted in a bigger box that stands for the whole planet (referred to as the a-spatial model). The model depicts environmental compartments in interaction with each other (Figure 1). The transfer of a substance from one compartment to another is based on mass balance equations. Improvement to this model in the last years has given new information that allows better predictions of impacts on human health (carcinogenic and non-carcinogenic damages) and aquatic ecotoxicity (referred to as the regionalised model).

This short/long term division is kept in this study, as the focus is on the behaviour of polluted soil. More steps will be evaluated during these two phases as the evolution of the impacts is not necessary linear.

2.3 Life Cycle Impact Assessment method: IMPACT

In LCA the IMPACT2002+ dataset covers a wide range of effects on the environment. The midpoint categories are expressed in mass of substance equivalent, which is a reference substance that affects the category with a weighted impact. For example, 1 kg of CH₄ emitted in the atmosphere will correspond to 7 kg of CO₂ for the impact category "climate change". A substance can damage more than one category. For water three endpoint are calculated: ecotoxicity (expressed in kg equivalent of triethylene glycol into water "kg TEG water"), acidification (kgeq SO₂ into air "kg SO₂") and eutrophication (kg equivalent PO₄³⁻ into a P-limited water "kg PO₄ P-lim"). In addition to this, 9 other impact categories are evaluated, such as emission of carcinogenic substance (in kg C₂H₃Cl equivalent) or global warming impact (kg CO₂ equivalent). Further, the reference-substance equivalent amounts are grouped in endpoint categories, to compare the damage provoked. In the IMPACT2002+ method, the damage categories express the impact on human health, ecosystem quality, climate change and resources.

Table 1 : IMPACT2002+ midpoint categories and standard damage factors

Damage category	Human Health	Unit :DALY
Carcinogens	2.8E-06	DALY / kg C ₂ H ₃ Cl
Non-Carcinogens	2.8E-06	DALY / kg C ₂ H ₃ Cl
Respiratory inorganics	0.0007	DALY / kg PM _{2.5}
Ionizing radiation	2.1E-10	DALY / Bq C-14
Ozone layer depletion	0.00105	DALY / kg CFC-11
Respiratory organics	2.13E-06	DALY / kg ethylene
Damage category	Impacts on Water	Unit : PDF*m²*yr
Aquatic ecotoxicity	5.02E-05	PDF*m ² *yr / kg TEG water
Aquatic acidification	0.065	PDF*m ² *yr / kg SO ₂
Aquatic eutrophication	3.11E-07	PDF*m ² *yr / kg PO ₄ P-lim
Damage category	Climate Change	Unit : kg CO₂
Global warming	1	kg CO ₂ / kg CO ₂
Damage category	Resources	Unit : MJ primary
Non-renewable energy	1	MJ primary / MJ primary
Mineral extraction	1	MJ primary / MJ surplus

Impacts on the different categories depend on the amount of the element or substance that will be transferred to water, air or soil. For instance, soil organisms would not be seriously affected by a very volatile compound, as it would almost entirely be transferred to

the gaseous phase in a very short time. On the other hand, other compounds can persist in the soil and not be volatilised at all, as is the case for most heavy metals. In this last case the impact on the soil ecosystem would be larger.

In LCA the functional unit is defined as an equivalent service or a product that is compared between multiple options. The comparison allows the discovery of the scenario with the most impact. The problem is: how to estimate the impact of a polluted (or contaminated) site, if no action is taken? Assuming that there is no impact because there is no action (thus no emission) would not be correct. The term contaminated itself implies the presence of substances affecting the environment.

The first part of this project will thus treat the evolution of the emission of substances from soils, trying to give a time scale, which will help describe the evolution of the impact with time. The idea is to look at the contaminated soil as a “pollutant reservoir” releasing pollutants to the surroundings; this approach is chosen following the current LCA way of reasoning. The additional question to solve is the temporal evolution of the emissions.

In the LCA literature several models treating the transfer of heavy metals (but also other pollutants) in soils (and landfills) can be found. The aim of this work is first to give an overview of these models and to search for information to determine metal emissions from soils over a time period of 100 years. Longer term metal behaviour in and emission from soils will be further addressed by considering pedological notions.

3 EXAMPLES AND MODELS FOR METAL EMISSIONS

The problem considered here derives from the question “how to consider and quantify the impact of emitted heavy metals in the long-term time scale?”.

In the Ecoinvent database, short term emissions are evaluated over a period of 100 years, while the long term is 60 000 years. This decision was taken based on Swiss climatic conditions, and supposing that after 60 000 years most of Switzerland will be covered by glaciers of the next ice age, which will thoroughly erode and redistribute matter present in today's surface soil (Doka et al. (c) 2005). In fact, when a glacier moves forward, it perfectly “cleans” the ground, removing the soil with the rocks that are carried at its base (Legros, 2007). This assumption is not valid for Europe as a whole because the extent of the glaciers in the last ice age was not total for the European continent, but this period of 60 000 years will be taken as a reference time, in order to evaluate the evolution of emissions.

Evidently, field data on such long term periods are impossible to collect. Many leaching tests have measured the leachable fraction of the concerned metal, but it must be stressed that such tests give good estimations of the leached fractions at a certain pH, but do not allow the prediction of the intensity and kinetics of metal release in the field (Tack et al., 1999). In addition, for long time periods weathering processes play a role in the chemistry of the soil, and can thus change the soil reactivity. Legislative leaching tests for landfill in Switzerland and in the European Union are performed on fresh, not weathered samples and are therefore merely a test for short-term behaviour of those wastes (Doka (d), 2007).

In the literature, many authors have focused on the fraction of a metal that can be leached from a particular type of soil and on identifying soil parameters that correlate with these fractions. Sauvé et al. (2000) elaborated a mathematical model to estimate the fraction of heavy metals leached from a soil, based on the study of previous models found in the literature (K_d linear coefficient, Freundlich isotherm and the competitive adsorption model). It is concluded that three leading parameters in the calculation of the solid-solution partitioning of metals are: pH, soil organic matter and total metal concentration in soil.

Gray and McLaren (2006) found that the most important factor affecting soluble metal concentrations is the total heavy metal content, whilst soil pH, total carbon content and Fe and Al oxides showed varying degrees of importance depending on the metal.

Thinking about the determination of long-term metal impact, the notion of time has to be integrated in these models. In fact, in laboratory experiments it is often assumed that the soil would reach a precise pH value within an estimated time frame due to local specific conditions. The evaluation of leaching consists of bringing the system to the foreseen pH, which normally corresponds to the worst case scenario for a given situation.

In this work a comparison between models described by different authors, treating emissions of the metals of interest in this study (cadmium, copper, lead, zinc) from the soil to the aquatic compartment. The vector of the movement is water; this is why the term leaching can be used. Emission would otherwise be a more general term to describe the lost of metal from a soil.

Four studies are illustrated:

- Ronde Venen measurements by Alterra (2000)
- ROAD-RES model done by Birgisdóttir et al (2007)
- Landfill model done by Obersteiner et al. (2007) based on empirical data
- Ecoinvent Waste treatment and Assessment of Long-term emissions by Doka (2005)

The comparison between these four cases is not totally rigorous because of the nature of the data presented. Absolute soil values are not always available. The aim here is to look for a trend that dominates the leaching (or emission) process of metals to the aquatic compartment. Where possible, the leaching ratio (concentration (or mass) present in the solid phase / concentration (or mass) leached after 100 years) is given, in order to have a visual support in finding the eventual trends.

3.1 Ronde Venen, Demmerik polder

The “toemaakdek” activities have been practiced for centuries in Dutch polders, and for this reason the treatment of data requires attention. Total concentration of metals in the soil and concentration in the pore water were measured by Alterra (Alterra, 2000). To evaluate the relation between the total concentration of each metal and its annual leaching, the pore water concentration [mg/l] was multiplied by the total amount of water flowing through the soil every year [l/yr]. The derived leaching [mg/l] is compared with the total metal content in figure 2.

The conditions used to describe the polder in the mathematical model are as follows: it has a surface of 1625 square metres, a polluted layer 10 centimetres deep, and an annual net infiltration in the soil¹ of 250 mm/m². The concentrations of metals are presented in table 2.

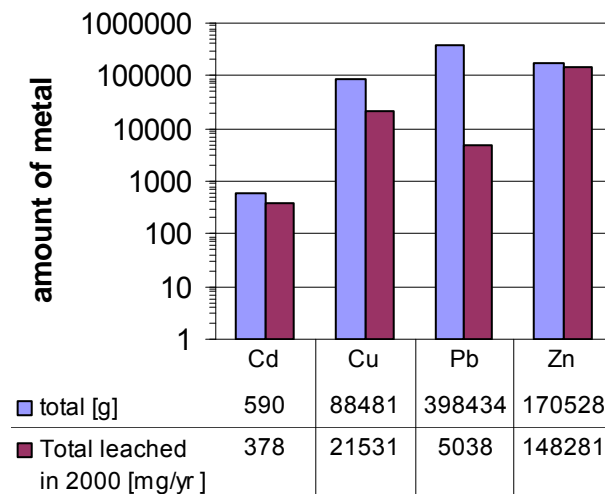


Figure 2 : Metal content [g] and metal leached in 2003 [g/yr] from the Demmerik polder, in Ronde Venen site (Rutgers, in press)

The comparison is between the total metal content of the site and the quantity of metal that has been leached during the same year. It shows that, compared to the other metals, lead is leached in very small amounts despite its high presence in the soil.

¹ The net infiltration is the fraction of rainfall that contributes to the groundwater table.

Looking at the results of the extraction by 0.01 M CaCl₂ in Table 2 (RIVM, 2000), the tendency of cadmium to be extractable is evident. In fact, the fraction released was about 8 % for this element, while for copper and it was under 0.6%. The value for zinc is 2.34 %, which is also high compared to lead and copper.

Table 2 : Metal concentration, pore water concentration, 0.01 M CaCl₂ extraction and CaCl₂ extractable fraction. Demmerik polder, Ronde Venen site (data by Alterra, 2003)

	Total destruction average [mg/kg]	Porewater concentration [mg/l]	CaCl ₂ extraction [mg/kg]	Extractable fraction [%]
Cd	1.09	0.00093	0.09	8.26
Cu	165	0.053	0.844	0.51
Pb	743	0.0124	1.653	0.22
Zn	318	0.365	7.441	2.34

The available data show the important relative leaching of cadmium and then zinc, and the resistance to this same process of lead and copper.

3.2 ROAD-RES Model

Birgisdóttir et al. (2007) described two disposal methods for 4400 tons of Municipal Solid Waste Incinerator (MSWI) bottom ashes in a life cycle assessment: the first one describes the landfilling of bottom ashes in a coastal landfill in Denmark, and the second one studies their recycling as subbase layer in an asphalt secondary road (the amount corresponds to the quantity of bottom ashes needed as subbase material beneath the lane of 1 kilometre of Danish traditional secondary road). Leaching phenomena are described as being controlled by two main factors: pH and redox potential. The differences between the starting concentrations of heavy metals in road water and in road sections with MSWI bottom ashes or with crushed rock as granular base were trivial, except for lead (Birgisdóttir et al. 2007). The functional unit is one kilometre of Danish secondary road.

To model the landfill, four time periods were considered: the first three during which the leachate of the landfill goes to the waste water treatment plant. It was assumed that on average 20% of the leachate would reach the environment due to defects in the impermeable liner layer at the bottom of the landfill and collection system. Leaching of heavy metals in the road scenario, during 100 years, represents less than 1% of the total amount in the bottom ashes (table 3).

Table 3 : ROAD-RES study, fraction of metals leached from landfill or road after 100 years (Birgisdóttir et al., 2007)

Element	Landfill %	Road %
Cd	0.0240	0.2000
Cu	0.0118	0.0314
Pb	0.0005	0.0045
Zn	0.0006	0.0049

The road material is more sensitive to the leaching of the metals, present as bottom ashes in the road structure. Especially for cadmium, the amount leached from the road is much more important than from the landfill; it is about 10 times bigger. Proportionally, cadmium is leached more easily in road scenario, while in the landfill copper is the metal most sensitive to be leached, even if its leached fraction is very small.

It is important to notice that all the values are equal or under 0.2 %, which means that after 100 years, a very small amount of metals could be released from the stabilisation that occurs in the creation of bottom ashes and in the inclusion of metals in the road subbase material.

3.3 Landfill model

Obersteiner et al. (2003) compare data of different kinds of landfills to show the evolution of leachates over a time period of 100 years. Three main phases are distinguished: from 1 to 5 years (called “operational period”, supposed to have the highest values), 6-30 years (“aftercare period”) and 31-100 years (medium time period, where active aftercare has stopped). Unfortunately, these results depend on the waste composition that is not given in the article. The Figure 3 shows absolute amount of leached metal (average and maximum) for sanitary landfills for the averaged data from different countries (Austria, Germany and Switzerland). Figure 4 weights the results with the fraction of waste composed by each specific metal.

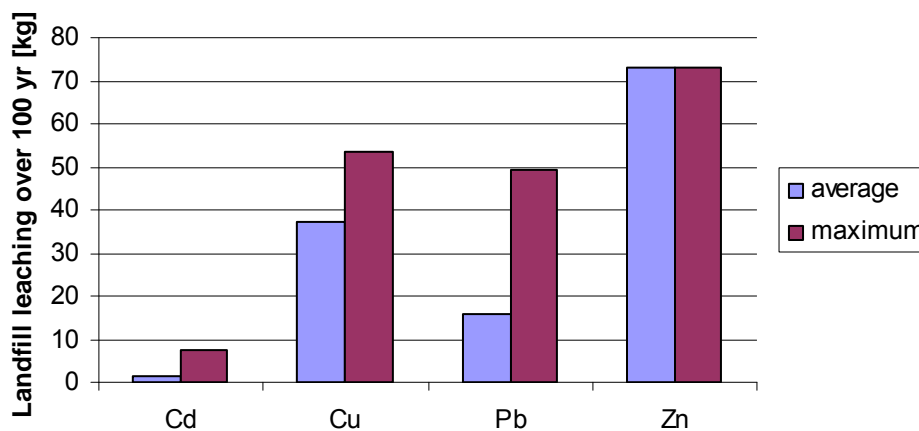


Figure 3 : Sum of leachate after 100 years. Obersteiner, 2007

Zinc shows only a very small difference between average and maximum leaching. It can thus be deduced that this metal is weakly dependent on local landfill conditions. At the opposite, lead, cadmium and copper seem to vary more between the landfills, as the maximum values are about 1.5 times higher than the averaged ones (extreme case for cadmium, where the maximum is 4.7 times higher).

Supposing that Germany, Austria and Switzerland domestic wastes have similar composition, and taking limit values for waste composition in sanitary landfill in Switzerland (OTD, Swiss waste ordinance, 1991) it is possible to normalise the plot.

The limit for zinc is 1000 mg/kg, while lead and copper have a limit of 500 mg/kg (the half) and 10 mg/kg for cadmium.

It means that if the landfill is at limit values of composition, the amount of cadmium is 100 times less than the amount of lead. With this hypothesis, the weighted data were plotted. Taking Zinc as a relative reference, Cd was multiplied by 100, Cu and Pb by 2 in order to have a relative “Swiss” standard waste composition.

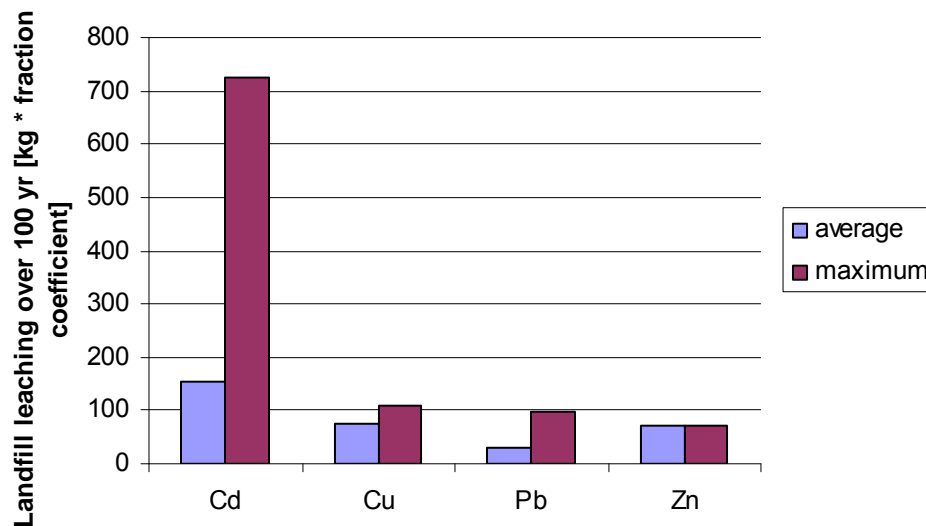


Figure 4 : Weighted sanitary landfill emissions.

The results underline the variability of cadmium leaching (notice the important difference between average and maximum leaching amounts), and also its higher proportional capacity to be emitted by the sanitary landfill compared to the other three metals. Lead seems to be the metal that proportionally remains more in the soil in long-term periods, but the difference between average value and the maximum is still considerable.

3.4 Ecoinvent waste treatment and metal emissions

Doka ((a) 2003, (b) 2004) elaborated the system used to determine transfer coefficients (TK) in the Ecoinvent database for the emission of several waste types from different landfills. Until 1996 the modelling was based on thermodynamics and laboratory leaching tests (with some refinements). The waste material was placed during 24 hours at pH 4, and the total leached amount was assumed to represent the long term available fraction. In Ecoinvent 1996, 50% of the total amount was used for landfills with little acidification potential and 100% for landfills with large acidification potential (sanitary landfills) (Doka, 2004).

Emissions from landfills used for calculations in SimaPro (the software used to calculate impacts in LCA) are split up into emissions that occur in the first 100 years after waste deposition (short term transfer coefficients) and emissions that occur afterwards (long term transfer coefficients, until 60 000 years).

The carbonate phase represents the period during which the pH is buffered by acid neutralising materials present in the landfill. Doka uses a landfill-waste specific transfer coefficient to calculate the emissions.

$$Emission\ media_{phase,i} [kg\ i/kg\ waste] = TK\ media_{phase,i} \times waste\ composition_i [kg\ i/kg\ waste]$$

The emissions from the waste to specific media are calculated from the transfer coefficient (TK) for the element i , for the concerned media (water or gas) and the landfill phase (short-term or long-term), multiplied by the concentration of the element in the waste.

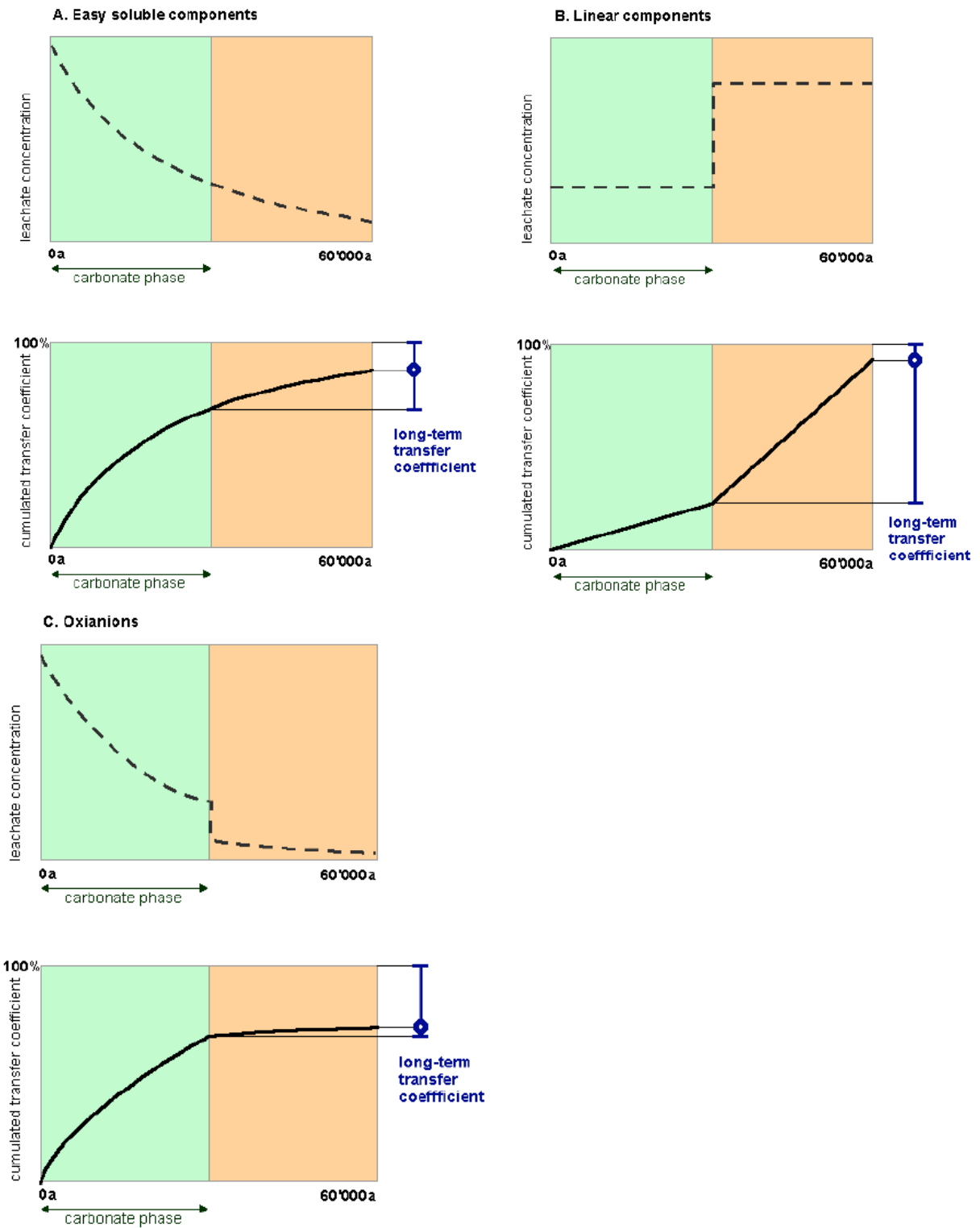


Figure 5 : Behaviour of Easily soluble components, Linear components and Oxyanions by Doka, 2003. Calculations scheme for long-term transfer coefficients for different elements: A.) Exponential decline for soluble elements with no change after the carbonate phase (left), B.) Constant concentrations for metal, Exponential decline of concentrations for metal oxianions with a decrease after the carbonate phase (right). The range indicated at the right side of each panel represents the derived uncertainty range for transfer coefficients

In the Doka model easily soluble elements (monovalent ions Na⁺, K⁺, Cl⁻, F⁻, Br⁻, I⁻) and oxyanion-forming elements (WO₄²⁻, HVO₄²⁻, Cr(VI)O₄²⁻, MoO₄²⁻, HBO₃²⁻, HSeO₄⁻, SbO₄³⁻, HAsO₄²⁻) and also nitrogen (as nitrate NO₃⁻) are supposed to decrease qualitatively in the same way (figure 5)

To have a general idea of the leaching of the four metals studied in this report, an extract from Appendix I is summarised in table 4.

Table 4 : Long term-transfer coefficient (Doka, 2007 (a)). Fraction of metal that will be leached after 60 000 years

Long term-transfer coefficient (%)						
	Sanitary Landfill		Residual Landfill		Slag compartment	
	Short term*	Long term	Short term	Long term	Short term	Long term
Cd	11.89	100	0.001133	0.68	0.0514	100
Cu	0.24	100	0.006426	3.86	0.003472	100
Pb	0.34	100	0.000866	0.52	0.001825	100
Zn	1.75	83	0.002046	1.23	0.002977	100

* The short term emission of a sanitary landfill depends strictly on the length of the carbonate phase, which keeps the pH in neutral-high values

Sanitary landfills are supposed to receive “all” kinds of waste (untreated municipal or household waste, building waste or wastewater treatment sludge)². Residual landfill has low-carbon wastes, like incineration residues or inorganic building materials. In Switzerland the total organic carbon in residual, inert and slag compartment landfill has to be lower than 5 % weight (3 % weight for slag compartments).

Residual landfills receive wastes that are not chemically or biologically reactive in water. They mainly receive MSWI filter ashes solidified with cement. This composition explains the huge difference between with the amount of leached metals of the sanitary landfill and the slag compartment.

In residual landfills the metal which undergoes the greatest (but still very limited) leaching is copper, with about the 4 % of total concentration. Zinc follows with 1.23% , while cadmium and lead leaching are under the 1%. Globally these values are extremely low. This is an expected result, since the residual material landfill has a large carbonate buffer, which is not depleted within 60'000 years, and also it bears waste with lower carbon content than sanitary or slag landfills and hence there is less potential for biogenic activity (Doka (d), 2007).

3.5 Conclusions on the quoted models

All examples were taken from European studies about long term metal leaching. As climate (and especially annual rainfall) determines the amount of rain water that flows (or could flow) through the soil, the specific location of the site of study has to be taken into account.

² However, since 2000, it is denied to landfill burnable waste in Switzerland.

In the Dutch Ronde Venen practical case study, an important leaching of cadmium and zinc was found. The difficulty to define an age for the site makes locating these emissions in the time scale difficult.

In the model elaborated by Birgisdóttir in Denmark, after 100 years the leaching of cadmium from the road material was significantly higher compared to the other metals, while for landfill copper was the dominant compound in leachates. Generally the emissions of metals were very low, under 0.2% of the total content for each metal.

Obersteiner et al. worked on data of sanitary landfills from Germany, Austria and Switzerland. Their results showed cadmium as the most leached metal compared to the others, but also its variability. Lead seemed to be the metal that proportionally remains more in the soil in long term periods, but the difference between average and the maximum value is considerable. The data are presented as absolute amounts, which do not allow a direct comparison with the Doka model.

The Ecoinvent model (based on Swiss data) presented by Doka also confirms cadmium leachability for short term periods in slag compartments, which proportionally is much higher than the fractions found for the other elements. The residual landfill is the only one that retains a large amount of metals, even after 60 000 years (the period after which sanitary and slag compartments have released the entire amounts of metals, except for zinc). If enough time is given, all phases could be weathered and turned into available phases. It would thus mean that there is no stop to leaching.

No obvious trend has been found in the review of these studies, although the magnitudes found can help to assess the possible evolution of emissions from a specific site, and consequently to estimate its impact on the environment. Qualitatively it can be said that cadmium has the tendency to be proportionally leached more than the other three considered metals. Lead is apparently well retained by the soil matrix for short term periods in all the models and analyses, while zinc and copper do not show a clear pattern of behaviour.

Although the situations presented are very different in context and soil composition, all authors put an accent on the importance of the acidity neutralisation capacity, which stabilises the pH, and indirectly reduces the leaching of most substances.

These factors are consequently going to be the basic parameters that are going to be used to estimate the leaching behaviour of metals for long term periods in the next section.

4 MODELLING EMISSION EVOLUTION

In the following paragraphs, the approach to qualitatively model the leaching of metals is explained. A graphical summary of the model of Doka ((b), 2004) is shown in figure 6. In this figure the different evolution of transfer coefficients for different elements is represented. Two main points are underlined: 1) the importance of the drop of pH on the emission of elements, especially for metals, and 2) the low value of the transfer coefficients for short-time periods compared to the long term.

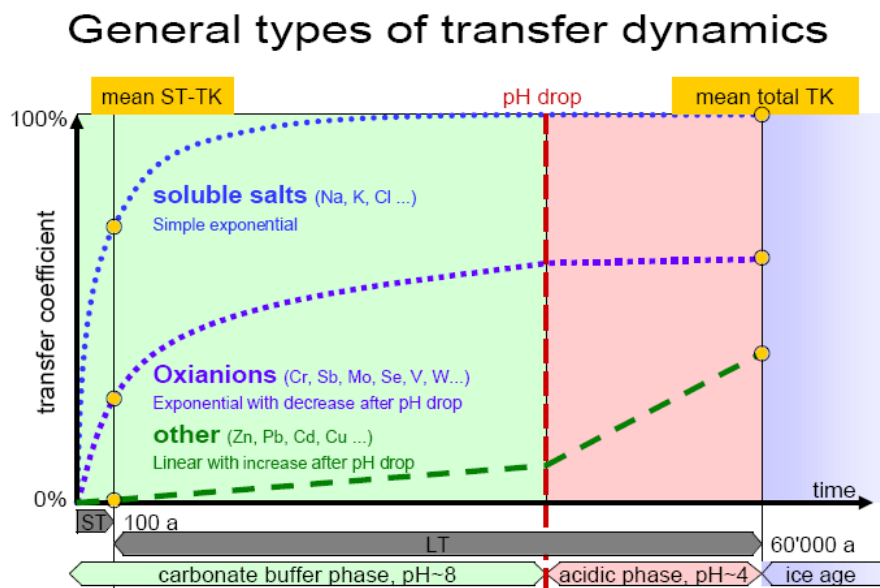


Figure 6 : Evolution of transfer coefficients (TK) used in SimaPro and proposed by Doka for different pollutant species. Transfer dynamics, Doka Life Cycle Assessment, Zurich, 2004

If the releasing of the element in the environment means that it has a greater “pollutant potential” (for instance it is more bioavailable, more mobile, etc) this model lets be assumed that most impacts generated by these species will appear in long time periods. In fact, only about 20% to 40% of the metals reach the groundwater directly through flow in continuous macro pores in the first decades (3-25 years). The remaining 60%-80% are retained more strongly by the soil matrix and their reach the water table in 400 to 3000 years for Cd^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+} and Cr^{3+} , while 5000 to 33 000 years are necessary for Pb^{2+} and Hg^{2+} . (Doka, 2007)

4.1 Basic ideas

To evaluate the environmental impact of the four metals it is not sufficient to determine their total content: their behaviour in a given soil fraction and their mobilisation capacity are both important (Alvarenga et al., 2007). Metal leaching and, more generally, emissions from soil are determined by the nature of the linkage between the metal ion and the soil form, the transformation that it can undergo and the evolution of the soil itself. In addition to physico-chemical factors, biology also plays a role in the soil metal dynamics. As stated by Gobat et al. (2003) microorganisms are key actors in:

- transformation of vegetable and animal debris

- oxidation, reduction, precipitation and dissolution of mineral ions
- fixation of molecular nitrogen
- control of bioelement cycles, in particular carbon, oxygen, iron nitrogen and sulphur cycles
- transformation of parent material

Abiotic and biotic processes in the soil are strictly linked. Microorganisms and vegetation influence the soil conditions, for example soil pH. The composition of litter depends on the type of vegetation that is present on the site (that depends on the climate, soil type, etc.). Soils are at the interface between atmosphere, biosphere, hydrosphere and lithosphere, which makes them difficult systems to describe. In the soil quasi-instantaneous processes, such as the capture of an iron atom by an organic molecule, coexist with much slower movements like progressive clay migration towards the deeper soil horizon and the consequent accumulation in horizon B (Gobat et al., 2003).

In the following description, focus will be on the lithosphere and its evolution, as well as on its interaction with the biosphere. The atmospheric and the hydrological aspects will be considered later, as “external” parameters in soil evolution.

4.2 Describing the soil which interacts with metals

First of all, a general description of the main constituents of the soil is presented, followed by the method used to analyse the metal bonds in the soils. As the metals can bind to several different soil components, the evolution of each will have consequences on the fate of the others. This fact will be at the base of the creation of a model to predict metal emission in time.

4.2.1 Mineral constituents

The soil minerals are primary, inherited directly from the parent rock or secondary, created by the chemical transformation and found in the weathering complex. This complex is composed by salts (e.g. calcium or magnesium carbonate) or silicates (e.g. micas and clays). Clays behave as colloids, as iron or aluminium hydroxides and other secondary minerals. If the weathering is “total”, it releases isolated ions but also micromolecules (Gobat et al., 2003). Physical disintegration and biogeochemical weathering produce a mix of constituents of very different size and mineralogy quality.

Climatic agents, such as wind, frost and water, break the rock down in smaller and smaller pieces. They physically degrade the soil but maintain the same chemical composition.

Biogeochemical weathering of rock involves water with oxygen, carbon dioxide or organic acids, and acts following five paths: hydration, dissolution, oxidation, reduction and hydrolysis.

Hydration first weathers the ferruginous rock, entering water molecules modifying the mineralogy, as for instance, hematite Fe_2O_3 hydrates to form goethite FeOOH .

Dissolution is present in alkaline environments, chelation and acid dissolution. An example of acid dissolution is the case of calcite, dissolved by carbonic acid H_2CO_3 .

Oxidation allows the liberation of Fe^{3+} from the Fe^{2+} present in the crystal lattice of some silicates.

Reduction dissolves Fe^{2+} from the oxides and hydroxides of Fe^{3+} found for example in cements of some sandstone. It takes place in poorly aerated environments.

Hydrolysis engenders important changes in crystal lattice. This process depends on the climatic conditions, and it increases with high temperature and humidity. It concerns practically all silicates and is often accelerated by microbial activity (Gobat et al., 2003).

4.2.2 Soil organic matter and organisms

Soil organic matter can be divided in two main groups: the first is inherited directly from the organic residues (litter) and the second are synthesised in the soil under humidification process. The first group is mainly composed of cellulose, lignin, proteins and lipids. In the second there are aromatic compounds with different levels of polycondensation, such as the highly stable macromolecules forming a part of humins. The limit between the two is difficult to locate, in particular for humins, which can be inherited from vegetable material or newly formed.

For these processes the time needed is extremely different. If on the one hand the exchangeable and the carbonate fraction can be degraded in relatively short time frames (less than 100 years), the complete (bio)degradation of organic matter is an extremely long process, which is influenced by “internal” (microbial activity) and “external” (atmospheric deposition) factors.

In the literature (Owen, 2001) half lives for fulvic acid and humic acids in an organic rich soil are estimate at 10-15 years and at more than 100 years respectively. Following Legros (2007) half lives of fulvic and humic acids are between 200 and 1000 years, while for formed humins it is more than 2000 years (if no changes in soil conditions and climate occur).

The organic matter in soils evolves with acidification, changes in hydrology and changing in land use (Salomons et al., 1995). These changes are reflected in higher dissolved organic matter content and increased leaching of dissolved organic matter to surface waters, which are positively correlated to the leachable amount of metal (Sauvé et al., 2000).

Although organic matter is able to retain chemicals in soils and sediments, its breakdown products are able to mobilise heavy metals and organic micro pollutants in particular (Salomons et al., 1995). This is due to the solubility of humic, but especially fulvic acids, which can chelate metals.

Metals can be bound or complexed with organic matter. It can thus immobilise metals in the solid phase or increase it, due to the presence of dissolved organic matter. In fact, dissolved organic matter has been shown to reduce metal sorption onto soil surfaces by competing for free metals and forming soluble organo-complexes or being preferentially sorbed onto surfaces instead of the metals it is competing with (Gray and McLaren, 2006)

Bacteria are an important organic component in structuring the soil. In fact, they synthesise some molecules, especially polysaccharides particularly resistant to enzymatic degradation, which contribute to the pool of organic matter in soils. The microbial humins (so these products are called) participate to the formation of microaggregates (Gobat et al., 2003).

The effects due to the soil microflora are mainly due to bacterial functions. They include mineralization of organic matter, oxidation of inorganic reduced molecules, anaerobic reduction of inorganic oxidised molecules, dissolving or precipitation of minerals, without forgetting the transformation for certain organic compounds to humins.

Soil fauna also plays an important role. For instance, macroarthropodes of temperate litter, termites in tropical soils, microarthropodes in peat lands, earthworm in mosts soils. Every one of these actors is involved with the transfer of matter and elements in the soil (Gobat et al., 2003).

The presence of vegetation cover and earthworms has a big impact on the macro-porosity of the soil upper layer (Hellweg et al., 2005). In addition, they play a key role in the bioturbation phenomenon, which allows the transfer of organic matter in the verticality of the soil.

4.2.3 Redox potential

Redox potential changes the valence of the metals. Under oxidising and slightly reducing conditions, the solubility of heavy metal cations decreases due to the precipitation of oxides, hydroxides or carbonate and only for neutral to mildly alkaline pH values, while lowering the redox potential has the effect to increase metal cation solubility (Legros, 2007). If reducing conditions are present (no oxygen available, long submersion time), leaching of metals is thus more important. In aquatic environments metal cations tend to desorb from solids as pH decreases. As pH increases, they adsorb or precipitate, but only up to a certain limit, after which they are again solubilised due to the negative charges present in the solution (Salomons, 1995).

Oxygen availability in soils determines the mobility of contaminants but also the presence or absence of iron and manganese(hydro)oxides. Redox potential variations change the valence of metals (Fe, Mn, As, etc.); under reducing conditions anions are more soluble, increased soluble concentrations of these metals have been observed in reducing environments such as ground waters and porewater of sediments. Indirectly, under reducing conditions sulphate reduction will take place and metal sulphides become a stable phase. Metal sulphides have an extremely low solubility and concentrations of metals in porewater of sediments (where the reducing conditions are normally found) are generally low. On the other hand, an increase in the redox potential induces metal sulphide to become unstable and thus dissolved concentration of the metal will increase. This abrupt change happens for instance when polluted (anoxic) sediments are exposed to oxidising conditions. The speciation of iron can be an important parameter. In fact, with the presence of sulphide (estuarine and marine environments), the iron hydroxides become unstable and are converted to iron oxides, which have a lower adsorbing capacity and the net result is a loss of adsorbing capacity from the system (Salomons et al., 1995).

Inundation and acidification also causes hydroxides to become unstable, when these phenomena occur the metals associated with iron and manganese hydroxides are mobilised (Salomons et al., 1995).

4.2.4 pH

Parallel to redox conditions, pH has to be considered. The retention strength of the ionic fixation depends on the nature of the element: atomic radius, valence (monovalent atoms are less retained than bivalent ones), hydration degree and pH are the determining factors (Gobat et al., 2003). The metal species that can exist in an environment are basically determined by these two factors, and shown in Eh-pH diagrams (figure 7) (Salomons et al., 1995). When pH drops (i.e. at the end of the carbonate phase), the metal cation concentration in leachate increases, while the metal oxyanions decrease as they are less soluble at low pH.

If pH drops (acidification) the release of heavy metals will occur more quickly. In actual cases, pH drops when the acidity neutralisation capacity (due especially to carbonates and organic matter) of the soil is consumed, this means that organic matter has been practically totally degraded (Legros, 2007). Oxyanions behave oppositely: they tend to adsorb and/or precipitate more as pH decreases (Salomons, 1995).

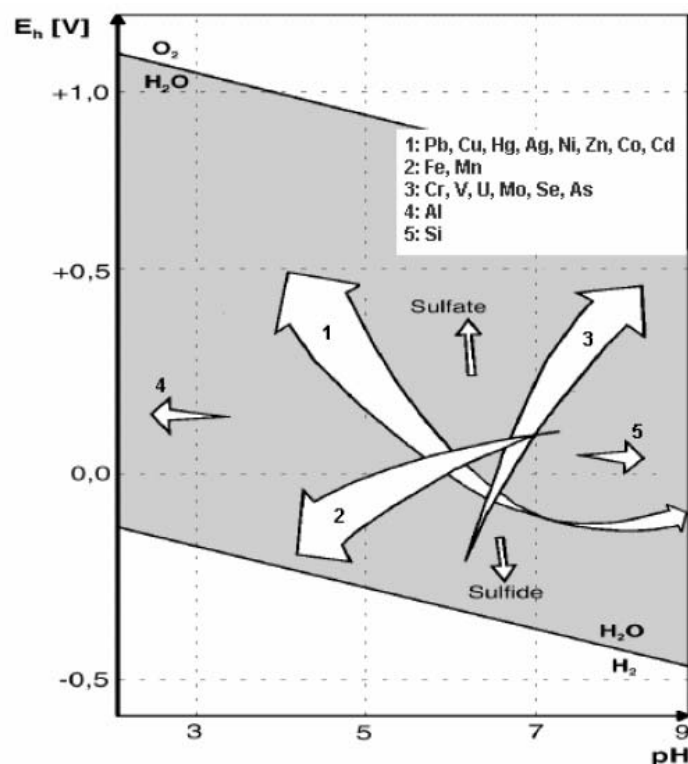


Figure 7 : Diagram of pH versus redox potential Eh and relative metal mobility. Arrows indicate direction of increasing relative mobility for the corresponding metals. (Doka, 2003, adapted from Förstner et al. 1989)

The retention strength of the ionic fixation depends on the nature of the element: atomic radius, valence (monovalent atoms are less retained than bivalent ones), hydration degree and pH are the determining factors (Gobat et al., 2003). For a given pH, small radius and hydration degree and high valence are the conditions to assure a stronger bond.

4.2.5 Climate

Climate (wind, rainfall, solar irradiation) plays a fundamental role in organic matter degradation, especially through the oxidation of organic matter. Higher temperatures and longer dry periods dramatically increase this phenomenon. Metals bound to iron and manganese oxides and organic matter, present stronger bonds than organic matter chelating metals. The degradation of organic matter destroys their bonds with the metals, increasing their release. Rainfalls have to be considered from two points of view: the hydrological one, which means the amount, length and frequency of rainfalls during the year, and the chemical one, which considers the composition of the water (for example, acid rains).

Temperature influences the weathering of the soil. With an increase of 10 celsius degrees, the rate of chemical reaction is expected to increase with a factor of two (Legros, 2007).

Seasonal contrasts in climatological conditions act on biological activity: organic matter is more easily mineralised. For example, there is less peat in the Alps than in the Massif Central due to the more contrasted climate in the Alps (Legros, 2007). Aridity helps speed organic matter degradation via oxidation, which brings to an increased sensitivity to erosion.

4.3 Modelling evolution emission of metals from soils

For long term predictions it is therefore not only necessary to consider variables like pH, competing ions, dissolved organic matter etc. that determine the initial adsorption, but even more so to consider the stability of the adsorbing phases which compose the soil.

Various chemical extraction procedures provide information about the reactivity of different metal pools in the soil (Pickering, 1981). Each pool thus has a different behaviour depending on chemical and physical parameters linked to the condition of the soil at a specific moment. Sequential extraction analyses give the partitioning of a specific metal among the soil; five fractions are defined by Tessier et al. (1979): exchangeable, bound to carbonates, bound to Mn/Fe oxides, bound to organic matter and residual.

Exchangeable and carbonate bound fractions are the most sensitive to natural degradation, and the metals bound to them are the most mobile. Once these fractions are not present in the soil anymore, metals that were bound to organic matter will be more and more present in the leachate, because of the degradation of the organic fraction of soil. This phenomenon is followed by the alteration of mineral oxides that consequently can liberate the metals bound to them. Iron and manganese oxides are important sorbents of trace metals (Sauvé et al., 2000). Both organic matter and oxide degradation strictly depend on external factors, such as temperature, annual rainfall amount and intensity, length of dry periods, etcetera. The residual fraction is also supposed to be released or degraded, for extremely long time periods. In this case, it is supposed to occur only after 60 000 years for cold regions subjected to the glacier expansion in the next ice age.

In general, with exception of selenium and molybdenum, metals are more soluble in soils at low pH due to the dissolution of carbonates, phosphates and other solid phases (Adriano, 2001). In the dynamics of metal leaching, pH is the most influencing factor (Sauvé, 2001). At low pH the sorption bonds of metals to adsorption sites on mineral surfaces is weakened and cation exchange capacity of organic matter is lower (Adriano, 2001).

The acid neutralisation capacity (ANC) of a soil is important to assess the sensitivity of the material to external influences, and crucial to address long term impact and stability of the components of a soil (Van der Sloot, 2001). With time, progressive acidification happens to most soils in humid and draining situations (Legros, 2007). This is due to the protons produced by organic matter and to the dissociation in the water of CO₂ of the soil. Minerals are destroyed and their bases are leached and drained. Van Breemen et al. (1983) defined acidification as following:

$$\text{ANC} = 6 [\text{Al}_2\text{O}_3] + 2 [\text{CaO}] + 2 [\text{MgO}] + 2 [\text{K}_2\text{O}] + 2 [\text{Na}_2\text{O}] \\ + 2 [\text{MnO}] + 2 [\text{FeO}] - 2 [\text{SO}_3] - 2 [\text{P}_2\text{O}_5] - [\text{HCl}]$$

[] represent concentration in mol.m⁻³.

Gobat et al. (2003) describe the buffering capacity of the soils, and the responsible species, depending on the pH. The summary is presented in table 5.

Table 5 : Soil buffering capacity (Gobat et al., 2003)

Soil mineral buffering specie	pH range of buffering capacity of the specie
Carbonates	8.6 – 6.2
Silicates	6.2 – 5.0
Clays	5 – 4.2
Aluminium hydroxides	4.2 – 2.8
Iron hydroxides	< 3.2

Under humid conditions soils have a natural tendency to lose their cations and thus acidify. For municipal solid waste incineration slag the dominant loss of acid neutralising capacity is not due to protons of acid rain or acid producing internal reaction, but from the wash-out of buffering

carbonate minerals. Thermodynamic calculations mentioned in the article by Doka (d) 2007) indicate that for a normal soil under a CO₂ partial pressure of 10⁻² atm (10 000 ppm) the carbonate washout and the carbonate buffer phase ends after 17'000 years. A study conducted on Hawaii Islands by Chadwick and Chorover (2001) show the decreasing curve of neutralisation capacity on the same basalt rock (average temperature 16°, annual rainfall 2500 mm). It reaches zero after about 10 000 years, but already after 1000 years it is under 100 mol/m³

The model elaborated in this study is based on four time frames of different lengths:

- The first period, during which the easily mobile metals are leached out of the soil basically due to convection movement, and the carbonates are dissolved in the water passing through the system. This leaching is very important especially for “young” pollution, which has not had the time to fix to the soil and thus is more mobile. This period ends with a pH value around 6 (see table 5). Heavy metals like Cd, Zn, Pb Cu are washed out 3 to 5 times faster after the carbonate buffer phase, due to the lowering of the pH.
- The second phase concerns organic matter, which is degraded by the decreasing pH which attacks the stable bonds. Vegetation cover and “external” factors, such as rains and climate, play an important role in the destabilisation of organic matter.
- The third phase sees (hydro)oxides as main actors. The pH has lowered, microbial activity is reduced and organic matter is no longer present. Physical disintegration and biogeochemical weathering have a stronger impact, as the soil is “naked”.
- The fourth and last period concerns the fraction of the soil where the metals are more strongly bound. The residual fraction contains the metals that are more strongly bound to the soil matrix, which normally correspond to clays, stabilised materials and rocks containing trace metals. The metal residual fraction is extremely stable in the soil. It corresponds to metals absorbed in clays or in minerals structure and it is very slightly sensitive to weathering (Legros, 2007). For the Swiss case, the metals are supposed to be emitted in the next ice age as hypothesised by Doka (a) 2003) and confirmed by the pedologic observation of Legros (2007). For the zones of Europe which are not supposed to be on glacier pathways, further studies have to be done, to evaluate the kind of soil that could be present following local data.

The length of each period varies importantly, depending on the leading factors, which characterise the leaching, and therefore stem from the location and situation of the site.

For the total degradation of organic matter and iron and manganese oxides practically no data from the literature are available. Most soils rich in organic matter have low pH and are prone to reduction when moisture increases. Present oxides are easily depleted by reductive dissolution enhanced by the presence of the high dissolved organic carbon concentration (Salomons, 1995).

As first assumption the length of this period is thus (roughly) approximate: after 10 000 years these two species are supposed to have completely degraded. In nature reality, these phenomena co-exist and take place at the same time, but with different rates.

After 60 000 years the whole soil is supposed to be degraded: 100 % of the metals have been liberated at that time.

Linear trends are hypothesised within the different phases. Figure 8 illustrates the trend that would have a specific metal emission from a soil during long term periods.

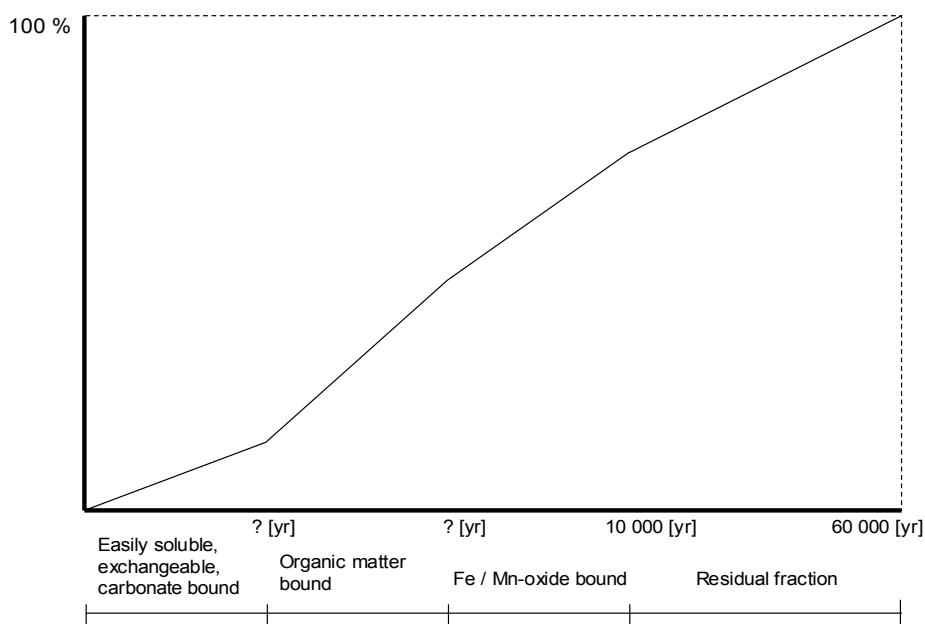


Figure 8 : General trend of metal emission from a soil during long term period

The shape of the curve varies depending on the soil conditions, as explained in the previous paragraphs and on local conditions. Depending on the nature of the metal and on its relative concentration, heavy metal cation solubility can vary from being entirely controlled by its direct interaction with an inorganic surface (cation-like) to being completely subjected to the sorption and solubility pattern of the organic matter (anion-like) (Salomons, 1995). The slopes of the segments would vary depending on the specific case.

Variation of soil pH and redox potential under natural conditions is due to several processes that can vary during time. pH is defined by the proton balance of the aquatic or terrestrial ecosystem. Atmospheric deposition and oxidation reactions (such as nitrification, sulphide oxidation, ferrous iron oxidation) supply protons, while weathering of carbonate and silicates minerals, the ion exchange and the reduction reactions (e.g. denitrification, sulphate reduction, iron oxide reduction) consume them. Redox conditions are influenced by the hydrology (flooding, rising water table), soil compaction (deterioration of the soil structure), excess of organic matter, increased biological activity due to the increased nutrient supply or temperature. Under natural conditions, most European soils present pH between about 4.5 and 8 (Legros, 2007).

To estimate the evolution of the four metals in time, it is fundamental to have an approximation of their distribution among the soil fractions.

In addition, it has to be considered that there is a fraction of the metal that will be leached very easily by rainfall in the “young” period of the pollution. This amount depends on the type of pollution and its application on the site, in addition to the rain characteristics (intensity, length, frequency).

5 CONCLUSIONS

As a conclusion, it is interesting to notice that current models in LCA are mainly based on rough assumptions such as a behaviour of metals in soils at 100 years or 60 000 years, and therefore it is not easily adaptable for assessing the transfer for soil to water. AT the same time, models comparing the mobility of Cd, Cu, Pb and Zn are coherent, highlighting the high mobility of Cadmium and Zinc afterward, while Cu and Pb appears to be more sensitive to the media conditions. Four key parameters are identified such as fraction of metals in soil, fraction of organic matter, Redox-potential and pH. The question of the most adapted way to consider and quantify the impact of emitted heavy metals on a long term period in LCA has to be addressed considering these parameters. Nevertheless, at this time we can only consider a general tendency and a relative impact of the different metals for cations. It is not easy to calculate which fraction of each metal will be released at 100 years and 1000 years. In spite of these limitations, it is possible to have an idea of the faction transferred of the cations that are commonly tested in ecotoxicology, such as copper, cadmium, etc. Models (such as the Free Ion Activity Models) can be used and eventually associated with a Biotic Ligand Model. This issue is even more complicated with anions since it is not feasible at this time to model the mobility and the effect of these metals and metalloids. It was not so problematic because considering the Ronde Venen case study; it was possible to focus on the 4 cations cited above. Nevertheless, anions are among the most impactant substances in LCA and it will be necessary to consider cases studies involving anions in further researches.

6 REFERENCES

- Bare, J. C., Norris, G. A., Pennington, D. W., & McKone, T. (2003). The Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts. *Journal of Industrial Ecology*, 6(3-4), 49-78.
- Bare, J. C., P. Hofstetter, et al. (2000). "Midpoints versus Endpoints: The Sacrifices and Benefits." *International Journal of LCA* 6(5): 319-326.
- Bayer, P., & Finkel, M. (2006). Life cycle assessment of active and passive groundwater remediation technologies. *Journal of Contaminant Hydrology*, 83(3-4), 171-199.
- Beinat, E., van Drunen, M. A., Nijboer, M. H., Koolenbrander, J. G. M., Okx, J. P., & Schütte, A. R. (1997). *REC: A Methodology for Comparing Soil Remediation Alternatives on the Basis of Risk Reduction, Environmental Merit and Costs* (No. NOBIS Report 95-10-3). Gouda NL.
- Benetto, E., Tiruta-Bama, L., & Perrodin, Y. (2007). Combining lifecycle and risk assessments of mineral waste reuse scenarios for decision making support. *Environmental Impact Assessment Review*, 27(3), 266-285.
- Blanc, A., Metivier-Pignon, H., Gourdon, R., & Rousseaux, P. (2004). Life cycle assessment as a tool for controlling the development of technical activities: Application to the remediation of a site contaminated by sulfur. *Advances in Environmental Research*, 8(3-4), 613-627.
- Cadotte, M., Deschenes, L., & Samson, R. (2007). Selection of a remediation scenario for a diesel-contaminated site using LCA. *International Journal of Life Cycle Assessment*, 12(4), 239-251.
- Carpenter, A. C., Gardner, K. H., Fopiano, J., Benson, C. H., & Edil, T. B. (2007). Life cycle based risk assessment of recycled materials in roadway construction. *Waste Management*, 27(10), 1458-1464.
- Cowell, S. J., Fairman, R., & Lofstedt, R. E. (2002). Use of risk assessment and life cycle assessment in decision making: A common policy research agenda. *Risk Analysis*, 22(5), 879-894.
- Diamond, M. L., Page, C. A., Campbell, M., McKenna, S., & Lall, R. (1999). Life-Cycle Framework for Assessment of Site Remediation Options: Method and Generic Survey. *Environmental Toxicology and Chemistry*, 18(4), 788-800.
- Ditor, M., (2006). "Integration of ecological risk assessment within life cycle impact assessment, used for the evaluation of remediation options of contaminated sediments". PhD thesis proposal. École Polytechnique de Montréal. 2008.
- Flemström, K., Carlson, R., & Erixon, M. (2004). Relationships between Life Cycle Assessment and Risk Assessment—Potentials and Obstacles. Naturvardsverket, 071-SNV Rapport 5379. Stockholm, Sweden: Swedish Environmental Protection Agency.
- Godin, J., Ménard, J.-F., Hains, S., Deschênes, L., & Samson, R. (2004). Combined Use of Life Cycle Assessment and Groundwater Transport Modeling to Support Contaminated Site Management. *Human and Ecological Risk Assessment*, 10(6), 1099-1116.
- Harbottle, M. J., Al-Tabbaa, A., & Evans, C. W. (2007). A comparison of the technical sustainability of in situ stabilisation/solidification with disposal to landfill. *Journal of Hazardous Materials*, 141(2), 430-440.
- Harbottle, M. J., Al-Tabbaa, A., & Evans, C. W. (2008). Sustainability of land remediation. Part 1: overall analysis. *Proceedings of the Institution of Civil Engineers-Geotechnical Engineering*, 161(2), 75-92.

- Hauschild, M., & Wenzel, H. (1998). *Environmental Assessment of Products- Volume 2: Scientific Background* (1 ed. Vol. 2): Chapman & Hall.
- Heijungs, R., J. B. Guinée, et al. (1992). *Environmental Life Cycle Assessment of Products. Guidelines and Backgrounds*. Leiden, The Netherlands, Centre of Environmental Sciences: 130.
- Huijbregts MAJ, Lundi S, McKone TE, and van de Meent D. 2003. Geographical scenario uncertainty in generic fate and exposure factors of toxic pollutants for life-cycle impact assessment. *Chemosphere* 51:501-508
- Huijbregts, M. A. J., U. Thissen, et al. (2000). "Priority assessment of toxic substances in life cycle assessment. Part I: Calculation of toxicity potentials for 181 substances with the nested multi-media fate, exposure and effects model USES-LCA." *Chemosphere* 41: 541-573.
- Jolliet, O., M. Margni, et al. (2003). "IMPACT 2002+: A New Life Cycle Impact Assessment Methodology." *International Journal of LCA* 8(6): 324-330.
- Jolliet, O., M. Saade, et al. (2004). *Analyse du cycle de vie - Des bases à la mise en oeuvre*. Lausanne, PPUR- In Press.
- Jolliet, O., R. Mueller-wenk, et al. (2004). "The LCIA Midpoint-damage Framework of the UNEP/SETAC Life Cycle Initiative." *International Journal of LCA* 9(6): 394-404.
- Lesage, P., Ekvall, T., Deschenes, L., & Samson, R. (2007). Environmental assessment of Brownfield rehabilitation using two different life cycle inventory models. *International Journal of Life Cycle Assessment*, 12(6), 391-398.
- MacLeod M, Woodfine DG, Mackay D, McKone T, Bennett D, Maddalena R. 2001. BETR North America: A regionally segmented multimedia contaminant fate model for North America. *Env Sci Poll Res* 8(3):156-163
- Page, C. A., Diamond, M. L., Campbell, M., & McKenna, S. (1999). Life Cycle Framework for Assessment of Site Remediation Options: Case Study. *Environmental Toxicology and Chemistry*, 18(4), 801-810.
- Payet J, and Jolliet O. 2005. Comparative assessment of the toxic impact of metals on aquatic ecosystems: The AMI method. In: Dubreuil A (Ed) *Life Cycle Assessment of Metals: Issues and Research Directions*. SETAC, Pensacola, FL, USA
- Payet, J. (2004). *Assessing Toxic Impacts on Aquatic Ecosystems in Life Cycle Assessment (LCA)*. École Polytechnique Fédérale de Lausanne, Lausanne.
- Pennington DW, Potting J, Finnveden G, Lindeijer E, Jolliet O, Rydberg T, and Rebitzer G. 2004. Life cycle assessment. Part 2: Current impact assessment practice. *Env Int* 30:721-739
- Pennington, D. W., Margni, M., Payet, J., & Jolliet, O. (2006). Risk and regulatory hazard-based toxicological effect indicators in life-cycle assessment (LCA). *Human and Ecological Risk Assessment*, 12(3), 450-475.
- Posthuma L, Suter GW II, and Traas TP. 2002. *Species Sensitivity Distributions in Ecotoxicology*. Lewis Publishers, Boca Raton, FL, USA
- Potting J. 2000. *Spatial Differentiation in Life Cycle Impact Assessment. A Framework, and Site-dependent Factors to Assess Acidification and Human Exposure*. PhD-thesis Universiteit Utrecht
- Russell, A. J. (2006). Human and ecological risk assessment and life cycle assessment: Intersections, collisions, and future directions. *Human and Ecological Risk Assessment*, 12(3), 427-430.
- Saouter, E., Hoof, G. v., Feijtel, T. C. J., & Owens, J. W. (2002). The Effect of Compact Formulations on the Environmental Profile of Northern European Granular Laundry Detergents, Part II: Life Cycle Assessment. *International Journal of Life Cycle Assessment*, 7(1), 27-38.
- Socolof, M. L., & Geibig, J. R. (2006). Evaluating human and ecological impacts of a product life cycle: The complementary roles of life-cycle assessment and risk assessment. *Human and Ecological Risk Assessment*, 12(3), 510-527.

- Sonnemann, G., Castells, F., & Schuhmacher, M. (2003). *Integrated life-cycle and risk assessment for industrial processes*. Washington DC: Lewis Publishers.
- Suèr, P., Nilsson-Paledal, S., & Norrman, J. (2004). LCA for Site Remediation: A Literature Review. *Soil & Sediment Contamination*, 13, 415.
- Toffoletto, L., Deschênes, L., & Samson, R. (2005). LCA of Ex-Situ Bioremediation of Diesel-Contaminated Soil. *International Journal of Life Cycle Assessment*, 10(6), 406-416.
- Udo de Haes, H. A., G. Finnveden, et al. (2003). *Life-Cycle Impact Assessment: Striving Towards Best Practice*, SETAC PRESS.
- Udo de Haes, H. A., Sleeswijk, A. W., & Heijungs, R. (2006). Similarities, differences and synergisms between HERA and LCA - An analysis at three levels. *Human and Ecological Risk Assessment*, 12(3), 431-449.
- USEPA (Environmental Protection Agency). (1998). *Guidelines for Ecotoxicological Risk Assessment*. EPA/630/R-95/002F. Washington: Office of Solid Waste, US EPA.
- Vignes, R. (2001, février 2001). Use of Limited Life-Cycle Analysis for Environmental Decision-Making, 40-54.
- Volkwein, S., Hurtig, H.-W., & Klöpffer, W. (1999). Life Cycle Assessment of Contaminated Sites Remediation. *International Journal of Life Cycle Assessment*, 4(5), 263-274.
- Wenzel, H., M. Hauschild, et al. (1998). *Environmental Assessment of Products, Volume 1: Methodology, Tools and Case Studies in Product Development*. Boston, Kluwer academic publisher.
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