Lechner P. (Hrsg.): Waste matters. Integrating views. 2nd BOKU Waste Conference 2007, 16. - 19. April 2007, Wien. Proceedings; Facultas Verlags- und Buchhandels AG, ISBN 978-3-7089-0060-5

An Approach to Determine Long-Term Emissions of Metals from Landfills with Specific Consideration to Waste Pretreatment and Landfill Processes

E. den Boer[a] and J. den Boer[b]
[a] *Den Boer Waste Consulting, Darmstadt, Germany;*
[b] *Darmstadt University of Technology*

Abstract
The present paper focuses on investigations performed to assess the time-dependent leachability of heavy metals from landfills. Emission of heavy metals from landfills represent the main contributors to the potential human toxicity impact of a waste management system (WMS), a crucial impact category within an LCA. Using selected results the impact of waste pretreatment on the mobility of heavy metals is demonstrated here. Results obtained following several years of investigations into the behavior of raw and pretreated waste in landfill simulating lysimeters are also evaluated here, providing significant progress into understanding the mobility of pollutants from various waste types under landfill conditions. The pretreatment options considered are aerobic mechanical-biological pretreatment (MBP) and incineration of residual waste. The investigated metals include Cd, Cu, Cr, Fe, Mn, Ni, Pb and Zn.

1 Introduction
Due to their elevated contents of heavy metals, wastes constitute a significant source of environmental pollution. Moreover, as heavy metals are not degradable and disperse very slowly into the ground, they accumulate in a landfill and continue to pollute the underlying soil and groundwater over exceedingly long periods. In natural environments metals can be immobilized by electrostatic forces, by adsorption and sorption in minerals e.g. carbonates, Mn-Fe oxy-hydroxides, silicates and by binding to organic matter. Chemical forms of heavy metals in solid waste differ to some extent from those found in natural environments. In solid waste heavy metals may be present either in their elementary form or embodied in materials such as additives, e.g. in plastics, glass and paper (Prudent et al. 1996). Before metals can be emitted in the leachate they must be released from their solid waste matrix into the percolating water. In the case of metallic materials, the release process is corrosion. In case of additives release may occur through decomposition of the solid matrix or through diffusion in and from the

solid matrix.

Once released into the water, the metals may be precipitated or sorbed to the solid phase by similar mechanisms to those occurring in natural environments. The stability of metals varies according to modifications in environmental conditions, thus determining the actual leaching rates. Municipal waste is a very heterogeneous material, thus it is very difficult to predict and model changes of its composition both within treatment processes and during final disposal. Additionally, waste treatment and landfilling in its current form have been practiced only over the last decades. Accordingly, no long-term observations of waste behavior in landfills are available as yet. Indeed, to date the majority of estimations of long-term leaching rates have been based on extrapolation of short-term leaching observations, not taking into account future changes in a landfill environment. In this paper an alternative approach is presented, in which long-term changes in landfill environment are accounted for.

2 Material and methods

2.1 Types of waste investigated

This paper presents the results of investigations performed to determine forms of binding of heavy metals in non-pretreated (raw) and pretreated residual waste, and respective degrees of leachability. For this purpose raw waste, mechanically-biologically pretreated waste (MBP waste) and thermally pretreated waste (incineration slag) were analyzed. All waste samples originated from Germany.

To determine the impact of storage under landfill conditions input and output samples from landfill simulating lysimeters as well as leachate thereof were analyzed. A series of continuous lysimeter experiments has been conducted since 1996 at the Technische Universität Darmstadt. The lysimeters used in the investigations varied in terms of their size (80 l, 300 l and 2000 l) and the simulated environmental conditions. They were equipped with a watering system allowing an even water distribution on the surface of waste body. Since it is difficult to obtain realistic temperatures in the relatively small volume containers, the lysimeters were placed in climate chambers with constant temperatures (18°C, 30°C and 40°C). The formation of water and gas releases from different kinds of pretreated waste has been investigated. The investigated wastes included raw waste, MBP waste and incineration slag. As the biological activity in the lysimeters containing waste from two mechanical-biological pretreatment plants (MBP1 and MBP2) significantly declined, it was decided to finalize these experiments. The lysimeters were re-opened and the waste output analyzed. In view of the fact that experiments with raw waste and incineration slag are on-going, only leaching data obtained for these types of wastes could be used for the purpose of the present study.

2.2 Methods for analysis and assessment of leachability of metals from waste

The long-term leachability of metals may vary according to both the form in which they occur in waste and conditions in the waste body, such as pH and redox potential as well as the presence of sorbents. The initial landfill phase is likely characterized by the most rapid chemical reactions. As an anaerobic methane phase is achieved biological activity gradually declines. In this study it is assumed that landfill remains in anaerobic conditions for the first 100 years. Within this period organic degradation is very slow and no other significant changes occur. Hence the data on metals leaching from lysimeter can be used to estimate metal leaching behavior within the first hundred years of landfilling. After this period it is assumed that due to gradual failure of the performance of landfill barriers (Witt and Zeh 2005), oxygen starts to penetrate into the waste body and the humic phase develops. Re-establishment of aerobic conditions results in an increased rate of metal leaching (Caille et al. 2003, Prantl et al. 2004). During oxidation metals can be first released, as a result of oxidation of sulphides, organic matter and other reduced species. An additional long-term process enhancing metal leachability is acidification of the environment. This may occur due to both acid producing reactions taking place within the waste body and infiltration of rain water. Thus, as opposed to the long-term metal leaching estimations based on extrapolations of emissions occurring within the observable time span, in this study an alternative approach is selected in which long-term changes in waste body are simulated and their effect on metal leachability assessed. The long-term developments considered here are decomposition of organic matter, oxidation of sulphides and loss of waste pH buffering capacity resulting in a pH drop in the long-term.

The forms of chemical binding of metals in waste can be determined by means of speciation analysis. By determining the proportion of metals bound to organics and sulphides and the rate of depletion of these species it is possible to estimate the time-related metal leaching rates. In the present study a 3-step sequential speciation method of the Community Bureau of Reference (BCR, modified) (Rauret et al. 2001) has been used. This method allows differentiation of 4 metals fractions: exchangeable (soluble species, bound to carbonates and cation exchange sites), reducible (bound to iron and manganese oxy-hydroxides), oxidizable (bound to organic matter and sulphides) and residual.

Leachability of metals at different pH conditions was also investigated and the acidity producing processes occurring in waste were quantified. These included time-related organic decomposition and sulphide oxidation as well as acidity due to infiltration of rain water. The latter is determined based on a long-term liquid/solid (L/S) ratio in a landfill, obtained from the LCA-IWM Landfill model (den Boer et al. 2005).

3 Results

3.1 Heavy metal speciation in waste

Results of metal speciation analyses performed on raw wastes are presented in Figure 1. It can be seen that different metals display different binding mecha-

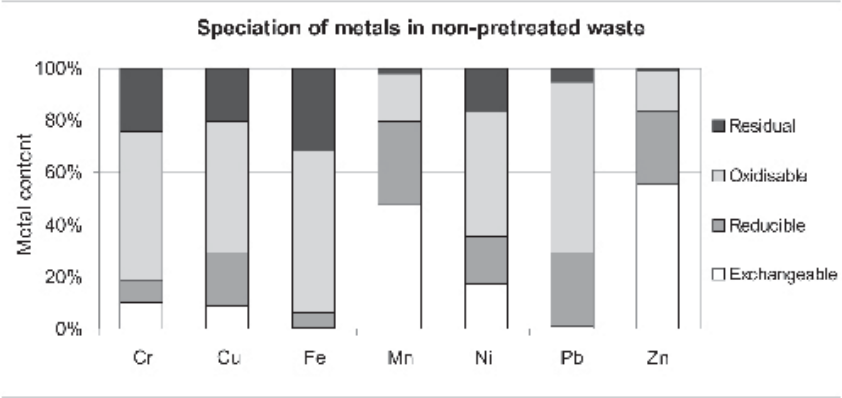


Fig. 1: Average metal speciation in raw waste, based on den Boer (2007)

nisms, but as a general rule the oxidizable fraction (organic matter and sulphides) binds the highest proportion of metals. These metals can be released under oxidizing conditions, e.g. in an aerobic MBP process where aeration takes place. A significant proportion of metals occurs in the reducible fraction i.e. as sorbed at oxy-hydroxides of iron and manganese. These metals can potentially be released in a reducing environment, e.g. in a landfill anaerobic stage. Some metals, Zn and Mn for example, are characterized by a high content in the exchangeable fraction, meaning that they are unstable under acidic conditions. The remaining metals bound in the residual fraction are considered the least mobile.

3.2 Impact of waste pretreatment on heavy metal speciation

Figure 2 shows the impact of aerobic MBP on metal speciation. The results for Cu, Fe and Zn were selected to demonstrate general trends of changes. These metals are at times characterized by different speciation patterns in raw waste. Reports present in literature illustrate how Cu shows very high affinity to the oxidizable fraction (oxides and sulphides) (Szpadt 1999, Sidełko 2004). Zn, similarly to Mn, occurs in a relatively high proportion in the exchangeable fraction. Finally, the speciation of Fe shows similar trends to the speciation of Cr, Pb and Ni. Furthermore, it is of particular importance to understand the behavior of Fe during treatment and disposal processes due to the fact that oxy-hydroxides of Fe provide significant sorption capacity for other metals. The main effects observed for aerobic MBP are a decrease of metals bound in the exchangeable fraction and an increase in the reducible metal fraction (oxy-hydroxides). The latter change was to be expected due to aeration occurring within the considered process. For several metals, e.g. Cu, an increase in the oxidizable fraction (organics and sulphides) was demonstrated, although the total volume of the organics decreased within the MBP process. Metal concentrations in the process leachate were also deter-

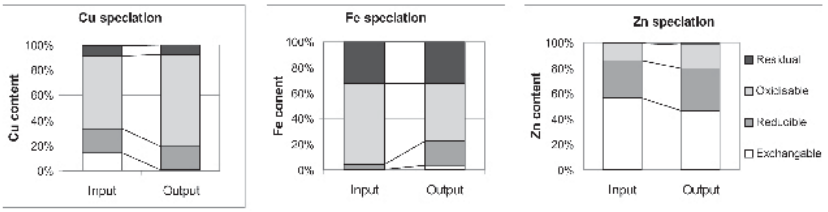


Fig. 2: Impact of MBP on heavy metal speciation (den Boer 2007)

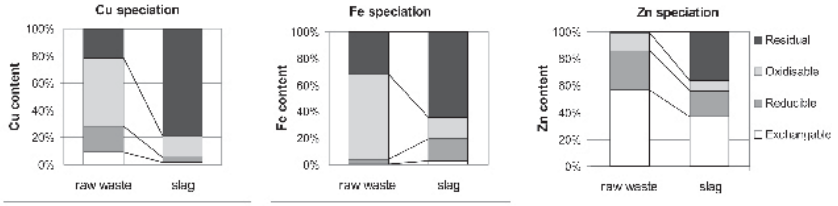


Fig. 3: Impact of thermal pretreatment on metal speciation (den Boer 2007)

mined. After leachate recirculation, final emission rates for all investigated metals were significantly lower than 1% of their respective total contents in waste.

The potential consequences of aerobic MBP on the mobility of metals under landfill conditions are presented in the following. Due to a decreased content of metals in the exchangeable fraction a higher stability is achieved. On the other hand, an increased content of metals in oxy-hydroxides may imply enhanced mobilization of metals under anaerobic landfill conditions.

The impact of thermal pretreatment on speciation of selected metals is demonstrated in Figure 3. The main effect of thermal pretreatment is represented by an increase of metal content in the residual fraction. This is compensated by a lower content of metals in the exchangeable and in the oxidizable fraction (organic and sulphides). The latter however remains relatively high, likely implying an incomplete combustion. As was to be expected a slight increase in metals bound in the reducible (oxy-hydroxides) fraction was observed. Thermal pretreatment generally enhances metal binding in the solid matrix, an extremely positive effect in terms of reduced emissions from the incineration slag.

3.3 Impact of the storage under landfill conditions on metals speciation

The lysimeter output samples were only available for MBP waste. Experiments performed using non-pretreated waste and incineration slag are still running.

Tab. 1: Progress of organic decomposition after more than 8 years storage in landfill simulating conditions (den Boer 2007)

Sample	**Organic dry mass content [% d.m.]**	**Mass reduction within storage [% d.m.]**
Input MBP1 waste	21.2[1]	-
Output MBP1 waste, lysimeter 30°C	18.2	3.6
Input MBP2 waste	37.7[1]	-
Output MBP2 waste, lysimeter 40°C	30.5	10.3

[1] Dach 1998

Lysimeters containing MBP waste were opened in February 2005, after more than 8 years of storage. Lysimeters containing the MBP1 waste revealed a very densely compacted waste in which water had gathered on the surface and was not able to percolate into the waste body. The waste itself was very dark, almost black in color. The waste was sieved and fraction <10mm was subjected to further analysis.

The MBP2 waste was less densely compacted than the MBP1 waste and as a result it was also significantly drier. The color of the output waste was brown-grey. In Table 1 indicators of the decomposition of organic matter during storage under landfill simulating conditions of MBP1 waste and MBP2 waste are summarized. Generally, the MBP1 waste was characterized by a much lower organic content than MBP2 waste. The decomposition of organic matter in the MBP1 waste was quite low compared to MBP2.

Impact of storage under anaerobic landfill conditions on speciation of selected metals in MBP waste is presented in Figure 4. As a general trend it can be concluded that during the storage of waste under anaerobic landfill conditions the expected release of metals from oxy-hydroxides took place only to a limited extent. The oxy-hydroxides of Mn proved to be less stable under simulated landfill conditions than the oxy-hydroxides of Fe. The literature reports how reduction of Mn^{4+} occurs at a relatively high redox potential (Eh: 100 ÷ 300 mV), while for the reduction of Fe^{3+} a significantly lower redox potential is needed (Eh: -100 ÷ 100

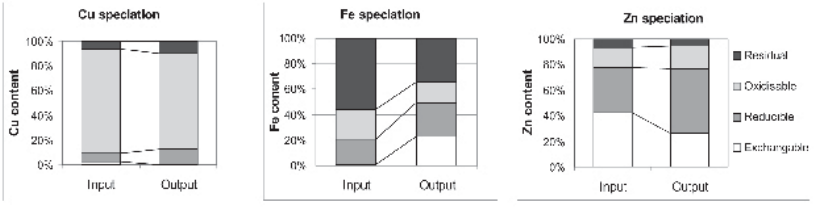


Fig. 4: Impact of storage under landfill conditions on metal speciation (den Boer 2007)

mV) (Flyhammar 1997). Relatively high redox potentials in lysimeters containing MBP waste, as opposed to those containing raw waste, were confirmed by monitoring of the Eh value during the experiment.

Additionally, low leaching of metals from lysimeters containing MBP waste indicates that if metals are released from one fraction, they are immediately immobilized in the others. Particularly in this case, the oxidizable fraction (organic matter & sulphides) and the exchangeable fraction seem to act as important metal sinks. Taking into account the final metal speciation obtained in wastes following storage under anaerobic landfill conditions, it can be concluded that in the landfill humic phase the rate of metal leaching will be governed by the gradual depletion of sorption capacity of the organic matter and sulphides (due to their oxidation). Additionally, pH reduction in waste due to these processes and infiltration of rain water may influence metal mobilization rates.

3.4 Estimation of time dependant metal emissions from landfilled waste

3.4.1 Short-term emissions

Data obtained with regard to emissions from lysimeters can be applied to predict the short-term (first 100 years) emission of heavy metals from wastes under landfill conditions. It is assumed that in the first 100 years anaerobic conditions are maintained in a landfill body and infiltration of rain water is very low due to a properly functioning landfill cover. Estimated metal leaching rates were extrapolated from lysimeter experiments by relating the L/S ratio in a lysimeter to the expected L/S ratio under real landfill conditions. The L/S ratio within 100 years storage is assumed to be app. 1.3 l/kg. In lysimeters L/S ratios from 0.15 for MBP1 waste to 0.96 for the MBP2 waste were achieved during the experiment. The 100 year leaching rates related to the total metal content for all types of waste are summarized in Table 2. The estimated short-term leaching rates of metals from raw waste are significantly higher than from pretreated waste. Leaching rates from both MBP waste and incineration slag are in all cases lower than 1% of total metal content in waste. Incineration slag provides the strongest binding for metals.

Tab. 2: Short-term (100 years) leaching factors for different kinds of waste (den Boer 2007)

	Ca	Cd	Cr	Cu	Fe	Ni	Pb	Zn
				[%]				
Raw waste	28.2	38.7	0.6	0.7	3.4	5.8	0.5	20.9
MBP1 waste	0.63	0.14	0.15	0.05	0.16	0.00	0.06	0.63
MBP2 waste	0.49	0.12	0.01	0.10	0.29	0.04	0.18	0.49
Incineration slag	0.09	0.04	0.00	0.002	0.002	0.04	0.001	0.00

3.4.2 Long-term emissions

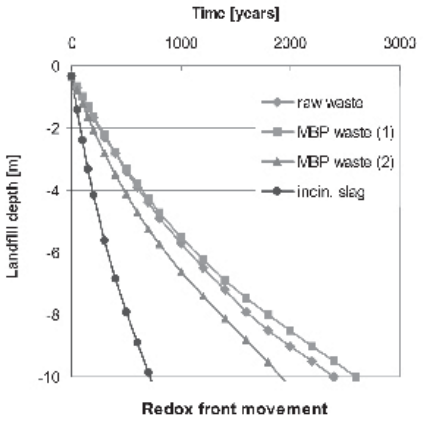


Fig. 5: Progress of organics and sulphide depletion

As discussed in section 2.2, in time waste may lose its redox and acid buffering capacities, leading to an increased leaching of metals. Here the two main driving forces for metal mobilization are considered: (i) the decomposition of organic matter and oxidation of sulphides (loss of metal binding capacity) and (ii) onset of negative pH in a landfill body due to acidity release from the aforementioned processes and infiltration of acid rain water. The decomposition of organics in the landfill body is regulated according to the availability of oxygen. Assuming degradation of a landfill cover in the long term, leading to a 10-fold higher oxygen diffusion coefficient of $2 \cdot 10^{-7}$ m^2/s, the influx rate of oxygen to the landfill can be estimated at approx. 0.29 kg $O_2/m^2/a$ (Bozkurt 2000). In Figure 5 the movement of the organics and sulphide oxidation front over time is calculated for all types of wastes investigated in a 10 m high landfill.

Calculations show how the depletion of sorption capacity for metals due to organic decomposition and sulphide oxidation will progress very slowly.

In order to estimate potential long-term pH reduction in waste a maximum acidity due to both oxidation reactions was estimated. The infiltration of acidic rain water is another source of acidification of the waste body considered in the calculations. In laboratory experiments, acid neutralization capacities of all waste types were determined. Results obtained showed that all investigated waste types had very high buffering capacity. Thus, even in long-term horizons of up to 3000 years only very slight pH change (up to one pH unit) is to be expected.

By relating the leachability of metals at a given pH to the pH development and to the L/S ratio in landfill the accumulative leaching over a given time period was calculated. Additionally, it was assumed that a gradual decomposition of organics and sulphides causes a gradual release of metals immobilized in this fraction (oxidizable fraction derived from the speciation analysis). To obtain the "worst case" i.e. the maximum leachability rates, a complete depletion of the sorption capacity of organics and sulphides was assumed. Moreover, relatively acidic rain water of pH 4 was assumed for calculations. In Figure 6 both the short- and long-term "worst case" leaching rates of Zn (selected example metal) from different waste types are presented. For the sake of comparison the range of average Zn contents in soils in Poland as well as the proposed limit values for Zn in European soils (5<pH<6) are also shown.

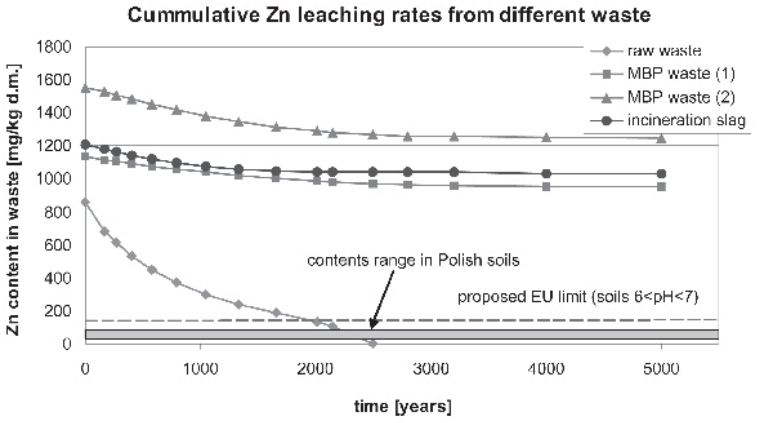


Fig. 6: Time dependent Zn leaching ("worst case") from different waste types

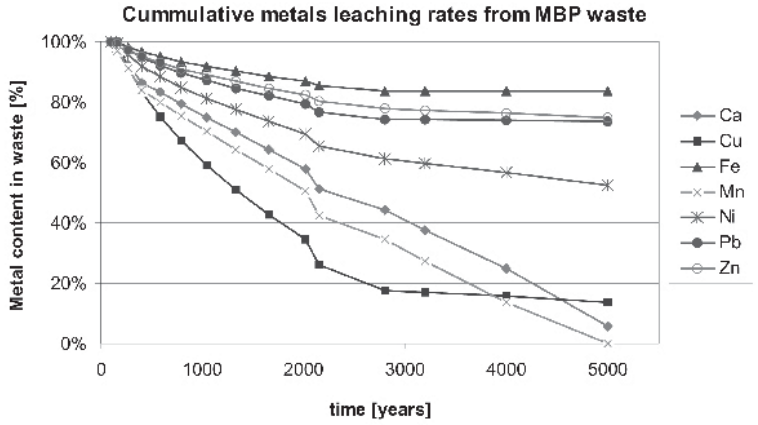


Fig. 7: Time dependent metal leaching ("worst case") from MBP1 waste

The obtained leachability rates show that leaching of Zn from waste is a very slow process. It is also apparent that the estimated leaching from raw waste progresses much faster than from the pretreated waste. Similar pattern of behavior was obtained also for other metals, implying a positive impact of waste pretreatment on metal binding. On comparison of Zn levels in waste to its natural contents in Polish soils and to the proposed soil limits, it can be concluded that landfills will continue to pollute the environment for exceedingly long time horizons.
In Figure 7 leaching rates of different metals from MBP1 waste are presented. Out of all metals Cu was estimated to leach the fastest over the first 3000 years. This is

due to a strong affinity of Cu with the oxidizable fraction which is expected to be gradually depleted within the first 2500 years of storage (see Figure 6). Mn and Ca also showed relatively high leaching rates. In this case leaching was pH-dependant, due to the high concentration of these metals in the exchangeable fraction. Similar leaching patterns and lowest leaching rates were displayed by Fe, Zn and Pb, likely due to the concomitant presence of these metals in the reducible fraction of Fe oxy-hydroxides.

4 Conclusion

The present paper presents the results of investigations performed to determine the behavior of heavy metals in waste pretreatment and disposal processes. Results of landfill simulating lysimeter experiments were used to estimate the short-term (up to 100 years) leaching rates of metals from raw and pretreated waste. Over the first 100 years of landfill storage leaching rates are very low, not exceeding 1% of total metal content in waste. Further on, an innovative approach for assessment of long-term leachability of metals from landfills was proposed. Its crucial points are: (i) to analyze metal speciation and changes within treatment and disposal processes and (ii) to include long-term processes, such as organic decomposition and pH development together with empirical investigations of metal behavior in different conditions into modeling of metal leaching. Generally, the results obtained in leaching tests indicate that the release of metals from waste is a very slow process, thus implying that landfills will continue to pollute the environment for thousand of years.

References

Caille, N., Tiffreau, C., Leyval, C., Morel, J.L. (2003): Solubility of metals in an anoxic sediment during prolonged aeration, The Science of the Total Environment Vol 3001, pp. 239-250

den Boer (2007): E. A Novel Approach for Integrating Heavy Metals Emissions from Landfills into Life Cycle Assessment Consideration of Waste Pretreatment, Landfill Processes and Long-Term Effects, Dissertation (in press), Technische Universitaet Darmstadt, Darmstadt

den Boer, E., den Boer, J. and Jager, J. (Eds.) (2005): Waste management planning and optimisation. Handbook for municipal waste prognosis and sustainability assessment of waste management systems, ibidem-Verlag, Stuttgart

Prantl R., Tesar M. and Heiß-Ziegler C. In-Situ Aerobisierung von Altablagerungen – Ergebnisse aus Labor- und Feldversuchen. In: Lorber K.E., Staber W., Novak J., Prochaska M., Maier J., Kastl I. (Eds.) (2004): Konferenzbericht der 7. DEPOTECH Fachtagung, 24. – 26. November 2004, Leoben

Prudent, P., Domeizel, M. and Massiani, C. (1996): Chemical sequential extraction as decision-making tool: application to municipal solid waste and its individual constituents, The Science of the Total Environment Vol. 178 pp. 55-61

Rauret, G., Lopez-Sanchez, J.F., Lück, D., Yli-Halla, M., Muntau, H. and Quevauviller, Ph. (2001): The certification of the extractable contents (mass fractions) of Cd, Cr, Cu, Ni, Pb and Zn in freshwater sediment following a sequential extraction procedure, BCR-701 Reference Materials, European Commission Directorate-General for Research, EUR 19775 EN