### **Analysis of Heavy Metal Contaminated Soils**

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**Abstract:** Heavy metal contaminated soils can be a long-term environmental concern and potential financial liability to landowners. Hence, the assessment of heavy metal contaminated soil has received much attention in the last few decades. For a reliable and cost-efficient investigation, a well-planned sampling strategy, appropriate selection and implementation of analytical methods, and careful interpretation of results are prerequisites. This paper presents a brief overview of the preparatory, sampling and analytical stages of an investigation of heavy metal contamination of soils, particularly in the analysis of heavy metal contaminated soils.

Keywords: Soil; Heavy metals; Contaminated land; Analysis; Assessment.

#### Introduction

Land degradation has become a major environmental issue following the rapid industrial development that has taken place in many parts of the world in recent years. Elevated concentrations of heavy metals in soils are of potential long term environmental and health concerns because of their persistence and cumulative

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tendency in the environment, and their associated toxicity to biological organisms (Nriagu, 1979 & 1988; Nriagu and Pacyna, 1988; Thornton, 1993). Furthermore, restricted use of contaminated lands and the costs of soil remediation also pose liabilities and financial burdens on landowners and other stakeholders. As a consequence, environmental assessment of lands with respect to heavy metal contamination, and identification its environmental and health implications have become increasingly important in environmental research.

For a reliable and cost-effective investigation of heavy metal contamination of soils, a well-planned sampling strategy, appropriate selection of analytical methods, and careful interpretation of results are of vital importance. In this paper, an overview of the investigation of heavy metal contaminated soils is given, particularly on analysis of heavy metal contaminated soils. The primary objectives of this overview are to discuss the various stages involved in the investigation of heavy metal contaminated land for site engineers and other related personnel, especially on the sampling and analytical methods involved, as shown in Fig. 1. A study on heavy metal contamination of urban soils in Hong Kong is provided as a case example.

#### **Preparation for the assessment**

Like other kinds of environmental assessment, it is important to understand the specific purposes of the investigation. Therefore, at the initiation of the investigation, its primary objectives must be clearly defined and stated, since the objectives will be used as guidelines according to which all subsequent sampling and analytical procedures will be developed. For instance, if the goal of the investigation is to determine whether the soils are contaminated with heavy metals, analysis of the heavy metal concentrations of the soils will be adequate, and sampling of the soils will be relatively simple. However, if knowledge of the spatial distribution of heavy metals in soils is also sought, a systematic sampling approach will be required. In the preparatory stage, site information, such as soil type, parent materials, topography, and surrounding human activities, should also be collected. This information will assist planning of the sampling strategy and interpretation of analytical results. Furthermore, it is also important to gather all relevant and applicable legislative regulations, such as soil regulatory standards, during the preparatory stage of the investigation for assessment and clean-up guidelines. Recognition of these legal and regulatory principles will ensure proper evaluation of soil contamination and fulfillment of necessary clean-up requirements (Jensen and Bourgeron, 2001; Jain, 2002)

#### Soil sampling and preparation

#### Soil sampling

In general, soil sampling strategies can be grouped into three major categories: random, systematic and stratified sampling methods. The random sampling strategy is the simplest of the three, where soil samples are collected randomly and stochastically independently across the site of interest. It can be used as a quick sampling program of a pilot study. A major disadvantage of this sampling strategy is that soil samples may not represent the whole study site. Therefore, this sampling strategy is usually employed in relatively homogenous sites and applicable to investigations where the major objective is to determine whether heavy metal concentrations of the soils are

elevated above background and/or legislative standards (Scholz et al., 1994; Petersen and Calvin, 1996).

In a relatively heterogeneous site, stratified and systematic sampling strategies are required, as they are able to produce a more detailed and accurate description of a given site with respect to the spatial and vertical distribution of heavy metals in the soil. According to Petersen and Calvin (1996), in a stratified sampling program, the population is broken into a number of subgroups, and a simple random sample is taken from each subgroup. This sampling strategy allows a detailed study on each of the subgroups and increases the precision and accuracy of the estimate over the entire population. In a systematic sampling, soil samples are collected in a systematic manner, such as at a regular distance from each other across the study area, and some of the fixed sampling grids, including the bottle rack grid and the rectangular grid, are illustrated in Scholz et al. (1994). The systematic sampling strategy is often employed in the geochemical mapping of heavy metals, since it enables detailed characterization of the spatial distribution of heavy metals in a large region (Appleton and Ridgeway, 1993; Xie and Cheng, 2001).

Other factors that should also be considered during soil sampling include sampling density, sampling depth and the use of composite soil samples. In an ideal situation, the larger the number of soil samples collected, the better the sample population can reflect the conditions of the site. However, in reality, sampling density is often a compromise between representativeness of the site and the availability of resources. Sampling depth is determined based upon the purpose of the investigation and/or the specific requirements of a regulatory guideline. Also, in cases where heavy metal contamination of subsurface soils is suspected or groundwater contamination is a concern, sampling of soil profiles or subsurface soils may be necessary. The two common approaches are metric (depth-related) sampling and soil –horizon-related sampling. In general, the metric sampling approach is used for the purposes of screening analysis of potentially contaminated land. In more detailed environmental assessments, a horizon-related sampling approach is recommended (Paetz and Crößmann, 1994). The use of composite soil samples offers the advantage of increased accuracy/representativeness through the use of large numbers of sampling units per sample. A composite soil sample is formed by combining equal portions of individual sub-samples. It is based on the fundamental assumption that analysis of the composite sample yields a valid estimate of the mean, which is obtained by averaging the results of analysis from each of the sampling units contributing to the composite (Tan, 1996). Ultimately, a suitable sampling strategy should maximize the representativeness of the study area with a minimal number of soil samples and resources to be utilized, while meeting the requirements of the investigation.

It is suggested that, in a preliminary investigation, surface soil samples may be collected randomly or systematically at a low sampling density. If contamination of subsurface soils is suspected, soil profiles may also be obtained. Analytical results of this preliminary assessment can provide an initial confirmation of the contamination. If signs of contamination are found, a more comprehensive systematic and strategical sampling program can be employed for the next stage of the study. In general, a sampling strategy should be tailored specifically to the intended study area to reflect the objectives and site conditions.

#### Soil sample preparation

To facilitate the dissolution and subsequent analysis of heavy metals in soils, drying, sieving and grinding of the soil samples are usually required. The collected soil samples are air- or oven-dried to remove moisture. For non-volatile heavy metals, such as Cd, Cu, Pb and Zn, the soils can be air- or oven-dried at temperatures between 50 and 105°C. Oven-drying is preferred since it can accelerate the speed of drying and limit changes of the sample condition due to microbial activity (Paetz and Cröβmann, 1994). For some volatile metals, e.g. Hg, soils should be air- or freeze-dried to minimize loss of the volatile metals.

After drying, the soil samples are usually sieved to remove coarse debris and rubble (>2.0mm). A non-metallic sieve is used to avoid contamination. This fraction of the soil with a particle size of <2.0mm, which is commonly designated as fine earth, is used for most chemical analyses. For most heavy metal analyses, the soil samples should be milled to fine particles (<250  $\mu$ m) manually or mechanically in a mortar with a pestle to increase homogeneity (Paetz and Crößmann, 1994). Commercially available mechanical mills are constructed of a wide variety of materials, including chrome steel, tungsten carbide and agate. Chrome steel has good wear resistance but contributes significant amounts of Fe, Cr, Mn, Ni, Co and V. Tungsten carbide is very hard and usually causes less contamination, but still contributes W and Co. Among the various types of materials available, agate, which is a natural silicate material, is recommended due to its hardness and the negligible contribution of metallic contaminants. However, it is far less hard-wearing than steel, prone to fracture, and more expensive (Miles, 1999).

#### Analyses of heavy metal contaminated soils

Appropriate selection of analytical parameters and careful implementation of corresponding analytical procedures are critical to the accuracy of the analytical results and the fulfilment of the ultimate objectives of an investigation of heavy metal contaminated soils. Total heavy metal concentrations of the soils are generally assessed for regulatory purposes, since soil contamination with heavy metals is evaluated based on absolute heavy metal concentrations in major soil regulatory guidelines, such as the Canadian Environmental Quality Guidelines (CCME, 1997) and the Netherlands Soil Contamination Guidelines (Department of Soil Protection, the Netherlands, 1994). It is increasingly acknowledged that chemical speciation of heavy metals plays an influential role in governing the fate and ecological toxicity of contaminants (Jackson et al., 1993; Sauve et al., 1997; Traina and Laperche, 1999; Li et al., 2000). Therefore, determination of the chemical speciation of heavy metals is often desired for assessing the potential ecological and health effects of heavy metals at a contaminated site. In addition, isotopic analysis of heavy metals, particularly Pb, has been used in the investigation of heavy metal contaminated soils to identify anthropogenic inputs and to distinguish possible contaminant sources.

#### Determination of the total heavy metal concentrations of soils

Elemental concentrations of soils and rocks can be determined non-destructively by neutron activation analysis (NAA) and X-ray fluorescence spectroscopy (XRFS), and destructively by inductively coupled plasma (ICP) and atomic absorption spectrometry (AAS) after the dissolution of heavy metals in solution. The selection of a suitable analytical method is often governed by sample type, target elements, and laboratory conditions. The NAA requires access to a research nuclear reactor or other neutron source, and therefore it is not widely used (Helmke, 1996). XRFS operates by measuring the characteristic secondary radiation emitted from a sample that has been excited with an X-ray source. It is rapid, reliable, non-destructive and often quicker than conventional chemical analysis techniques (Karathanasis and Hajek, 1996). More commonly, heavy metal concentrations of soils are determined by the more conventional analytical instruments ICP and AAS (Wright and Stuczynski, 1996).

In order to analyze heavy metal concentrations of soils by ICP and AAS, decomposition of the soils and the dissolution of heavy metals in solution are required by using strong acid digestion or fusion agents. Strong acid digestion is probably the most commonly used decomposition technique for the determination of heavy metal concentrations of soils due to low-cost, readily available inorganic acids and the low salt content of the digested solutions. In general, strong acid digestion requires the use of concentrated inorganic acids, such as HF, HNO<sub>3</sub>, HCl, HClO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>, to decompose and dissolute the soil matrix into a solution form in conjunction with high temperatures and, sometimes, high pressure (e.g. microwave digestion). The use of inorganic acids is highly dependent on the soil type and the target metals to be analyzed. Complete dissolution of silicate minerals can only be achieved using HF. Therefore, HF must be handled in polytetrafluoroethylene (Teflon) rather than a glass apparatus, and strong acid digestion using HF must be conducted in Teflon or platinum containers and specially-designed fume cupboards. In the absence of HF, strong acid digestion using other inorganic acids, sometimes referred to as pseudo acid digestion, can be performed in glass containers, e.g. beakers and test tubes. For instance, concentrated HCl and HNO<sub>3</sub> may sometimes be used independently, and capable of readily dissolving carbonates when concentrated and hot. Since HNO<sub>3</sub> is preferred for the dissolution of sulphides, tellurides and arsenides, and dissolution of iron and manganese oxides, borates and sulphates other than barite is better achieved by HCl, these two acids are commonly used together as *aqua regia* (HCl/HNO<sub>3</sub>: 3/1 by volume) to attack a wide range of soil and geological materials (Hossner, 1996; Miles, 1999).

Briefly, soil samples are weighed into glass or Teflon containers. One or more types of strong acid are added to the samples. The mixtures are heated on a heating block or in a microwave until the soils completely dissolved. The residual solutions are then filtered to remove solid residuals and made to a final volume using dilute acid, usually 2-5% HNO<sub>3</sub> or HCl. In cases where the solutions are to be analyzed by ICP-MS, weak HNO<sub>3</sub> should be used to avoid polyatomic interferences induced by Cl. It should be noted that volatile elements, e.g. Hg and Se, may be lost during the heating process. Extraction of these volatile elements from the soils can be achieved either at low-temperature acid digestion or by microwave digestion in enclosed containers. Concentrations of these volatile elements can be determined alternatively by the cold-vapor method and/or hydride methods (Miles, 1999).

Microwave digestion is performed in closed Teflon vessels heated with microwave radiation, which prevents the loss of volatile compounds. It is also comparatively time-efficient and capable of decomposing resistant solids using a smaller volume of acid. However, owing to the use of Teflon vessels, the initial cost involved in the microwave digestion system is usually higher than that of the heating block method. Fusion agents are normally employed for decomposition of substances, such as cassiterite, chromite, corundum, rutile, spinel, zircon, and tourmaline, that are insoluble in acids or resistant to acid attack. Its decomposing effect is mainly by high fusion temperate and fusion agents. The commonly used agents for soil and mineral analyses include anhydrous sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) and sodium peroxide (Na<sub>2</sub>O<sub>2</sub>). However, dissolution by the acid digestion method is usually preferred to fusion decomposition, owing to the lower concentration of extraneous materials in the final solution and less interference in the determination of the solution concentrations of elements by AAS and ICP (Hossner, 1996; Miles, 1999). The advantages and disadvantages of strong acid digestion, fusion agents and strong acid digestion by microwave are given in Table 1. A comparison of the conventional analytical instruments ICP, FAA, and GFAA is given in Table 2.

#### Determination of chemical partitioning of heavy metals

Heavy metals exist in many chemical forms in soils. Many extraction procedures are available to differentiate the various forms of metals in soils. Some methods are aimed at evaluating potential bioavailability (e.g. extraction methods by 0.1 N HNO<sub>3</sub>, EDTA, DTPA, and other ion exchange reagents), while others (e.g. sequential chemical extractions) may be used to examine the possible chemical speciation of heavy metals, from which solubility, bioavailability and chemical associations may be estimated (Tessier et al., 1979; Gibson and Farmer, 1986; Mahan et al., 1987; Li et al., 1995; Sun et al., 2001).

Sequential chemical extraction is used to operationally define heavy metals into different geochemical phases, usually in order of increasing stability. A five-step sequential chemical extraction, commonly referred to as Tessier's method, is probably one of the most widely used sequential chemical extraction methods (Tessier et al., 1979), and defines metals into five fractions with increasing stability through the use of progressively reactive extractants. The extracted metals from these five consecutive steps are operationally defined into five geochemical fractions: 1) readily soluble and exchangeable, 2) carbonate-bound, specifically adsorbed, and weak organic and inorganic complexes, 3) bound to iron and manganese oxides, 4) bound to stable organic and/or sulphide complexes, and 5) residual fractions containing primary and secondary minerals held within their crystal structure, respectively. It is acknowledged that the reactivity and potential bioavailability of heavy metals generally increases with increasing solubility. Thus, the first two forms are usually considered the two most mobile forms of metals in soils, and are potentially bioavailable to plants and animals. The last three are relatively immobile and stable, but may sometimes become mobile and bioavailable with changes of soil conditions.

#### Isotopic analysis of heavy metals in soils

Revelation of the origin of the contaminants and, possibly, fractional contributions of different sources can sometimes be achieved through the use of isotopic analysis of heavy metals. In particular, isotopic analysis of Pb is well established and frequently applied in environmental studies of heavy metals. Pb isotope as a tracer has been documented in many publications (Farmer and Eades, 1996; Gelinas and Schmit, 1997; Marcantonio et al., 1998; Munksgaard et al., 1998; Marcantonio et al., 1999; Hansmann and Koppel, 2000; Zhu et al., 2001).

In the environment, Pb has four isotopic forms, Pb<sup>204</sup>, Pb<sup>206</sup>, Pb<sup>207</sup> and Pb<sup>208</sup>, and the relative abundance of these natural isotopes are 1.4%, 24.1%, 22.1%, and 52.4% respectively. Among the four Pb isotopes, only <sup>204</sup>Pb is non-radiogenic and therefore remains stable over time. The other three radiogenic isotopes, <sup>206</sup>Pb, <sup>207</sup>Pb, and <sup>208</sup>Pb, are derived from <sup>238</sup>U, <sup>235</sup>U, and <sup>232</sup>Th respectively. The Pb isotope composition of a given sample therefore depends on the age and U/Pb and Th/Pb ratios of the parent material(s) from which the Pb is derived. Because of these inherited isotopic characteristics of Pb in the environment, Pb isotopic composition has become a useful tool in anthropogenic Pb detection and source identification (Sturges and Barrie, 1987; Munksgaard et al., 1998; Hansmann and Koppel, 2000).

The inherited differences in isotopic ratios, usually indicated by Pb<sup>206</sup>/Pb<sup>207</sup>, between natural and anthropogenic Pb sources are commonly utilized to distinguish and/or identify sources of the contaminants in soils as well as other environmental compartments. The <sup>206</sup>Pb/<sup>207</sup>Pb ratios of naturally-derived Pb, e.g. rock-released Pb, are usually higher than 1.20 (Sturges and Barrie, 1987; Hansmann and Koppel, 2000). The <sup>206</sup>Pb/<sup>207</sup>Pb ratios of anthropogenic Pb derived from ore bodies, ranging from 0.92 to 1.20, are usually low in comparison with those of natural origin. Usually, the <sup>206</sup>Pb/<sup>207</sup>Pb ratios of anthropogenic Pb derived from lead sulphide ore deposits in the U.S., Canada and Australia are 1.213-1.221, 1.148-1.153 and 1.04 (Sturges and Barrie, 1987).

Due to the subtle differences in isotopic ratios between various Pb sources, isotopic analysis of Pb requires careful sample preparation and treatment and the use of advanced analytical instruments, such as thermal ionization mass spectrometry (TIMS) and inductively coupled plasma – mass spectrometry (ICP-MS) (Halicz et al., 1996).

The potential usefulness of isotopic analysis of other heavy metals, e.g. Cu and Zn, has yet to be fully explored (Maréchal et al., 1999).

#### Quality control and assurance

During sampling and laboratory analysis of heavy metal contaminated soils, care should be devoted to prevent sample contamination and to ensure the reliability and quality of analytical results. First of all, the use of metallic tools should be avoided whenever possible. Soil samples should be collected using tools made of stainless steel and stored in non-metallic containers, such as glass bottles or polyethylene bags, at  $4^{\circ}$ C prior to laboratory treatment. All glass- and plastic-ware should be soaked in weak inorganic acid, e.g. 10% (v/v) nitric acid, and rinsed thoroughly with distilled and deionized water before use, to ensure that there is no contamination of the laboratory accessories.

In order to provide valid and reliable data in a timely manner, a quality control system must be implemented throughout the analytical process. Quality control is defined as a system of procedures and practices which result in an increase in precision and a decrease in bias. The use of duplicate analysis, spiked samples, standard reference materials, and QC check samples are all mechanisms used to demonstrate the control of quality (Klesta and Bartz, 1996). In general, to detect contamination and evaluate the reproducibility and effectiveness of the analytical procedures, procedural blanks, duplicates and certified standard reference materials, such as those offered by the National Institute of Standards & Technology (NIST), should be included in the analytical program.

#### A case study of heavy metal contamination of urban soils in Hong Kong

In the urban environment of Hong Kong, where population and traffic densities are high, human activities exert tremendous pressure on the environment. Previous studies have shown that the urban soils of Hong Kong are enriched with heavy metals, including Cd, Cu, Pb and Zn (Lau and Wong, 1982; Wong, 1996; Wong and Mak, 1997; Chen et al., 1997; Li et al., 2001). In order to further understand urban soil contamination with heavy metals in Hong Kong, a study was conducted to evaluate Pb and Zn contamination of urban soils, to examine chemical partitioning of the heavy metals and to distinguish natural and anthropogenic Pb in the soils. Composite urban soil profiles between 0 and 20 cm at 10 cm intervals were collected from an urban park and a vegetated road divider, Site A and Site B respectively, in Kowloon using a stainless steel auger. A transaction line strategy was employed in the pilot study. At Site A, each composite soil sample was made of 9 subsamples that were collected at 1m intervals from a 2m×2m sampling grid. Because of the elongated shape of Site B, one composite soil sample was made of 6 subsamples collected in a straight line along the study area.

For the analysis of heavy metal concentrations, chemical partitioning and the Pb isotopic composition of the soils, the soils were dried at 50°C and sieved through a 2.0 mm polyethylene sieve. Since high Pb and Zn concentrations of the soils were anticipated, a porcelain mortar with a pestle was used to mill the soils. For heavy metal concentrations, the prepared soil samples were digested in concentrated HNO<sub>3</sub> and HClO<sub>4</sub> (4:1) in pre-cleaned test tubes in an aluminum heating block. The acid digestion was performed in open-vessel test tubes at temperatures ranging from 50°C to 190°C.

The solutions were then made into a final volume of 10.0ml using 5% (v/v) nitric acid and stored in polyethylene tubes for the determination of heavy metal concentrations by ICP-AES. For quality assurance, blank samples and replicates, representing 10% and 20% of the sample population respectively, were inserted into the analytical program to detect contamination and to evaluate the reproducibility of the results. Furthermore, a standard reference material, representing 10% of the sample population, was also included to evaluate and monitor the effectiveness of the analytical method. The analytical results are shown in Table 3.

Some of the solutions obtained from the acid digestions were extracted and analyzed for Pb isotopic composition using ICP-MS. Due to the high sensitivity of ICP-MS, dilution of the solutions with 5% high-purity HNO<sub>3</sub> was necessary. A stringent quality control program was also implemented, in which a standard reference material, NIST Common Pb Isotope 981, was used for calibration and quality control. The Pb<sup>206</sup>/Pb<sup>207</sup> ratios of the soils are given in Table 3. In addition, the heavy metals of the urban soils were operationally defined into five geochemical fractions using a modified Tessier's method (Li et al., 1995). Quality control measures similar to those used in acid digestion were also implemented. Although some variability was observed among the individual samples, the averaged partitioning distribution of each of the soil groups was used and is shown in Fig. 2.

Since Hong Kong has not established its own soil regulatory standard, the Netherlands Soil Contamination Guidelines (Department of Soil Protection, the Netherlands, 1994) were used. The Guidelines contain a set of target (T) values, and a set of intervention (I) values. Heavy metal concentrations below the T values indicate that the concentrations are within the maximum background levels, and heavy metal concentrations exceeding the T values suggest possible soil contamination. If the concentrations exceed the I values, undertaking of an immediate investigation and possible remediation will be demanded. A comparison of the Zn and Pb concentrations of the urban soils with the Guidelines indicated that the Pb and Zn concentrations of the soils at the two investigation locations exceeded the corresponding T values recommended by the Guidelines. Thus the soils were considered to be contaminated with Pb and Zn. It was also observed that the contamination tended to be more serious in the surface layer (0-10cm) than in the subsurface layer (10-20cm), suggesting surface enrichment with the contaminants. The Pb<sup>206</sup>/Pb<sup>207</sup> ratios of Pb in the soils ranged from 1.13 to 1.18. The comparatively low Pb<sup>206</sup>/Pb<sup>207</sup> isotopic ratios of Pb in the surface layer (0-10cm) further substantiated anthropogenic Pb inputs into the soils. Since both of the study areas were in close vicinity to high traffic volumes (annual average daily traffic > 40,000 vehicles per day), it was strongly indicated that some of the excessive Pb in the soils could be attributed to gasoline Pb in the past.

In general, the analytical results of the sequential chemical extraction indicated that the Pb and Zn in the soils were primarily associated with the Fe-Mn oxide fraction and secondarily with the carbonate and residual fractions, and the Pb and Zn in the exchangeable fraction represented small percentages of the total metal contents (see Fig. 2). Although the results suggest that large percentages of Pb and Zn were relatively stable in soils, the relatively significant associations between the contaminants and the carbonate fraction imply that the contaminants in this fraction might be moderately soluble and potentially bioavailable, representing a potential environmental concern.

#### Conclusions

A reliable and cost-effective investigation into heavy metal contaminated soils should consist of three essential components. The first is clearly defined objectives and adequate background research, where relevant legislative and site information is gathered and thoroughly studied. The second component is a well-designed sampling plan, from which soil samples representative of the study site are collected in such a manner that the objectives can be achieved. The third component is the selection of appropriate analytical parameters and methods and careful implementation the methods to obtain accurate and reliable results.

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| Dissolution  | Advantages  | Disadvantages  |
|--------------|---|--|
| Method       |   |  |
| Acid         | Inexpensive, semirapid, high-purity acids available, low salt       | Loss of volatiles (e.g., Hg & Se) from open crucible, attack     |
|              | matrix in final solution, can remove Si as $\mathrm{SiF}_4$ in open | glass (HF), corrosive and potentially explosive $(HClO_4)$       |
|              | crucible  | acids  |
| Fusion       | No corrosive and potentially explosive acids, Teflon-lined          | High salt matrix in final solution, high potential for           |
|              | digestion bombs not required  | contaminants in fusion salts, relatively slow, loss of volatiles |
|              |   | (e.g., As, Hg, Se, Tl), expensive crucibles (Pt)                 |
| Microwave    | Rapid, high-purity acids available, low salt matrix in final        | Equipment expensive, loss of volatiles from open containers,     |
|              | solution  | corrosive acids, low recovery of Cr and Ti                       |
| Erom Hogenor | (1006)  |  |

# **Table 1.** A Comparison among the Strong Acid Digestion, Microwave Digestion and Fusion Agents

From Hossner (1996).

| Factor                       | ICP                                | FAA  | GFAA                           |
|------------------------------|------------------------------------|--|--------------------------------|
| Detection limits             | Best for refractory elements, rare | Similar to ICP, but better for                               | Generally 10-100 times more    |
|                              | earths and elements with           | group I metals and selected                                  | sensitive than FAA or ICP when |
|                              | resonance lines below 190 nm       | esonance lines below 190 nm volatile elements Na, K, Pb, Zn, |                                |
|                              | such as P and S                    | Cd   |                                |
| Linear concentration range   | $10^4 - 10^6$                      | 10 <sup>3</sup>  | 10 <sup>2</sup>                |
| Within run precision         | 0.3-2% RSD                         | 0.1-1% RSD   | 0.5-5% RSD                     |
| Interferences:               |                                    |  |                                |
| Chemical                     | Lowest                             | Intermediate   | Highest                        |
| Spectral                     | Highest                            | Lowest   | Intermediate                   |
| Ionization                   | Lowest                             | Highest  | Intermediate                   |
| Speed of standardization and | Most rapid for 6 or more           | rapid for less than 6 elements per                           | Slow                           |
| analysis                     | elements per sample                | sample   |                                |
| Cost: Initial                | Highest                            | Lowest   | Intermediate                   |
| Operating                    | Highest                            | Lowest   | Intermediate                   |
| Other factors                | Does not use combustible gases     | Uses combustible gases and                                   | Does not use combustible gases |
|                              | and can be used for unattended     | cannot be left unattended                                    | and can be used for unattended |
|                              | overnight operation                |  | overnight operation            |

**Table 2.** A Comparison among ICP, FAA and GFAA

From Wright and Stuczynski (1996).

| <b>Table 3.</b> Zh and Po concentrations and Po/ Po ratios of soils at Site A and B |                 |   |                  |                  |                                      |  |  |  |
|---|-----------------|---|------------------|------------------|--------------------------------------|--|--|--|
|   | Soil depth (cm) | N | Zn conc. (mg/kg) | Pb conc. (mg/kg) | <sup>206</sup> Pb/ <sup>207</sup> Pb |  |  |  |
| Site A  | 0-10            | 4 | 318 ± 139        | $249\pm95.8$     | $1.169\pm0.027$                      |  |  |  |
|   | 10-20           | 4 | $203\pm131$      | $235\pm101$      | $1.178\pm0.036$                      |  |  |  |
| Site B  | 0-10            | 2 | $645 \pm 128$    | $185\pm20.5$     | $1.131\pm0.008$                      |  |  |  |
|   | 10-20           | 2 | $172\pm48.1$     | $85.3 \pm 18.4$  | $1.160\pm0.013$                      |  |  |  |
| T value*  | -               | - | 140              | 85               | -                                    |  |  |  |
| I value*  | -               | - | 720              | 530              | -                                    |  |  |  |

**Table 3.** Zn and Pb concentrations and  ${}^{206}$ Pb/ ${}^{207}$ Pb ratios of soils at Site A and B

\* The Netherlands Soil Contamination Guidelines (1994)

## **Stage I. Preparation**

- Q1. What are the major objectives of the investigation?
- Q2. What are the site conditions (e.g. soil type, topography & surrounding human activities)?
- Q3. What are the relevant and applicable legislative regulations and soil standards?

## Stage II. Soil sampling and processing

- Q1. What type of sampling strategy should be used?
- Q2. How about sampling density, sampling depth and sample quantity?
- Q3. How are the collected samples prepared?

## Stage III. Soil analyses

- Q1. What kind of analytical parameters are required?
- Q2. What kind of analytical methods should be used?
- Q3. What kind of quality control measures should be taken?

Fig. 1. The various stages of an investigation into heavy metal contaminated soils



Fig. 2. Chemical partitioning of Pb and Zn in urban soils at Sites A and B.