ASSESSMENT OF METAL MOBILITY IN SLUDGES AND SOLID WASTES

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1. Introduction

Among the criteria to assess which element or elemental species, beside its toxic potential, may be of major concern in ecological evaluations, one question deserves primary attention (Nriagu, 1984): Is the element mobile in geochemical processes because of either its volatility or its solubility in natural water, so that the effect of geochemical perturbations can propagate through the environment? In this context, "mobility" mostly deserves a negative aspect of environmental "speciation" - here in terms of "describing the distribution and transformation of metal species in various media" (Bernhard et al., 1986) - in that faster transfer from one environmental medium into another generally involves greater reactivity and bioavailability of potentially toxic elements.

Problems with solid "speciation" - now with the second meaning of "operational procedures for determining typical metal species in environmental samples" (Bernhard et al., 1986) - are connected to the complexity of heterogenous systems, e.g. of soils, sediments and aerosol particles, and to disequilibria between dissolved and particulate fractions. It has been stressed, that due to the important role of kinetically controlled processes in these systems, the actual speciation is often different from what can be expected (Andreae et al., 1984). Particularly in polluted solid systems, an even greater increase of entropy will induce a concomitant increase in instability in both physical and chemical context; this can mainly be seen in the difficulties in sample handling and storage prior to analysis (Wood et al., 1986). On the other hand, it is just these systems, where action is immediately needed.
and where for an assessment or prognosis of possible adverse effects the species and the transformations of pollutants have to be evaluated.

The present review on metal mobility in relation to "speciation" in typical examples of solid waste materials is a follow-up study to our earlier compilations, e.g. from the NATO Advanced Research Workshop on Trace Element Speciation held at Nervi/Italy in 1981 (Fürstner & Salomons, 1983), the Dahlem Konferenzen on Chemical Speciation in Environmental Processes held at Berlin in 1984 (Fürstner, 1986), the NATO-/ISSS Workshop on Soil Colloid/Solution Interface held at Gent in 1986 (Fürstner, 1989a), and from an international workshop on Speciation of Metals in Water, Sediment and Soil Systems held at Sunne/Sweden in October 1986 (Fürstner, 1987). Here we will focus on the progress, which - to our opinion - has been achieved since the latter conference with respect to the conceptual aspects and operational procedures in the subject area of distribution and transformation of metal species in solid waste materials.

2. Dynamic Behaviour of Solid Metal Species in the Environment

In addition to the manifold procedural aspects of speciation, which form the major focus of the present symposium, we consider it as an important challenge in this new field of environmental research that the findings established on the molecular level are transferred into a macroscopic scale, where practical action can take place.

2.1 The Mobility Concept in Relation to Metal Speciation

Typically for systems involving solution/solid interactions, "mobility" reflects the flux of metal species in a certain medium, which contains both accelerating and inhibiting factors and processes. The former influences comprise effects of pH-lowering, redox changes, inorganic and organic complexation, and microbially mediated species transformations such as biomethylation. Among the spectrum of "barriers", physical processes include adsorption, sedimentation, and filtration;
chemical barriers comprise mechanisms such as complexation and precipitation; biological barriers are often associated with membrane processes, which can limit translocation of metals, for example, from plant roots to the shoots and fruits. "Complexation" in its various forms can both inhibit and accelerate metal fluxes, particularly in biological systems consisting of different types of membranes. Four different ways can be envisaged for the assessment of metal mobility in typical environmental compartments:

1 The most comprehensive approach involves evaluation of all species changes along the pathway of the element through the system ("full-system speciation").

2 For many objectives, e.g. for studying effects on biota, determination of the elemental species distribution at a critical section within the system or at its efflux may be sufficient ("part-system speciation").

3 Model considerations, which are aimed to generalize typical distribution or transformation processes, need data on dominant species combined with typical mobili- zing/inhibiting parameters such as pH, and pH2S in the dissolved phase and surface properties of the solid phase ("model species/mobility approach").

4 Long-term prognosis of the behaviour of metals at critical sites requires both the knowledge of interactions of element species in solid matter and solution, and an estimation of the future borderline conditions in a dynamically evolving medium ("prognostic mobility/species approach").

In the present contribution we will mainly discuss the two latter approaches, which typically include solid/solution interactions of metal species. As will be shown later, long-term prognosis of such interactions (approach 4) at this stage is still based mainly on characteristic changes of total metal fluxes, i.e. on mobility variations derived from laboratory experiments, rather than on informations on real "speciation".

2.2 Metal Mobility in Dynamic Environments

Under the aspect "dynamic behaviour of metal species in the environment" (Session 1 of the Symposium) typical "macro-environments" can be considered, where the assessment of metal mobility is of particular relevance for estimating both the
actual and future effects of critical components. Such "dynamic" sites, which have been described during the present symposium, include: (1) Excessive treatment of soil with organic-rich agricultural waste materials (Del Castillo); (2) transformation of metal-rich components in mining residues in tropical regions (Salomons); (3) behaviour of polluted particulate matter in the estuarine mixing zone (Calmano); (4) long-term development of municipal and industrial waste materials (this contribution). In these dynamic environments characteristic factors and processes are acting as "driving forces":

- High-energy mechanical processes, such as resuspension of particles by wave action, bioturbation, and dredging activities;

- Strong chemical gradients, e.g. of salinity, as well as of redox conditions, pH-values, and organic ligand concentrations, the latter three variables mainly induced by the degradation of organic matter;

- Distinct temporal variations and developments, such as seasonal changes of biological activity in aquatic systems and typical successions in metabolic transformations, e.g., reductive processes in waste materials.

From a practical view, for example, for application in wastewater treatment and solid waste disposal techniques, knowledge on "speciation" of characteristic elements may be useful; however, it seems that with the concept of mobility assessment, the often complex information on interactions between solid and dissolved species can be narrowed down to more simple parameters, which can both be measured under field conditions and used for generalizations in models. The questions arising in this context are:

1 Can the actual metal species in both solid and dissolved phase of a given system satisfactorily be described?

2 What are the typical variables, apart from metal species distribution, which can be measured in a dynamic system?

If these informations are available, experimental and/or model designs can be developed, from where - under expected boundary conditions - interrelations between metal species and typical variables can be studied and extrapolated for a long-term prognosis of metal behaviour in critical cases.
3. Modeling Solid/Solution Interactions of Metal Species

One of the greatest challenges of environmental chemistry has been to describe the behaviour of trace elements in natural aquatic systems based solely on knowledge of their fundamental physical-chemical properties. Initial efforts for applying quantitative models have been undertaken for the prediction of metal speciation in solution (Baham, 1984). The theoretical foundations for solving the problem of chemical speciation, which is usually not solvable by use of experimental analysis, are based upon a model that relates the equilibrium activities of metals and ligands to the formation of complexes in solution (see contributions by Buffle and other authors in this volume). These models are also being used increasingly to predict the mobilizable fraction of metals in the sediment (Baes & Sharp, 1983) and the transport of toxic metals and radionuclides in ground waters (Lewis et al., 1987), to assess pollution potential to the ecosystem in general (Luoma & Davis, 1983), and to develop sediment quality criteria (Jenne et al., 1986). Quantification of competing effects is difficult, and thus the equilibrium partition approach for sediment quality assessment of metals is still limited (Honeyman & Santschi, 1988; Shea, 1988; see contribution by Calmano et al. in this volume).

3.1 Factors Affecting Distribution Coefficients (K_D-Values)

Mobility of an element in the terrestrial and aquatic environment is reflected by the ratio of dissolved and solid fractions. Evaluation of the current literature indicates at least three major factors affecting the distribution of trace metals between solution and particulates: (i) the chemical form of dissolved metals originating both from natural and human-caused sources (Förstner & Salomons, 1983); (ii) the type of interactive processes, such as sorption/desorption- or precipitation-controlled mechanisms (Salomons, 1985); and (iii) concentration and composition of particulate matter, mainly with respect to surface-active phases.
Typical curves for the adsorption of metals onto inorganic substrates, such as iron oxyhydrate, increase from almost nothing to near 100% as pH increases through a critical range 1-2 units wide (Benjamin et al., 1982). It is important to note, that the location of the pH-adsorption-"edge" depends on adsorbent concentration. This effect is due to the existence of a range of specific site-binding energies. High-energy adsorption sites, since they are fewer in number than lower energy sites, become limiting first. As lower energy sites are gradually filled, the overall binding constant decreases. In the few cases, where kinetics of sorption have been investigated, surface reactions were not found to be a single step reaction (Anderson, 1981). Experiments performed by Benjamin & Leckie (1981) showed an initial, rapid and almost complete metal uptake process perhaps lasting no more than a few minutes to hours, followed by a second, slower uptake process requiring from a few days to a few months. The first effect was thought to be true adsorption, and the second to be slow adsorbate diffusion into the solid substrate or coagulation of colloidal to filterable particles (Santschi & Honeyman, 1989). Extrapolations to geologic time scales have been made by Förstner & Schoer (1984) by a comparison of the extractibility of stable metal isotopes and their unstable counterparts - the latter supplied from radioactive emissions of nuclear power and reprocessing plants; using reducing extraction agents, for example, only 15% of the natural stable manganese was mobilized from a river sediment sample, while the artificial, more recently (during the past 20-30 years) induced isotope Mn-54 from the reprocessing plant is extracted by more than 80% during the same treatment.

For systems rich in organic matter, metal adsorption curves cover a wider pH-range than is observed for inorganic substrata. Typically, a reduced reversibility of metal sorption has been observed in these organic systems (Lion et al., 1982). Such effects may be important restrictions for using distribution coefficients in the assessment of metal mobility in rapidly changing environments, such as rivers, where equilibria between the solution and the solid phases can often not be achieved completely due to the short residence times. In prac-
tice, applicability of distribution coefficients may find further limitation from methodological problems. Sample pretreatment (e.g., dry or wet conditions), solid/liquid separation technique (filtration or centrifugation), and grain size distribution of solid material is strongly affecting $K_D$-factors of metals (e.g., Calmano, 1979; Duursma, 1984; Table 1). Such effects also have to be considered for the interpretations of in-situ processes, where the above-mentioned influences of reversibility usually are playing a minor role than in the case of open-water conditions.

With respect to the possible differences of metal sorption between natural and polluted systems it can be argued from the preceding information that the higher concentrations of metals expected in contaminated systems will tend (see also Brümmer et al., 1986):

- to be less strongly bound to the substrate,
- to form precipitates rather than to interact via adsorption, and
- to be subject to more intensive transformations, including competition between various substrates, than do the natural constituents in aquatic and terrestrial systems.

In addition, mobility of metals is influenced by the chemical form of the inputs. Direct emissions, for example of Cd, into the environment from waste materials are approximately 10-fold greater from solid materials such as pigments, phosphate

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Factors and Mechanisms Influencing Distribution of Elements between Solid and Dissolved Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor/mechanism</td>
<td>Reference</td>
</tr>
<tr>
<td>Sample preparation (e.g. drying)</td>
<td>Duursma (1984)*</td>
</tr>
<tr>
<td>Separation (filtration/centrifugation)</td>
<td>Calmano (1979)*</td>
</tr>
<tr>
<td>Grain size distribution</td>
<td>Duursma (1984)*</td>
</tr>
<tr>
<td>Suspended matter concentration</td>
<td>Salomons (1980)</td>
</tr>
<tr>
<td>Kinetics of sorption/desorption</td>
<td>Schoer &amp; Förstner (1985)*</td>
</tr>
<tr>
<td>Non-reversibility of sorption</td>
<td>Lion et al. (1982)</td>
</tr>
<tr>
<td>Colloids</td>
<td>Santschi &amp; Honeyman (1989)*</td>
</tr>
</tbody>
</table>

* Experiments with artificial radionuclides
fertilizers, sewage sludge, municipal and mining wastes, and smelting residues, than from dissolved inputs such as lead-zinc mines, sewage treatment plant, effluents from battery factories, and electroplating plants. For atmospheric precipitation the percentage of dry deposition (by which aerosols or gaseous compounds are deposited on surfaces such as soil particles and plant leaves) has been observed between 10% and 90% of bulk cadmium deposition, depending upon the emission sources, climatic conditions and - in particular - upon pH (Nriagu, 1980; Nürnberg et al., 1983).

3.2 Equilibrium Models for Interstitial Waters

The use of equilibrium models has been to some extent successful for anoxic environments. "Buffering" of metal ion mobility not only involves interactions with numerous inorganic and organic ligands, but also with inorganic and organic (biological) surfaces - via coordinative bonding -, and heterogenous equilibria between metal precipitates and dissolved metal species (Stumm & Morgan, 1981). In sediment pore water and landfill leachates precipitation as sulfides is considered as the dominant mechanism limiting the solubility of many trace elements (Boulegue et al., 1982; Peiffer, 1989). Sulfide coordination is particularly strong for metals exhibiting so-called "B-character" (see contribution by Buffle in this book), such as Cu(I), Ag, Hg, Cd, Pb, and Zn; it is an important mechanism for transition elements in decreasing order of the Irving-Williams-series Cu(II) > Ni(II) > Co(II) > Fe(II) > Mn(II). There is strong direct (Luther et al., 1980; Lee and Kittrick, 1984) and indirect (Lu and Chen, 1977) evidence that the concentrations of copper, zinc and cadmium in sulfidic pore waters are determined by precipitation-dissolution processes, and in this case the metal concentrations in the pore waters are independent of the concentrations in the solid phase; on the other hand, the concentrations of arsenic and chromium in anoxic pore waters are probably controlled by adsorption-desorption processes, and mainly depend on the concentrations in the solid phase (Salomons, 1985).
According to Davies-Colley et al. (1985) two situations can be distinguished in natural systems, either the existence of a certain sulfide precipitation capacity (SPC), or - when exceeding the SPC - the accumulation of free sulfide (as \( \text{H}_2\text{S} \) or \( \text{HS}^- \)) in the water phase. Concentrations of sulfate and reducible iron seem to be the principle factors influencing different evolutionary sequences in anoxic fresh and marine waters (Salomons et al., 1987; Kersten, 1988). At excess sulfide concentrations (e.g., in Fe-poor environments), metal solubility can be increased by the formation of thio-complexes. There is still a discussion about the stability of thio-complexes, which possibly has been underestimated in most equilibrium models (Peiffer, 1989).

There is a remarkable agreement that complexation by natural organic ligands is not important for most metals except for copper, mainly due to the competition by ions such as \( \text{Ca}^{2+} \), \( \text{Mg}^{2+} \), \( \text{Fe}^{2+} \), and \( \text{Mn}^{2+} \) (Stumm & Bilinski, 1973; Chian & De Walle, 1977; Tauchnitz et al., 1983; Van den Berg & Dharmvanij 1984; Salomons et al., 1987). Even at high concentrations of organic substances (and high complexing capacity) in solutions from digested sewage sludge only copper and lead seem to be slightly competitive with Ca- and Mg-ions (Fletcher & Beckett, 1987). It has been stressed by Peiffer (1989) that only in the presence of selective, basic complexing agents exhibiting small molar masses - such as organic sulfur and nitrogen compounds - significant oversaturation of Cu and Pb can be expected. With respect to copper speciation, the formation of more soluble polysulfides as a result of oxidation of \( \text{H}_2\text{S} \) by waste-borne oxidants may play a certain, not yet quantified, role (Peiffer, 1989).

4. Metal Mobilization from Aquatic Sediments and Solid Wastes

Regarding the potential release of contaminants from sediment, soil and solid waste material changing the pH and redox conditions are of prime importance (Table 2). It can be expected that changes from reducing to oxidizing conditions, which involve transformations of sulfides and a shift to more acid
conditions, increase the mobility of typical "B-" or "chalco-
philic" elements, such as Hg, Zn, Pb, Cu, and Cd. On the other
hand, the mobility is characteristically lowered for Mn and Fe
under oxidizing conditions. Elements exhibiting anionic spe-
cies, such as S, As, Se, Cr, and Mo are solubilized, e.g.,
from fly ash sluicing/ponding systems at neutral to alkaline
pH-conditions (Dreesen et al. 1977, Turner et al. 1982.)

Table 2  Relative Mobilities of Elements in Wastes and Soils
as a Function of Eh and pH. (After Plant & Raiswell,
1983)

<table>
<thead>
<tr>
<th>Relative Mobility</th>
<th>Electron activity</th>
<th>Proton activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very low mobility</td>
<td>Al, Cr, Mo, V, U, Se, S, B, Hg, Cu, Cd, Pb</td>
<td>Al, Cr, Fe, Mn, Hg, Cu, Ni, Co, Si</td>
</tr>
<tr>
<td>Low mobility</td>
<td>Si, K, P, Ni, Zn, Co, Fe</td>
<td>Si, K, P, Pb, Fe, Zn, Cd, K, Fe(III)</td>
</tr>
<tr>
<td>Medium mobility</td>
<td>Mn</td>
<td>Co, Ni, Hg, Cu, Zn, Cd, Mn</td>
</tr>
<tr>
<td>High mobility</td>
<td>Ca, Na, Mg, Sr</td>
<td>Ca, Na, Mg, Sr, Ca, Na, Mg, Cr, Mo, V, U, Se</td>
</tr>
<tr>
<td>Very high mobility</td>
<td>Cl, I, Br</td>
<td>Cl, I, Br, C, Cl, I, Br, S, B, Mo, V, U, Se</td>
</tr>
</tbody>
</table>

4.1 Metal Mobilisation from Aquatic Sediments

Release of potentially toxic metals from contaminated
sediments pose problems both in aquatic systems and subsequent
to land deposition of dredged materials (Pörstner, 1989).
Examples are given by various authors, indicating the major
factors, processes and rates of metal mobilisation:

- Field evidence for changing cadmium mobilities was given
  by Holmes et al. (1974) from Corpus Christi Bay Harbor;
  During the summer period when the harbor water was stag-
  nant cadmium was precipitated as CdS at the sediment/-
  water interface; in the winter months, however, the in-
  creased flow of oxygen-rich water into the bay resulted
  in a release of the precipitated metal.
- In the St. Lawrence Estuary, Gendron et al. (1986) found evidence for different release mechanisms near the sediment-water interface: The profiles for cobalt resemble those for manganese and iron with increased levels downwards, suggesting a mobilization of these elements in the reducing zone and a reprecipitation at the surface of the sediment profile. On the other hand, cadmium appears to be released at the surface, probably as a result of the aerobic remobilization of organically-bound cadmium.

- Biological activities are typically involved in these processes: Remobilization of trace metals has been explained by the removal of sulfide from pore waters via ventilation of the upper sediment layer with oxic overlying water, allowing the enrichment of dissolved cadmium that would otherwise exhibit very low concentrations due to the formation of insoluble sulfides in reduced, H$_2$S-containing sediments (Emerson et al., 1984); the authors suggest a significant enhancement of metal fluxes to the bottom waters by these mechanisms. It was evidenced by Hines et al. (1984) from tracer experiments that biological activity in surface sediments greatly enhances remobilization of metals by the input of oxidized water; these processes are more effective during spring and summer than during the winter months.

- From enclosure experiments in Narragansett Bay it has been estimated by Hunt and Smith (1983) that by mechanisms such as oxidation of organic and sulfidic material, the anthropogenic proportion of cadmium in marine sediments is released to the water within approximately 3 years; for remobilization of copper and lead, approximately 40 and 400 years, respectively, is needed, according to these extrapolations.

Typical early diagenetic geochemical changes and subsequent element mobilization via the porewater result from dredging activities. A study performed by Darby et al. (1986) in a human-made estuarine marsh demonstrates characteristic effects of oxidation (Table 3): Compared to the river water concentration, the channel sediment porewater is enriched by a factor of 200 for iron and manganese, 30-50 for nickel and lead, approx. 10 for cadmium and mercury, and 2-3 for copper and zinc. When the expected concentration of metals following hydraulic dredging, which were calculated from a rate of porewater to river water of about 1:4, were compared with the actual measurements at the pipe exiting the dredging device, negative deviations were found for iron and manganese, suggesting reprecipitation of Fe/Mn-oxide minerals; the positive deviations of
zinc (factor 80), copper, lead and cadmium (factors 7-8) indicate, that during dumping of the sludge-water mixture significant proportions of these elements were mobilized and transferred into the effluent water.

Table 3 Mobilization of metals and nutrients during dredging (after Darby et al., 1986). Concentrations in mg/l

<table>
<thead>
<tr>
<th>Metal</th>
<th>Channel sediment porewater (a)</th>
<th>River water concn. (b)</th>
<th>a/b</th>
<th>Effluent at man-made marsh</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Expected concn.</td>
</tr>
<tr>
<td>Mn</td>
<td>6.94</td>
<td>0.03</td>
<td>230</td>
<td>1.34</td>
</tr>
<tr>
<td>Fe</td>
<td>57.3</td>
<td>0.26</td>
<td>220</td>
<td>11.12</td>
</tr>
<tr>
<td>Ni</td>
<td>0.054</td>
<td>0.001</td>
<td>54</td>
<td>0.011</td>
</tr>
<tr>
<td>Pb</td>
<td>0.077</td>
<td>0.002</td>
<td>38</td>
<td>0.016</td>
</tr>
<tr>
<td>Hg[µg/l]</td>
<td>3.2</td>
<td>0.26</td>
<td>12</td>
<td>0.82</td>
</tr>
<tr>
<td>Cd</td>
<td>0.009</td>
<td>0.001</td>
<td>9</td>
<td>0.0025</td>
</tr>
<tr>
<td>Cu</td>
<td>0.012</td>
<td>0.004</td>
<td>3</td>
<td>0.0055</td>
</tr>
<tr>
<td>Zn</td>
<td>0.12</td>
<td>0.052</td>
<td>2</td>
<td>0.065</td>
</tr>
</tbody>
</table>

These results demonstrate the problematic effect of dispersing anoxic waste materials in ecologically productive, high-energy nearshore, estuarine, and inlet zones (Khalid, 1980). Similar effects may also pertain to procedures such as "sludge-harrowing", which is occasionally performed in the cold season in some sections of Hamburg harbor. By application of these techniques highly contaminated sediments are transferred into zones of lower pollution intensity; oxygen-consuming substances, such as ammonia, are released from the pore water; increased turbidity affects "light climate" and thus the ecosystem in the lower reaches of the estuary.

4.2 Metal Mobility in Solid Wastes

Subsequent to landfilling, the raw waste compounds undergo a variety of early diagenetic processes accompanying microbiologically mediated degradation of the organic compounds (Aragno, 1989). The metabolic intermediates of organic matter decay (e.g. HCO₃⁻, HPO₄²⁻, carbohydrates and other low molecular organic acids) and those of the coupled inorganic reduction processes (e.g. Fe²⁺, Mn²⁺, S²⁻, NH₄⁺) accumulate in the interstitial
water until concentrations are limited by physical convection/dispersion, by subsequent microbial utilization, or by diageneric formation of secondary ("authigenic") minerals such as metal sulfides. This secondary inventory of a reactor landfill is critical both in buffering leachate water chemistry (Stumm & Morgan, 1981) and in affecting transport of pollutants to underlying groundwater aquifers.

In municipal solid waste landfills initial conditions are characterized by the presence of oxygen and pH-values between 7 and 8. During the subsequent "acetic phase", pH-values up to 5 were measured due to the formation of organic acids in a more and more reducing milieu; concentrations of organic substances in the leachate are high. In a transition time of 1 to 2 years chemistry of landfill changes from acetic to methanogenic conditions; the methanogenic phase is characterized by higher pH-values and a significant drop of BOD₅ (biochemical oxygen demand)-values from more than 5,000-40,000 mg/l in the acetic phase to 20-500 mg/l. By comparison of the long-term evolution of a sewage sludge landfill to similar natural sediments (peat, organic soils) and their diagenesis it has been suggested by Lichtensteiger and Brunner (1987), that the transformation of organic material will last for geological time scales (10³ to 10⁷ years).

Particular problems occur when leachate collection pipes are plugging during the acidic decomposition period (Ham et al., in Baccini, 1989). Typically increased concentrations of metals have been found for iron, manganese and zinc in leachates during this phase compared with the "methanogenic phase" (Table 4). The lack of significant differences for other trace elements may be related to difficulties in sampling and chemical analysis since similar effects, for example, of pH on zinc mobility can be expected for other related elements such as Cd, Ni, Pb, and Cu. Comparison of inorganic groundwater constituents upstream and downstream of 33 waste disposal sites in West Germany (Arneth et al., 1989) indicates characteristic differences in pollutant mobilities, which may partly be related to releases during the acidic phase of the landfill development. High contamination factors (contaminated mean/uncontaminated mean) have been found for boron (>63), ammonia (62),
and arsenic (CF = 34; this element may pose particular problems during initial phases of landfill operations; Blakey, 1984); heavy metals such as cadmium (CF >6.5), chromium (>5), lead (5.0), copper (4.7) and nickel (3.0) are significantly enriched in the leachates as well.

Table 4 Concentrations of trace elements (µg/l) in leachates from municipal solid waste landfills (review by Ehrig, 1989)

<table>
<thead>
<tr>
<th>Element</th>
<th>&quot;Acetic Phase&quot;</th>
<th>&quot;Methanogenic Phase&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>average range</td>
<td>average range</td>
</tr>
<tr>
<td>Iron</td>
<td>780 20 - 2100</td>
<td>15 3 - 280</td>
</tr>
<tr>
<td>Manganese</td>
<td>25 0.3 - 65</td>
<td>0.7 0.03 - 45</td>
</tr>
<tr>
<td>Zinc</td>
<td>5 0.1 - 120</td>
<td>0.6 0.03 - 4</td>
</tr>
<tr>
<td>Arsenic</td>
<td>160 5 - 1600</td>
<td></td>
</tr>
<tr>
<td>Cadmium</td>
<td>6 0.5 - 140</td>
<td></td>
</tr>
<tr>
<td>Chromium</td>
<td>300 30 - 1600</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>80 4 - 1400</td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>90 8 - 1020</td>
<td></td>
</tr>
<tr>
<td>Mercury</td>
<td>10 0.2 - 50</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>200 20 - 2050</td>
<td></td>
</tr>
</tbody>
</table>

It has been inferred that oxidation of sulfidic minerals by intruding rainwater may mobilize trace metals from landfills subsequent to the methanogenic phase, and the impact on the underlying groundwater could be even higher if a chromatographic-like process, involving continuous dissolution and reprecipitation during passage of oxidized water through the deposit, would preconcentrate critical elements prior to final release with the leachate (Förstner et al., 1989). Experimental investigations performed by Peiffer (1989) on long-term development of sewage sludge materials provide detailed insight into the sequence of processes taking place in the post-methanogenic stage of such deposits: Transition from anoxic to oxic conditions involves a pH-decrease from 6.7 to 6.4, an accumulation of sulfate on the expense of sulfide, and a release of Mn- and Ca-ions, either by cation exchange (by protons) or by an indirect redox effect via oxidation of Fe²⁺ to Fe³⁺; organic substances act as an acid buffer. Time-dependent release
of zinc and cadmium is similar to as calcium and manganese, whereas lead and copper are not remobilized under these conditions. It has been inferred by Peiffer (1989), that due to slow oxidation kinetics of the sparingly soluble metal sulfides ZnS, CdS, PbS and CuS ion exchange will become the rate-determining mechanism in this system. From the current pH-decrease it can be expected that zinc and cadmium are being exchanged for protons, whereas lead and copper do not, because of their stronger bonding to the solid substrate. Because of their eminent practical significance, these initial findings need further confirmation. The same is valid for the effect of residual organic carbon in municipal solid waste incinerator slag as a potential proton producer due to microbial degradation to CO₂ (Krebs et al., 1988).

5. Assessment of Metal Mobility in Solid Materials

Since adsorption of pollutants onto particles is a primary factor in determining the transport, deposition, reactivity, and potential toxicity of these materials, analytical methods should be related to the chemistry of the particle's surface and/or to the metal species highly enriched on the surface. However, as it has been stressed before, the greater the instability of the polluted system the more difficulty is in sample handling and storage prior to analysis. Many of the analytical techniques are handicapped by disruptive preparation techniques which may alter the chemical speciation of inorganic components or lead to loss of analyte before analysis, e.g. freezing, lyophilization, evaporation, oxidation, changes in pH, light catalyzed reactions, reactions with the sample container, time delays before analysis with biologically active samples, and sample contamination.

5.1 Leaching Procedures

Various laboratory techniques have been reported for the characterization of reactivity and mobility of pollutants generating leachates from hazardous waste, and are generally grouped into batch and column extraction methods. The batch
extraction method offers advantages through its greater reproducibility and simplistic design, while the column method is more realistic in simulating leaching processes which occur under field conditions. It has been noted by Jackson et al. (1984) that relative standard deviation of experimental data was over twice as great for the column method than for the batch method; this result was attributed to varying degrees of "channeling" that may have occurred during leaching of waste constituents using the column method.

Apart from the procedures aimed for the study of metal species distribution and transformation, other parameters controlling the mobility of elements have to be measured, preferentially in a continuous way during the time of the experiment. In many cases, the variables to be determined are pH, electric conductivity, oxygen potential, and sulfide activity. For the latter parameter, a pH$_2$S (glass/Ag$^0$, Ag$_2$S) electrode can be used, which has been introduced by Prevert & Galster (1978) and successfully applied for geochemical studies in anoxic systems, even at very low H$_2$S-concentrations (Peiffer & Prevert, 1987).

Initial estimation of potential release of metal from contaminated solids is mostly based on elutriate tests, which, apart from the characterization of the reactivity of specific metals - can provide information on the behavior of metal pollutants under typical environmental conditions. Common single reagent leachate tests, e.g. U.S. EPA, ASTM, IAEA, ICES, and DIN use either distilled water or acetic acid (Theis & Padgett, 1983). A large number of test procedures have been designed particularly for soil studies. These partly used organic chelators such as EDTA and DTPA, both as single extractants or in sequential procedures (Sauerbeck & Styperek, 1985). Physiological solutions have been applied, e.g. for the estimation of organ-specific effects of atmospheric particulates (Harris & Silberman, 1988).

A "mobility test" procedure for soils based on variations of pH-values has been proposed by Kiekens & Cottenie (1985). Application to a large number of polluted and non-polluted
soils indicate that typical mobilisation patterns are obtained for the different heavy metals. Beside the nature of the element, the pH-curves reveal typical textural features of different soil substrates. Best results with respect to the estimation of middle-term effects can be attained by "cascade" test procedures at variable solid/solution ratios: A procedure of the U.S. EPA (Ham et al., 1979) designed for studies on the leachability of waste products consists of a mixture of sodium acetate, acetic acid, glycine, pyrogallol, and iron sulfate. For the study of combustion residues a standard leaching test has been developed by the Netherland Energy Research Centre (Van der Sloot et al., 1984). In the column test the material under investigation is percolated by acidified demineralized water (pH = 4; for evaluating most relevant effects of acid precipitation) to assess short-term leaching (< 50 years). In the cascade test the same quantity of material is extracted several times with fresh demineralized water (pH = 4) to get an impression of medium-term leaching behavior (50-500 years). As a time scale the liquid/solid ratio (L/S) is used (De Groot et al., 1987).

Single reagent leaching tests, in particular short-term batch procedures, can be used for easily soluble components such as halides or sulfates, but in most cases are not adequate for assessing mobility of trace metals. For example, cascade test procedures demonstrated much high increases in the percent elution of elements such as arsenic than can be expected from the increase of the solution/solid ratio (Van der Sloot et al., 1985). Another example, from the time-dependent leachability of cadmium and lead in filter-dust samples, indicated much greater percentages of released metals after short-time treatment (0.5 and 5 hours) than after longer contact (50 hours) between dissolved and solid metal species; a reverse time-dependency was observed for lead in dust samples solidified with cement; both developments can be interpreted as resulting from pH changes (Brunner & Baccini, 1987). Most important is the effect of time-dependent change in metal release from waste materials containing oxidizable components: In a low buffered industrial waste containing less than 1% sulfide minerals, proton activity decreased from initial pH 10.2 to pH
5.5 after 50 days, whereas \( E_h \) increased from -200 mV to +500; it is obvious, that application of standard elutriate procedures would have provided totally wrong results, also with respect to the design of remedial measures (see section 6).

In connection with the problems arising from the disposal of solid wastes, particularly of dredged materials, chemical extraction sequences have been applied which are designed to differentiate between the exchangeable, carbonatic, reducible (hydrous Fe/Mn oxides), oxidizable (sulfides and organic phases) and residual fractions. The undisputed advantage of this approach with respect to the estimation of long-term effects on metal mobilities lies in the fact, that rearrangements of specific solid "phases" can be evaluated prior to the actual remobilisation of certain proportions of an element into the dissolved phase (Förstner, 1985). One of the more widely applied extraction sequences of Tessier and co-workers (1979) has been modified by various authors (Table 5).

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Extractant</th>
<th>Operational Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable</td>
<td>1 M NH₄OAc, pH 7</td>
<td>Exchangeable ions</td>
</tr>
<tr>
<td>Carbonatic</td>
<td>1 M NaOAc, pH 5 HAc</td>
<td>Carbonates</td>
</tr>
<tr>
<td>Easily reducible</td>
<td>0.01 M NH₄OH HCl</td>
<td>Mn-oxides</td>
</tr>
<tr>
<td>Moderately reducible</td>
<td>0.1 M oxalate buffer pH 3</td>
<td>Amorphous Fe-oxides</td>
</tr>
<tr>
<td>Sulfidic/organic</td>
<td>30% H₂H₂O₂ pH 2, 0.02 M HNO₃ extracted 1 M NH₄OAc-6% HNO₃</td>
<td>Sulfides together with organic matter</td>
</tr>
<tr>
<td>Residual</td>
<td>hot HNO₃ conc.</td>
<td>Lithogenic Material</td>
</tr>
</tbody>
</table>

The widely used extraction sequence of Tessier and collaborators (1979) consists of five steps. Applications of these methods have been given for atmospheric particulates (e.g., Lum et al., 1982), street dust and roadside soils (Harrison et al., 1981), sewage sludge (Rudd et al., 1986), incinerated sludge ash (Fraser et al. 1982), and in a review by Kersten and Förstner (1989) for sediment-related studies. It has been stressed that - providing the use of a proper sampling and
preparation protocol - the more sophisticated extraction schemes such as Tessier's, significantly improves the specificity and efficiency of extraction.

Despite the advantages of a differential analysis over investigations of total metal concentrations and the fact that sequential chemical extraction is probably the most useful tool for predicting long-term adverse effects from contaminated solid material, it is obvious that there are still many questions and uncertainties associated with these procedures (Kersten & Förstner 1986; Rapin et al. 1986), for example:

- Reactions are not selective and are influenced by the duration of the experiment and by the ratio of solid matter to volume of extractants. An excessive solid content, together with an increased buffer capacity may cause the system to overload; such an effect is reflected, for example, by changes of pH-values in time-dependent tests.

- Labile phases could be transformed during sample preparation, which can occur especially for samples from reducing sites.

In this respect, earlier warnings have been made by various authors, not to forget changes of the sample matrix during recovery and treatment of the material. This, in particular, relates to the anoxic sediment material, where changes are quite obvious.

5.2 Applications

From a practical view the following questions indicate the significance of informations on the mobility of critical elements in aquatic and terrestrial ecosystems (Förstner, 1987):

- How reactive are the metal compounds introduced with solid materials from anthropogenic activities (hazardous waste, sewage sludge, atmospheric fallout) in comparison to their natural existence?

- Are the mechanisms and kinetics of interaction between dissolved and solid metal phases comparable for natural and contaminated systems (this particularly pertains to the question, how fast a quasi-stable state is reached for the latter systems)?

- What are the factors and processes of remobilization to become particularly effective, when either the solid inputs or the solid/solution interactions lead to weaker bonding of critical metal species in contaminated compared to natural systems?
In the following examples emphasis will be given to the latter aspect - the assessment of remobilization of potentially toxic elements from polluted solid materials in both aquatic systems and land deposits.

5.2.1 Evaluation of Threshold Values for Soil Pollutants

Among the various factors affecting the transfer of metal pollutants to plant, lowering of pH - locally from oxidation of sulfidic components and regionally by acid precipitation - is the most important. Generally the lowering of pH by one unit will increase metal solubility by a factor 10. For the example of zinc, Figure 1 (after Herms & Brümmer, 1980) indicates how the permissible limit of total metal concentration in the soil is affected by pH as the dominant factor with respect to metal solubility. At pH 7, the limit of 1 mg Zn per liter soil equilibrium solution, which already may lead to slight depressions in yield for cabbage (Hara & Sonoda, 1979), would be attained at approx. 1200 mg Zn per kg soil. However, at pH 6, the maximum permissible Zn concentration in soil equilibrium solution would be reached at approx. 100 mg Zn per kg soil, at pH 5 even at approx. 40 mg Zn per soil. Under the latter conditions (pH 5), adverse effects can be found even in unpolluted soils.

Figure 1

Solubility of Zn in Relation to pH and Total Zn-Content of Soils Not or to A Different Degree Polluted with Zn (Herms & Brümmer, 1980)
5.2.2 Applications for Sediment Quality Criteria

New objectives regarding the improvement of water quality as well as problems with the resuspension and land deposition of dredged materials require a standardized assessment of sediment quality. Numerical approaches are based on (1) accumulation, (2) pore water concentrations, (3) solid/liquid equilibrium partition (see above), and (4) elution properties (e.g., Förstner et al., 1990). In Table 6, an example is given for the possibilities of standardizing the data from elution experiments with respect to numerical evaluation. An "elution index" for sediment samples from various rivers in West Germany is based on the metal concentrations exchangeable with 1 N ammonium acetate at pH 7. These metal fractions are considered to be remobilizable from polluted sediments at a relative short term under more saline conditions, for example, in the estuarine mixing zone. Comparison of the release rates from oxic and anoxic sediments clearly indicates, that the oxidation of samples gives rise to a very significant increase in the mobilization of the metals studied. This effect was particularly important for Cd. When proceeding further in the extraction sequence, more long-term effects can be estimated, but generally with a reduction of prognostic accuracy.

Table 6  Elution-Index for Selected River Sediment, as Determined from Exchangeable Proportions (1 M Ammonium-Acetate). Calculated Relative to Background Data from Elbe River Sediments. These Values are Multiplied by a Factor of 100

<table>
<thead>
<tr>
<th></th>
<th>Neckar</th>
<th>Main</th>
<th>Elbe</th>
<th>Weser</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>&lt;1</td>
<td>-</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Lead</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Zinc</td>
<td>7</td>
<td>10</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>Cadmium</td>
<td>22</td>
<td>22</td>
<td>25</td>
<td>-</td>
</tr>
<tr>
<td>Total oxic</td>
<td>30</td>
<td>33</td>
<td>67</td>
<td>11</td>
</tr>
<tr>
<td>(Anoxic)</td>
<td>0.5</td>
<td>0.3</td>
<td>&gt;4</td>
<td>4</td>
</tr>
</tbody>
</table>
5.2.3 Metal Partitioning in Combustion Residues and Their Transfer to Other Environmental Compartments

Waste incineration ashes usually exhibit relative high concentrations of trace metals - Zn and Pb up to the percent range - and particularly strong enrichment factors compared to natural contents have been observed for these elements and for cadmium and silver (Brunner and Zobrist, 1983). Sequential extractions performed by Wadge and Hutton (1987) indicate (Figure 2), that about 20% of total Cd and 1% of total Pb in coal fly ash was in exchangeable fraction; in contrast, the single largest fractions of Cd and Pb in refuse ash, at 72% and 41%, respectively, were present in the exchangeable form. It is suggested that this effect is mainly due to higher concentrations of metal associations with chlorides (Baccini and Brunner, 1985).

Figure 2 The Chemical Associations of Cadmium and Lead in Coal Fly Ash and Refuse Fly Ash (Wadge and Hutton, 1987). Extraction Sequence After Tessier et al. (1979)
The release of cadmium and other metals from particulate matter during interactions with saline waters is an important effect in the estuarine mixing zone and at the seawater interface. Such mobilization of cadmium in estuaries has been observed in several examples (Salomons & Förstner 1984); it seems that microbially mediated oxidation of particulate organic carbon is a prerequisite for that effect (Prause et al. 1985). According to Chester et al. (1986), the latter mechanism could be the major factor in the transfer of metals from aerosols to seawater. Figure 3 indicates, that a certain proportion of metals associated with contaminated aerosols, which is related to the more labile fractions, may be solubilized at the seawater interface. Percentage of released metals is greatest for cadmium, followed by zinc, lead and copper, whereas components such as chromium, aluminium and iron are only solubilized to a very small extent. Via selective accumulation in organic solids, released metals can be transferred into the marine food chain. It has been suggested that with such pathways the enrichment of Cd, Pb, and Hg, can be explained in both pelagic and benthic organisms of the northern and central part of the North Sea (Kersten et al., 1988).

![Figure 3](image)

**Figure 3**

Relation between Water Solubility of Trace Metals from Polluted Atmospheric Aerosols and the Percentage Associated with Loosely Bound Fractions (Chester et al., 1986)

### 5.2.4 Study of Diagenetic Processes in Sediment Core Profiles

Partitioning studies of sediment from core profiles are particularly useful, since they provide information on the relative changes of elemental phases irrespective of the method app-
lied, and thereby an insight into diagenetic processes taking place after deposition of the sedimentary components. Two examples are presented here, both indicating significant changes in the partition of zinc and cadmium during a relative short period of time.

Figure 4 Total Concentrations and Partitioning of Zinc, Cadmium and Lead in a Floodplain Soil Profile in the Manifold Catchment (Bradley, 1988)
Floodplains on the River Manifold contain sediments with large metal concentrations (Bradley & Cox, 1986, 1987). The sedimentary units described were deposited during concerted mining, and as mining ceased in 1870, pedogenic processes have influenced these sediments for over 100 years. A general decrease of total Zn concentrations over time, which can primarily be interpreted as the result of improvements in the processing of ores, is given here (Fig. 4, right bars). Phase differentiation (Fig. 4, left) indicate that there has been a significant temporal increase of the percentage of exchangeable Zn. These changes can be interpreted from pedogenic processes. Since these transformations will result in a reduction of the bonding strength, it cannot be excluded, that the decrease of total metal concentrations is partly due to a diagenetic remobilisation of metals from the floodplain deposit. However, Pb concentrations have decreased similar to Cd and Zn, without the respective changes of chemical fractions. Thus, it is suggested that the process of diagenetic release generally is not a significant factor in this environment.

Metal release from tidal Elbe River sediments by a process of "oxidative remobilization" has been described by Kersten (1989). Short (30 cm) sediment cores were taken from a site, where diurnal inundation of the fine-grained fluvial deposits takes place; subsamples were analyzed with sequential extraction according to the methods described in section 5.1. In the upper part of the sediment column, total particulate cadmium content was approximately 10 mg kg\(^{-1}\), whereas in the deeper anoxic zone the total particulate concentration of Cd was 20 mg kg\(^{-1}\). The results of the sequential extractions of the core sediment samples separated at 2-cm levels (Figure 5) indicate, that in the anoxic zone 60-80% of the Cd was associated with the sulfidic/organic fraction. In the upper - oxic and transition - zone the association of Cd in the carbonatic and exchangeable fractions simultaneously increase up to 40% of total Cd. Thus, high proportions of mobile cadmium forms correlate with the reduction in total cadmium contents. This distribution of total and partitioned Cd in the "Heuckenlock" sediment profile suggest that the release of metals from particulate phases into the pore water and further transfer into
biota is controlled by the frequent downward flux of oxygenated surface water. In the oxic zone, Cd is leached from the labile particulate-binding sites, where the predominant mechanism controlling the availability of Cd is adsorption/desorption. With the downward flux of pore water, the mobilized metal moves into the anoxic environment, where Cd is reprecipitated by the formation of sulfidic associations. From the observed concentrations, it would be expected that long-term transfer of up to 50% of the Cd from the sediment subsurface would take place in the anoxic zone located further below the sediment-water interface. By this process of "oxidative pumping" (Kersten & Förstner 1987b) a maximum downward flux of 0.4 g Cd/m² per year can be estimated in the Heuckenlock sediments.

![Graph showing sediment accumulation and Cd partitioning](image)

**Figure 5** Total Concentrations and Partitioning of Cadmium in a Tidal Flat Sediment Profile in the Heuckenlock Area Sampled in 1984 and 1988. Sedimentation Rates were Determined by the 137-Cs-Method. Cd Pore Water Profile was Determined at Low Tide (Kersten, 1989)
5.2.5 Long-Term Prognosis of Metal-Release from Solid Waste

Because of the reasons mentioned above, long-term behaviour prognosis of metals in the environment based on models alone are of limited value. In such cases direct measuring of changes of chemical forms of typical soil and waste constituents at in-situ conditions with respect to interstitial water composition, e.g. by inserting dialysis bags or PVDF sheets containing typical substrates with varying metal concentrations into boreholes.

Because these approaches neither involve reaction-mechanistic nor kinetic considerations, they are of limited value with regard to prediction of long-term effects in waste-deposits. This lack can be avoided by an experimental approach, originally been used by Patrick et al. (1973) and Herms and Brümmer (1978). Metal mobility can be estimated by comparing sequential extraction results before and after treatment of waste material by controlled significant intensivation of relevant release parameters such as pH-value, redox-potential and temperature using an ion-exchanger system for extracting and analysing the released metals at a adequate frequency (Figure 6).

Figure 6 Experimental Design for Long-Term Prognosis of Metal Release (Schoer and Förstner, 1987)
This system was used for the evaluation of the long-term behaviour of metal contaminants (including arsenic, cadmium, thallium and vanadium) in metal oxide residues from heat processing, which were deposited into borrow pits from sand removal along the river Rhine. The way of interaction between the water and the deposit - flow-through at high and flow-by at low permeability of the deposit compared to the surrounding groundwater aquifers; intensive interaction between water and critical components under extreme conditions - which may result from erosion of waste materials - can also be reproduced by the experimental design.

For most elements, the acidity is more effective concerning the release than changes in redox potential. Remobilized element percentages in a typical sample were approximately 20 to 40 % of total concentration for Zn, Co and Cd at pH 5. Temporal release patterns were also different for the individual elements. The experimental data clearly indicated the much reduced mobilisation of metals in the flow-by experiments (sample in a dialysis bag) compared to flow-through conditions. For cadmium, lead and zinc, maximum release during the flow-by experiment was less than 1 % of the flow-through experiment at the same chemical conditions.

The combination of mobilization kinetics and the chemical metal forms enable to predict the long-term release behaviour of metals from the landfill under estimation. For this purpose the "quick-motion" factor of the experimental design has to be evaluated. For zinc under the flow-through conditions at pH 5 and 400 mV, from the total release (437 mg per kg) and the amount of water passing through the landfill material (140 l), an experimental zinc release of approx. 3 mg/l can be calculated. The measured concentrations in the pore-water of the deposition site are between 0.04 mg Zn/l and 1.40 mg Zn/l, in the groundwater just beside the landfill approx. 0.02 mg Zn/l. If all this zinc in the nearby groundwater would have been originating from the landfill ("worst case" assumption), a "black-box-experimental-factor" of 150 can be calculated from the ratio between predicted and measured zinc concentrations. If this factor is multiplied with the duration of the experiment (10 weeks), a time period of nearly 30 years is represen-
ted by the experiment. From solid speciation data it can be concluded, that the release of the rest of "oxalate-bound" zinc would take another 12 experimental weeks; this would be equivalent to nearly 40 years in nature. In total, a time period of at least 50 to 100 years would be covered by the experiment, and a prognosis within this time scale can be drawn from the present results.

6. Demobilization of Metals in Solid Waste Materials

"Geochemical and biological engineering" emphasize the increasing efforts of using natural resources available at the disposal site for reducing negative environmental effects of all types of waste material, in particular of acid mine wastes. Practical examples for improvement of storage quality of metal-containing waste, including measures for recultivation of old and recent mining waste disposal sites and physico-chemical methods to water processing, have been reviewed (Salomons & Förstner, 1988a,b).

Most stabilization techniques aimed for the immobilization of metal-containing wastes are based on additions of cement, water glass (alkali silicate), coal fly ash, lime or gypsum (Calmano, 1988). Generally, maintainance of neutral pH-values beyond favors adsorption or precipitation of soluble metals (Gambrell et al., 1983).

Incorporation in naturally formed minerals, which remain stable over geological times, constitutes favourable conditions for the immobilization of potentially toxic metals in large-volume waste materials both under environmental safety and economic considerations. There is a particular low solubility of metal sulfides, compared to the respective carbonate, phosphate, and oxide compounds (Kersten, 1988). Marine conditions, which are favourable due to the higher production of sulfide ions, in addition, seem to repressing the formation of mono-methyl mercury (Craig & Moreton, 1984). This type of waste deposition under stable anoxic conditions, where large masses of polluted materials are covered with inert sediment became known as "subsediment-deposit"; the first example was
planned for highly contaminated sludges from Stamford Harbour in the Central Long Island Sound following intensive discussions in the U.S. Congress (Morton, 1980). Other advantages of near-shore capped mound deposits (Kester et al., 1983) include the protection of groundwater resources, since the underlying water is saline, and enhanced degradation of organic priority pollutants (Kersten, 1988).

With regard to the immobilization of contaminants in municipal and industrial waste materials the term "final storage quality" has been brought into discussion (Baccini, 1989a). Solid residues with final storage quality should have properties very similar to the earth crust (natural sediments, rocks, ores, soil; Table 7). Treatment includes several possible steps, e.g. assortment, thermal, chemical and biological treatments. In most cases this standard is not attained by simply incinerating municipal waste, i.e. by reduction of

Table 7 Comparison of Inventories of Chemical Components in the Two Landfill Alternatives and in the Earth Crust

<table>
<thead>
<tr>
<th>Reactor Landfill</th>
<th>Final Storage</th>
<th>Earth Crust</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major Solid Constituents</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solid &quot;Inert&quot; Waste</td>
<td>Silicates, Oxides</td>
<td>Quarz, Fe-Oxide Clay, Carbonates</td>
</tr>
<tr>
<td>Putrescible Waste</td>
<td>[Gypsum, NaCl]</td>
<td>(Gypsum, NaCl)</td>
</tr>
<tr>
<td>Grease Trap Waste</td>
<td>(Char)²</td>
<td>Kerogenic Comp.</td>
</tr>
<tr>
<td>Minor Solid Constituents</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organic Micropollutants</td>
<td>Organic Micropol.</td>
<td>-</td>
</tr>
<tr>
<td>Metals in Reactive Chemical Forms</td>
<td>Metal-Rich Minerals</td>
<td>Metals Mainly in Inert Forms</td>
</tr>
<tr>
<td>Dissolved Constituents</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Protons, Electrons</td>
<td>(Protons)</td>
<td>(pH: Acid Rain)</td>
</tr>
<tr>
<td>Organic Compounds</td>
<td>(Organic Residues)</td>
<td>(Humic Acids)</td>
</tr>
<tr>
<td>Dissolved Salts</td>
<td>[Dissolved Salts]¹</td>
<td>(Dissolved Salts)</td>
</tr>
</tbody>
</table>

¹ [Partial Extraction by Pretreatment] ² (Minor Constituent)
organic fractions only. There is, in particular, the problem of easily soluble minerals, such as sodium chloride. Measures before incineration include the separate collection of (organic) kitchen and garden wastes (containing some chlorine and sulfur), which can be transferred into compost; a major decrease of chlorine content, however, would require a significant reduction of PVC in municipal solid waste. After incineration washing of the residues can be performed either with neutral or acidified water. Another possibility is to put the electrostatic precipitator dusts into a thermal process to remove metal like zinc, cadmium and lead as chlorides at high temperatures (>1200°C). These salts should then be used as educts for metal production (Baccini, 1989b).

7. Conclusions

1. Conceptually, "mobility" reflects the flux of metal species in a system of solution/solid interactions, which is influenced by both accelerating and inhibiting factors and processes. Data for description of metal mobility include informations on dominant aqueous species, typical mobilizing/inhibiting system parameters such as pH and pH₂S, and surface properties of the solid phases.

2. Thermodynamic models may give suggestions as to the possible species to expect, but due to the important role of kinetically controlled processes, the actual speciation is often different. Particular difficulties with modeling are found for systems rich in organic matter, due to the lack of information on specific ligands and the reduced reversibility of metal sorption processes.

3. Typical "dynamic" macro-environments are characterized by high-energy mechanical processes, such as bioturbation and dredging activities, by strong chemical gradients, e.g. of redox conditions, and by distinct temporal variations, such as seasonal changes of biological activity in aquatic systems and characteristic successions in metabolic transformations, for example, in waste deposits.

4. In anoxic sediment pore water and landfill leachates precipitation as sulfides is considered as the dominant mechanism limiting the solubility of metals exhibiting so-called "B-character", such as copper, lead, zinc and cadmium. While complexation by natural organic ligands does not seem relevant for most metals except for copper, formation of thio-complexes at excess sulfide concentrations could significantly influence metal mobility.
5. Due to the instability of polluted solid materials, sample handling and storage prior to analysis is problematic. Many of the analytical techniques for solid speciation are handicapped by disruptive preparation techniques which may alter the chemical speciation of inorganic components or lead to loss of analyte before analysis.

6. Simple "standard" leaching tests can be used for easily soluble components such as halides or sulfates, but in most cases are not adequate for assessing mobility of trace metals. With sequential extraction procedures rearrangements of specific solid "phases" can be evaluated prior to its actual remobilisation.

7. Estimation of long-term release of metals from solids can be made using a test procedure, which combines data from column experiments applying controlled intensification of parameters such as pH-value, redox potential and temperature with results from sequential extraction of the contaminated solids before and after exposure.

8. Partitioning studies on materials from core profiles are particularly useful, since they provide information on relative variations of elemental phases irrespective of the method applied, and thereby an insight into diagenetic processes taking place after deposition of the sediment or solid waste components.

9. Changes from reducing to oxidizing conditions in sediments, which involve transformations of sulfides and a shift to more acid conditions, increase the mobility of critical metals. These results demonstrate the problematic effect of dispersing anoxic waste materials in ecologically productive, high-energy nearshore, estuarine, and inlet zones.

10. Increased concentrations of metals have been observed for in leachates during the acidogenic phase of landfill evolution at low pH-values. Recent data from experiments on organic-rich wastes suggest that also subsequent to the methanogenic phase transition from anoxic to oxic conditions could affect a lowering of pH, which in turn could influence mobility of metals like zinc and cadmium. Such effects, together with the long-term emissions of nitrogen compounds, will pose additional questions as to the reliability of "reactor landfills" in the management of municipal wastes.

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