Wangzhao Zhu
ADVANCED INDUCTIVELY COUPLED PLASMA
MASS SPECTROMETRY ANALYSIS OF RARE EARTH ELEMENTS
ENVIRONMENTAL APPLICATIONS
Advanced Inductively Coupled Plasma Mass Spectrometry Analysis of Rare Earth Elements:

*Environmental Applications*

DISSERTATION
Submitted in fulfilment of the requirements of the Board for Doctorates of Delft University of Technology and the Academic Board of the International Institute for Infrastructural, Hydraulic and Environmental Engineering for the Degree of Doctor to be defended in public on Monday, 22 November 1999 at 10:30 h

by

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This research was funded by the TNO Institute of Environmental Sciences, Energy Research and Process Innovation, Delft/Apeldoorn, the Netherlands.

Dr ir E.W.B. de Leer of the National Metrology Institute of the Netherlands and Dr M. Kennedy of IHE made invaluable contributions to this research as mentors.

The project was carried out in the TNO Institute of Environmental Sciences, Energy Research and Process Innovation, Delft/Apeldoorn, the Netherlands. The work of Chapters 5 and 7 were a co-operation with the Water Quality Research Center, Beijing, China and the Zhongshan University, China respectively. The work of Chapter 8 was a co-operation with AB-DLO, Haren, the Netherlands.

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Published by
A.A.Balkema, P.O. Box 1675, 3000 BR Rotterdam, Netherlands
Fax: +31.10.4135947; E-mail: balkema@balkema.nl; Internet site: http://www.balkema.nl

A.A.Balkema Publishers, Old Post Road, Brookfield, VT 05036-9704, USA
Fax: 802.276.3837; E-mail: info@ashgate.com

ISBN 90 5410 422 8
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Printed in the Netherlands
To Yanling

To my parents
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Chapter 1

General Introduction

Abstract

The Rare Earth Elements (REEs), (La.,Lu), Y and Sc, show similarities in chemical behavior. They find increasing application in industry, and are also applied in agriculture. Their name is misleading, since they were formed in huge quantities during nucleosynthesis in the universe system. Ever since then, their similarity made them stay mostly together, and the ratios of their individual concentrations in for instance soil samples still largely reflect their primary ratios. However, due to geological, biological and industrial processes and mining not only their total concentrations differ, but the individual element ratios often exhibit strong deviations from their primary ratios. Knowing not only total REE concentrations, but also these deviations is the key to understanding these processes, and is also necessary to assess for instance the environmental effects of REEs.

The fractionation of the REEs can only be determined when analytical tools are available which are fast, cheap, reliable and sensitive. As well as providing individual element concentration data, they should be suitable for the relevant sample types (soil, airborne particles, (sea) water). Also for control of industrial separation and purification of REEs, such analytical tools are required. Among the techniques available, inductively coupled plasma mass spectrometry (ICP-MS) is an excellent candidate provided that certain drawbacks are minimized. Among these are spectral overlap, matrix effects and too high detection limits.

The aim of this work was to develop two auxiliary techniques to overcome two major current drawbacks, and to investigate whether the improved ICP-MS allows conclusions to be drawn on REE fractionation in environmental samples. First, a mathematical correction algorithm was developed which corrects for spectral
overlaps. Secondly a sample preconcentration method based on ion exchange was worked out. Studies on Yangtze river sediment samples, on atmospheric particulate matter in The Netherlands, and on Chinese and Dutch soils were performed. The leaching behaviour of various types of samples (sand, clay, peaty) was studied as a function of pH in a batch set-up as well as in a column set-up. In the last chapter the results are evaluated.

1.1. Chemical and physical properties of REEs

REEs comprise lanthanum (La, atomic number 57), the other lanthanides Ce-Lu (atomic numbers 58-71), yttrium (Y, atomic number 39) and scandium (Sc, number 21), see Figure 1.1. As in many REE studies, Sc is taken separately or not all at all taken into account in this work, unless indicated otherwise. The set of REEs may be divided into two groups: the light rare earth elements (Sc, La, Ce, Pr, Nd, Pm, Sm, Eu) and the heavy rare earth elements (Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), with Y having a separate position (Henderson, 1984).

In particular the REEs (La through Lu) possess similar physical and chemical properties and are therefore difficult to separate. Their common properties are associated with their particular atomic structure. Each has two outer electrons and eight or nine in the next inner shell (Schijf, 1992). The configurations of outer electrons for REE atoms and REE$^{3+}$ ions are given in Table 1.1. The addition of electrons to the inner shells makes little change in many of their physical and chemical properties. All REEs are relatively soft and malleable as pure metals, and have a bright silver lustre. When finely divided, the metal powder oxidizes quickly when exposed to air. When present in solid lumps, the metal will not undergo spontaneous combustion, but will oxidize slowly, comparable to the rusting of other metals. Because of the similarities in the chemistry of REEs, many authors discuss the characteristics of the REEs as a group. Within this group, however, there are substantial differences between the individual REEs and their compounds (Bulman, 1988). Some of the REEs exhibit more than one oxidation state, but all commonly favour the (III) oxidation state. Most REEs form REE$^{3+}$ ions by losing two electrons from the 6s shell and one electron from the 4f shell. However, for La, Ce, Gd, and Lu the third electron resides in the 5d shell and these REEs therefore have a significantly lower third ionization potential. In nature, all REEs strictly occur in the (III) oxidation state, except Ce and Eu, which also occur in the (IV) and (II) oxidation state, respectively (Schijf, 1992).
The lanthanide promethium (Pm, atomic number 61) has no stable isotopes, only radioactive isotopes with half-lives shorter than 18 year. Thus, this element is not considered any further in this study.

<table>
<thead>
<tr>
<th>Sc</th>
<th>Rare Earth Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>(REEs)</td>
</tr>
<tr>
<td>Y</td>
<td>Light REE</td>
</tr>
<tr>
<td>39</td>
<td>Heavy REE</td>
</tr>
<tr>
<td>La</td>
<td>Ce</td>
</tr>
<tr>
<td>57</td>
<td>58</td>
</tr>
</tbody>
</table>

Lanthanides

Sc: Scandium  
Y: Yttrium

La: Lanthanum  
Ce: Cerium  
Pr: Praseodymium

Nd: Neodymium  
Pm: Promethium  
Sm: Samarium

Eu: Europium  
Gd: Gadolinium  
Tb: Terbium

Dy: Dysprosium  
Ho: Holmium  
Er: Erbium

Tm: Thulium  
Yb: Ytterbium  
Lu: Lutetium

**Figure 1.1.** Rare earth elements.
### Table 1.1. Configuration of outer electrons of REE atoms and REE $^{3+}$ ions (Schijf, 1992).

<table>
<thead>
<tr>
<th>REE</th>
<th>Z</th>
<th>Configuration of outer electrons</th>
<th>Ion radius</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Atom 4f 5s 5p 5d 5f 6s Ion 4f 5s 5p Å</td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>57</td>
<td>2 6 1 2 2 6</td>
<td>1.06</td>
</tr>
<tr>
<td>Ce</td>
<td>58</td>
<td>1 2 6 1 2 2 6</td>
<td>1.03</td>
</tr>
<tr>
<td>Pr</td>
<td>59</td>
<td>3 2 6 2 2 2 6</td>
<td>1.01</td>
</tr>
<tr>
<td>Nd</td>
<td>60</td>
<td>4 2 6 2 3 2 6</td>
<td>0.995</td>
</tr>
<tr>
<td>Pm</td>
<td>61</td>
<td>5 2 6 2 4 2 6</td>
<td>0.979</td>
</tr>
<tr>
<td>Sm</td>
<td>62</td>
<td>6 2 6 2 5 2 6</td>
<td>0.964</td>
</tr>
<tr>
<td>Eu</td>
<td>63</td>
<td>7 2 6 2 6 2 6</td>
<td>0.950</td>
</tr>
<tr>
<td>Gd</td>
<td>64</td>
<td>7 2 6 1 2 7 2 6</td>
<td>0.938</td>
</tr>
<tr>
<td>Tb</td>
<td>65</td>
<td>9 2 6 2 8 2 6</td>
<td>0.924</td>
</tr>
<tr>
<td>Dy</td>
<td>66</td>
<td>10 2 6 2 9 2 6</td>
<td>0.908</td>
</tr>
<tr>
<td>Ho</td>
<td>67</td>
<td>11 2 6 2 10 2 6</td>
<td>0.894</td>
</tr>
<tr>
<td>Er</td>
<td>68</td>
<td>12 2 6 2 11 2 6</td>
<td>0.881</td>
</tr>
<tr>
<td>Tm</td>
<td>69</td>
<td>13 2 6 2 12 2 6</td>
<td>0.869</td>
</tr>
<tr>
<td>Yb</td>
<td>70</td>
<td>14 2 6 2 13 2 6</td>
<td>0.858</td>
</tr>
<tr>
<td>Lu</td>
<td>71</td>
<td>14 2 6 1 2 14 2 6</td>
<td>0.848</td>
</tr>
</tbody>
</table>

- *Z*: atomic number
1.2. Applications of REEs

1.2.1. REE utilization in industry

The application fields of REE compounds are diverse and expanding. REEs are presently used to improve the mechanical properties of steel, providing both strength and corrosion resistance. La, Ce, Pr and Sm are also used in the motion picture industry as a core material in carbon-arc electrodes and for studio and projection lighting; Ce, Pr, Nd are utilized in the manufacturing and polishing of glass products, including lenses. Cracking catalysts containing rare earth mixtures are consumed by the petroleum refining industry to produce light weight hydrocarbons, such as gasoline and fuel oil. The lighting industry utilizes Eu containing calcium phosphate as fluorescence powder. Other REEs have been used in color television tubes, laser materials, microwave equipment, nuclear reactor control rods, super-conductors, catalysts, etc. (Xu et al., 1995 and Yu and Chen, 1995). Indications of total uses are given in Table 1.2. (Slooff et al., 1993).

Table 1.2. Utilization of REEs by industrial sector in worldwide and in the Netherlands (Slooff et al., 1993).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ton .y(^{-1})</td>
<td>%</td>
</tr>
<tr>
<td>Catalyst</td>
<td>8300</td>
<td>33</td>
</tr>
<tr>
<td>Metallurgy</td>
<td>6300</td>
<td>25</td>
</tr>
<tr>
<td>Glass/ceramics</td>
<td>9300</td>
<td>37</td>
</tr>
<tr>
<td>Others</td>
<td>1300</td>
<td>5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>ton .y(^{-1})</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>800</td>
<td>67</td>
</tr>
<tr>
<td>Metallurgy</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Glass/ceramics</td>
<td>100</td>
<td>8</td>
</tr>
<tr>
<td>Others</td>
<td>300</td>
<td>25</td>
</tr>
</tbody>
</table>

Even though no primary production or manufacture of REEs takes place in the Netherlands, approximately 1200 tons of REEs are processed into the Netherlands, mostly for the catalyst industry.

In Figure 1.2, trends in the worldwide consumption of REEs are presented. Currently, Austria, the United Kingdom, Australia, the United States and Japan are relatively
important REE producing countries. In the future, China and India will become more
dominant. No primary production or manufacture of REEs takes place in the
Eighty percent of the REE mineral supplies are found in the P. R. of China (Annema,
1990).

![Graph showing global consumption of REEs from 1960 to 2000.]

**Figure 1.2.** Global consumption of REEs.

1.2.2. Processing of REE compounds

REE are found in concentrated form as compounds such as bastnasite
(REE₂(CO₃)REEF₃) or monazite (REEPO₄). These are digested in acids and bases in
various steps, yielding REE mixtures. REEs are subsequently separated by ion
exchange, solvent extraction, extractive chromatography or fractional crystallization
(Yu and Chen, 1995).

Another type of winning in the future could be by direct extraction during the solvent
mediated recrystallization of calcium sulfate hemihydrate into dihydrate, a step in wet
phosphoric acid production. Zielinski et al. (1993) extracted 85% of the lanthanides
with an equimolar mixture of M₂EHPA and D₂EHPA. In this way REEs can be won
as a byproduct.
Due to the similarities in the properties of REEs, it is very difficult to separate individual elements from mixtures of REE compounds. The modern separation methods of ion exchange, solvent extraction and extraction chromatography have been developed to obtain high purity REE compounds.

An interesting phenomenon is that the extraction efficiency is largely determined by the radius and charge of REE as well as the pH of the system. It was found to increase with a decrease in the atomic radius, in the following order (Yu and Chen, 1995 and Xu et al., 1995):

La < Ce < Pr < Nd < Sm < Eu < Gd < Tb < Dy < Ho < Er < Tm < Yb < Lu

Koopman et al. (1999), however, found for REE removal from phosphoric acid (from REE containing fluorapatite) solutions by solvent extraction a dependency on the type of ligand: phosphoric acid ligands yielded the same sequence, while sulfonate groups exhibited the reverse sequence with respect to the radius of the bare cations. This could be attributed to the increase in hydrated lanthanide radius with increasing mass contrary to the bare cations. It might be that for sulfonate groups the extraction takes place via the hydrated lanthanide ion. These changes in sequence offer additional possibilities for REE fractionation.

1.2.3. REE utilization in agriculture

The earliest study of REE usage in agriculture began in 1917. The scientists of the USSR initiated research in the early 1930s to investigate the effect of REEs on plant growth. Small amounts of La carbonate and Ce oxalate were employed to examine the effect on the vegetative growth of two wheat varieties. Research indicated that La had a stronger growth stimulation than Ce. In 1935, Dropkov used aquatic solutions of REE compounds to examine the effect on growth, development and yield of sweet pea, radish, cucumber and flax, and found considerable influence on both fresh weight and production yield. A primary conclusion drawn was that either mixed or individual REEs yielded considerable benefits, as did micro-nutrients, but their function was not known. Since the 1960s further studies have been conducted. However, few reports about REE utilization in practical farming were available during the 60s and 70s (Bremmer, 1994 and Yu and Chen, 1995).

In the past decade, a series of investigations indicated that REE nitrates could accelerate the development of roots and the photosynthetic rate. A field trial reported that the yield of wheat increased by 6-12%, rice 4-8%, peanuts 8-12%, beet 6-10%, cured tobacco 8-
10%, water melons 8-10% and pakchoi by 10-20% as a result of the use of REE enriched fertilizer (Wu et al., 1984 and Wu and Guo, 1995). The use of REE fertilizers in agriculture has been demonstrated and popularized in China in the 1980s. It was reported that the consumption of REE fertilizers is continuously increasing by about 20% every year (Yu and Chen, 1995 and Zhong and Min, 1995). As a result of the high economic benefits of REE fertilizer utilization, millions of tons of REE fertilizers are now used in agriculture every year in the world.

In recent years, REEs have been introduced as an additive in animal husbandry. Preliminary studies indicated that REEs increased the yield of grass and legume herbage by 7 to 21%. REE additives increased the survival rate of young chickens by 3 to 4%, and increased the daily weight gain of fattening pigs by 6% (Wu and Guo, 1995, Yu and Chen, 1995 and Zhong and Min, 1995).

1.3. **REE abundance and spread**

1.3.1. **Origin and “natural” spread**

REEs were formed during nucleosynthesis in the universe. The abundance of the different REEs in our solar system are primarily reflected by their concentrations in chondrites, meteorites approximately as old as the solar system. These abundances can be considered as their “natural” occurrences. Ever since their formation, the REEs have been subjected to fractionation due to geological, biological and recently, industrial processes. This has resulted for instance in a substantially enriched earth crust compared to the primary materials in the solar system.

Due to their resemblance in chemical behaviour they are mostly encountered together in individual concentrations which reflect the ratio in chondrites. This retention of ratio also results from their relative immobility. The fractionation of REEs is therefore best represented by plotting their individually normalized concentrations. This normalization can take place with respect to concentrations in for instance chondrites, earth crust, or other average values. The average concentrations of REEs, in the earth's crust are shown in Figure 1.3., together with their concentrations relative to the average concentrations in chondrites (Henderson, 1984 and McLennan, 1989). The abundance plots show a marked oscillation with atomic number, which stems from the greater stability of nuclei with even atomic number compared to those with odd atomic numbers. In addition it can be seen that the enrichment of the earth crust is
accompanied by a fractionation: the lighter lanthanides such as La are enriched a
hundred fold, while the heavier ones such as Lu are only a factor of ten enriched.

![Graph showing the concentration of REEs in the earth's crust compared to chondritic values.](image)

**Figure 1.3.** The average concentration of REEs, in the earth's crust and chondrite-normalized abundance (Henderson, 1984 and McLennan, 1989)

Some minerals contain much higher concentrations of REEs than the average concentration in the earth's crust. Generally spoken, the REEs are not nearly as rare as their name suggests. In fact, their average crustal abundance is not very different from that of cobalt, tin and lead and even substantially higher than that of silver and gold. In the earth's crust, REEs are found in over 180 different types of minerals. The ores with the highest concentrations of REEs are bastnasite (70%, mainly as Y, Ce and La), a fluorocarbonate of REEs, and monazite (55%, mainly as Ce, La, Y and Tm) and xenotime (42%, as Y₂O₃), the latter being both isomorphic mixtures of orthophosphate of thorium and REEs (Henderson, 1984). In addition, fluoroapatites contain up to a few % REEs, perhaps allowing economically attractive REE winning as a byproduct to phosphoric acid in the future.

During the spread of REEs by geological and biological processes, fractionation occurs. By reconstructing the partitioning behaviour of REEs in geological processes, the mechanisms of such processes can be elucidated. For instance, the REE ionic radius varies smoothly with atomic mass, and the degree of isomorphous substitution taking place during recrystallisation in geological processes shows a dependency on this radius (Henderson, 1996). Other natural processes, such as spread in water and reduction of Eu(III) into Eu(II), or oxidation of Ce(III) into Ce(IV) also lead to fractionation. This fractionating behaviour contributes strongly to the understanding of these processes.
Brown et al. (1990) indicated that REE behaviour in biological processes is related to their resemblance to calcium ions. This also leads to fractionating effects. Tjooe et al. (1983) showed that even within the human body different degrees of depletion of heavy REEs occurs. Conclusively, the REEs are therefore not only important as such, but are very useful as probes to understand geological and biological processes (Loveland, 1989). Anthropogenic activities lead to further spread and fractionation of REEs.

1.3.2. Influence of human activities on spread environmental aspects

1.3.2.1. REE dissipation from industrial sources

Since REEs are abundant everywhere, it is mostly more appropriate to speak of redistribution of REEs in the environment. In some cases, however, strong fractionation might be encountered of anthropogenic origin. Locally, even a strong increase in bioavailability might occur. It is very difficult to quantify the emission of REEs to the environment. Presently, hardly any detailed data on either industrial or non-industrial sources are available. Nevertheless, some examples are given below of the spread of REEs through human activities.

REE emissions during extraction operations strongly depend on the ores used. Furthermore, REEs are common trace elements in several ores and refined petroleum products (a consequence of the use of fluid catalytic crackers (FCC) containing REEs). Phosphate fertilizer usually contains a large natural amount of REEs. Investigations of REEs in the Nieuwe Waterweg (a major shipping canal near Rotterdam), The Netherlands, showed unexplained REE peaks, possibly connected to waste acid dumping by a TiO₂ production plant (Slooff et al., 1993).

Using FCC to absorb nickel and vanadium from crude oil is a potential emission source (Olmez et al., 1985, Mizohata, 1986, Kitto, 1991 and Kitto et al., 1992). Light REE containing catalysts (1-3% as oxides) are used in refineries for the cracking of petroleum. It was reported that REEs have been found in bottom fly-ash from oil-fired power plants (Olmez et al., 1991 and Ravichandran, 1996). The data indicate that refined petroleum products from Los Angeles are responsible for the light REEs enriched signature in the upper sediments of San Pedro Bay. They also show that La, Ce, Nd, and Sm may be 890 to 6900 times enriched over crustal material near an industrial outlet in the Bay.

Concentrations of REEs ranging from 2×10⁻⁵ to 2×10⁻³ mg/m³ have been found in urban air in a number of locations in the U.S.A. In Philadelphia, monitoring of 104
sites showed clear enrichment factors for the light REEs, as indicated by the reported La/Ce and La/Sm ratios, which are 73 and 20, respectively. In the earth's crust these ratios are 0.5 and 4.8 respectively (Annema, 1990). Similarly, Mizohata (1986) found very high REEs concentrations and La/Sm ratios in the emission from a catalyst-regeneration tower of a FCC in a Japanese refinery. The data from a sampling network in several Japanese cities showed a dramatic increase in the La/Sm ratio. From 1984 to 1986, six sites throughout Osaka showed a La/Sm ratio of 22-42 for fine particles (<1.5 mm).

In principle, air pollution in urban areas arises from a multitude of sources of which anthropogenic activity is a major contributor. However, the concentration of rare earth elements in air has not been widely studied. REEs are increasingly emitted into the atmosphere and monitoring of their concentration may be one of the good indicators for the assessment of air quality. Therefore, it is important to determine their concentration in ambient air.

Near a fertilizer plant in Russia, REE concentrations ranging from $7 \times 10^{-3}$ to $2 \times 10^{-2}$ mg/m$^3$ have been found (Volokh et al., 1990). Yasuda et al. (1992) showed that the concentration of many REEs in the soil in an area close to a solid waste incineration plant were substantially larger than outside that area. In the U.K., high concentrations of La, Pr, Nd, and Sm were found in the Warrington sewage sludge; the Nd content of this sludge was ten times higher than any reported figures in the literature, which seems quite exceptional. There are a number of factories involved in glassmaking in the Widnes area, and the REEs probably came from these factories (Vivan, 1986). No data are available on the amounts of REEs present in domestic waste in The Netherlands or elsewhere.

High Gd concentrations were found in drinking water sludge in a purification plant in the north of The Netherlands (van Dijk and Montizaan, 1986). REEs concentrations ranging from below 0.001 to 245 mg.l$^{-1}$ were found in some shallow groundwater samples in The Netherlands (Stuyfzand, 1991 and 1992). For these high REE concentrations in ground water, air and soil pollution generally seem to be the most important anthropogenic cause.

In recent years, more attention has been given to the behavior of REEs in sediments and in particular, to aquatic environmental aspects of REEs (Cullers, 1994, Jarvis et al., 1994, Albarete and Semhi, 1995, Ross et al., 1995, Wang et al., 1995 and Kraemer et al., 1996). This is important because, under different environmental conditions, sediments act as efficient sinks for metals released into aquatic
environments or as a source thereof. However, in general, information on REE occurrence and their ratio distribution in sediment are very sparse.

1.3.2.2. Environmental impact of REEs originating from agricultural activities

Since the 1990s, REE enriched fertilizer, which is widely applied in agriculture, has generated much concern about REE toxicity and its effect on the environment. The water-soluble fraction of REEs (SREEs) determines their bioavailability (Liu, 1993). Generally the fraction of SREEs is substantially lower than the total amount of REEs in the soil sample. To evaluate changes in speciation of the REEs after applying REE containing fertilizer to soil, a simulation test was undertaken (Ran and Liu, 1993 and Chen, et al., 1995). After adding SREEs to the soil for one month, the chemical forms of REEs had changed. The distribution in the soil varied with the type of soil and REE; the SREEs added to the soil were mainly transformed into the residual form. Also, the influence of acid rain on the environmental chemical behaviour of REEs was investigated by a simulation experiment (Chen et al., 1995). Acidity of the solution apparently caused the REEs to leach from the soil. The leaching properties varied depending on the type of soil and the individual REE.

In The Netherlands large amounts of drinking water are prepared from ground water. Ground water is being threatened nowadays by air-borne acidification of the soil, which may result in progressive dissolution of trace metals and REEs in the soil. Moreover, a threat of REE contamination of groundwater might exist as a result of the application of phosphate fertilizer for agricultural activity.

To shed light on the effect of REEs from agricultural and industrial activities on the environment, it is necessary to focus on both fundamental and field-level research to show: (a) how REEs are distributed between the environmental compartments and soil; (b) the relationship between total and soluble REEs in different types of soil; and (c) the availability of REEs to plant and what factors influence the leaching behavior of REEs in soil.

1.4. REE ecotoxicology and bioaccumulation

Although many studies have appeared on the biological impact of REEs, it is still not possible to assess the toxicity under realistic conditions. Model studies with well soluble REE compounds are sometimes able to provoke toxic effects (Slooff et al., 1993, Yu and Chen, 1995, van Dijk and Montizaan, 1986, Posthumus and Knaap, 1990,
Gerritsen and Bowmer, 1992, Hoofman et al., 1992). Because of the low availability in the environment dangerous exposures are unlikely to occur. An excellent review by Brown et al. (1990) gives a good impression on the complexity of REE biological effects.

Additional research is needed to increase the general knowledge of the influence of REEs on humans. A quantitative risk assessment for man is not yet possible, because of the lack of exposure data.

1.5. Analysis of REEs

1.5.1. Current techniques

Many analytical methods have been developed for the determination of REEs (Rollinson, 1995). Their applications depend on the sensitivity and accuracy required as well as on the availability of instrumentation. A very accurate and sensitive, but expensive technique is isotopic dilution mass spectrometry (IDMS). In the past decades, the major analytical techniques employed for the determination of REEs were e.g. complexometric methods, graphite-furnace/flame atomic absorption spectrometry (GF-AAS, FAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), X-ray fluorescence (XRF) and neutron activation analysis (NAA) (Littlejohn and Burns, 1994 and Kellner, 1997). The complexometric methods are often used to determine the total amount of REEs in combination with an extraction procedure for the removal of interfering elements. Detection limits are at the mg.l$^{-1}$ (ppm) level. The ICP-AES, FAAS, GF-AAS, XRF, etc., techniques are usually employed to determine individual REEs, with detection limits at ppm and sub ppm levels. Disadvantages of AAS (both flame and graphite-furnace) include the limited concentration range and the sequential nature of most systems. Though ICP-AES provides multi-element detection for REEs at sub ppm level, there are numerous limitations resulting from complex spectra and matrix interferences and the detection limits are not low enough to analyze REEs in most environmental sample matrices. XRF is a popular analytical technique in both research and industry for the estimation of major and minor elements in several matrices such as rock, alloy, etc. But this technique suffers from drawbacks such as interferences and poor detection limits for REE in the above matrices and this technique cannot handle solutions (Littlejohn and Burns, 1994, Balaram, 1995 and Kellner et al., 1998). Neutron Activation analysis (NAA) is a sensitive multi-element analytical method for the accurate and precise determination of elemental concentrations in unknown materials. The analysis of solid sample pieces is completely free of blank.
At present, this can be considered as the greatest advantage of activation analysis in comparison with other methods. Furthermore, highly accurate calibrations can be performed by simultaneous irradiation of samples and synthetic multi-element standards. However, the technique requires access to a nuclear reactor and a radiochemical laboratory, since for low-level measurements a radiochemical separation after neutron irradiation is required (Tielrooij, 1987, Schijff, 1992, Littlejohn and Burns, 1994 and Balaram, 1995).

Today, inductively coupled plasma-mass spectrometry (ICP-MS) is becoming competitive or even superior, because of (i) the full elemental coverage, (ii) the ability to analyze samples of different quality, and (iii) the low detection limits, particularly when using ultrasonic nebulization (Batly, 1991, Jarvis et al., 1992, Evans, 1993 and de Boer et al., 1995).

1.5.2. Inductively-coupled plasma mass-spectrometry

(i) The introduction of ICP-MS

The introduction of ICP (1964) as an excitation source in atomic emission spectrometry (AES) had a major impact on the field of elemental analysis. Since the introduction of the first commercial ICP-AES instruments in 1974, the technique has developed rapidly. However, it has also proved to have a number of drawbacks with respect to detection limits and interferences. The first quadrupole based ICP-MS systems were introduced to the market in 1983 by Sciex (Perkin Elmer Corporation), and by VG (Fisons Instruments). Many improvements have been made over the years so that a new generation of reliable and powerful instruments is now working successfully in many routine applications. Some years ago, a special low cost version for environmental analysis ('PQe') was introduced to the market by VG (Fisons Instruments) (Jarvis et al., 1992). An unique instrument with ICP as the source and incorporating a double focusing magnetic sector mass analyzer equipped with multiple ion collectors has been recently developed. It has been demonstrated recently that by combining laser ablation with high resolution ICP-MS, the isotopic composition of solids can be measured directly. High resolution ICP-MS shows very high sensitivities and less interferences. (Balaram, 1995 and Kellner et al., 1998).
(ii) **ICP-MS outline and principle**

In general, the instrument consists of three basic units (see **Figure 1.3.**): a) a conventional argon ICP operating at temperatures of 6000-9000 K with a nebulizer, spray-chamber, work coil and associated power supplies, b) a conventional quadrupole mass spectrometer and associated data collection electronics and c) an interface consisting of two water cooled nickel cones, each containing a small orifice at the center, which allows sampling of the plasma gases and transfer of the ion beam into the mass spectrometer (Evans, 1993, Littlejohn and Burns, 1994, Balaram, 1995 and Kellner *et al.*, 1998).

![Diagram](image)

**Figure 1.4.** A scheme of the sampling and plasma section of an ICP-MS.
ICP

In the ICP source the plasma is generated by an oscillating high frequency electric field of an induction coil. If a gas, X, is used, a plasma can be described by the following equilibrium:

\[ X = \sum X^n + \sum n * e \quad (n=1 \ldots q) \]  

(1.1)

where \( X^n \) is an ion with \( n \) times the electron charge and \( e \) is the electron. The plasma is therefore well-suited for inorganic mass spectrometry since it is an efficient source of ionization. In general, the gas used to generate the plasma is argon (Ar). Ar is an element with a high ionization energy (15.76 eV), and is chemically inert (Evans, 1993, Littlejohn and Burns, 1994, Balaram, 1995 and Kellner et al., 1998).

Samples are introduced as an aerosol into the central channel of the gas plasma, with a high temperature of about 8000K, where fast evaporation, atomization, and ionization take place on the way through the plasma. The ions are extracted from the plasma at atmospheric pressure by means of a special interface, which is necessary to reduce the pressure by differential pumping to the working range of the mass analyzer, which is nine orders of magnitude lower in comparison to the source.

Sample introduction

Many analytical applications of ICP-MS depend on the performance of a special sample introduction system. By far the most common method of sample introduction is pneumatic nebulization, which produces a fine aerosol of droplets of the sample solution. One special aim is the reduction of spectral and non-spectral interferences. For reduction of spectral interferences, the application of a desalination system has proved useful. The application of electrothermal vaporization (ETV) may also reduce the appearance of molecules arising from solvent derived atoms. Furthermore, several new developments concerning sample introduction systems are laser ablation (the direct analysis of solid samples without dissolution), slurry nebulization, hydraulic high-pressure nebulization coupled with flow injection and chromatographic preseparation techniques (Evans, 1993 and Kellner et al., 1998).

Sampling interface

ICP is operated at atmospheric pressure and high temperature, whereas the MS requires high vacuum conditions and ambient temperature. An interface is, therefore,
necessary to reduce both the pressure and temperature. Currently, the interface consists of two cones usually made of Cu and Ni. The first cone is called the sampler and the second one the skimmer. The orifices of the cones are of the order of 1 mm or less, and are aligned within the axis of the plasma. The pressure is reduced between the sampler and the skimmer by means of a rotary pump. High vacuum (typically $10^{-6}$ to $10^{-4}$ Pa) at the ion optics and quadrupole mass filter level is obtained through the use of turbomolecular pumps (Evans, 1993, Balaram, 1995 and Kellner et al., 1998).

**Mass analyzer and detector**

The magnetic sector MS resolves ions in space, the time-of-flight MS resolves ions in time, whereas the quadrupole device is a mass filter. The quadrupole mass filter is largely used because of its low cost, its reliability, and it has a vacuum that is not as high as for sector mass spectrometers. The major limitation of a quadrupole filter is the limited resolution, which is typically 1 amu over the mass range. Because of isobaric interferences, there is a need to use high-resolution mass spectrometry (HR-MS). The most commonly used detectors are the electron multiplier (continuous or discrete dynode type) and Faraday cup (Evans, 1993, Littlejohn and Burns, 1994, Balaram, 1995 and Kellner et al., 1998).

### 1.5.3. Application of ICP-MS for REE analysis

#### (i) Geological samples

The determination of REEs in geological samples has become increasingly important in recent years, as their physical and chemical characteristics are widely studied. ICP-MS is in an ideal analytical technique for the determination of this elemental group, with good sensitivity and detection limits. Since 1983, a number of articles has appeared in the literature on the use of ICP-MS for the determination of the REEs in geological samples (Crock and Lichte, 1982, Date and Hutchison 1987, Lichte et al., 1987, Doherty, 1989, Kawabata et al., 1991 and Watkins and Nolan, 1992). Jarvis (1989) carried out research on the use of slurry nebulization in ICP-MS. The result shows that the inter-sample precision is generally better than 5% RSD (relative standard deviation) for most elements.

#### (ii) Sea water

The content of REEs in seawater is in the ppt (ng/l) range, which is too low for direct analysis by most analytical techniques. Seawater contains large amounts of interfering
elements, such as alkali and alkaline earth elements. Starting with the classical work of REE measurement in seawater samples, the determination of REEs in seawater has been a real challenge. Since the mid-eighties, ICP-MS has successfully been applied to transition elements and also recently for the analysis of REEs in seawater (Moller et al., 1992).

Preconcentration is a key procedure in the determination of REEs in water by ICP-MS. The application of a mixture of (2-ethylhexyl) hydrogen phosphate (HDEHP) and 2-ethylhexyl dihydrogen phosphate (H$_2$MEHP) in heptane for the preconcentration of REEs in seawater is a well developed method. The recovery values for spiked REEs in seawater samples were more than 90%, whereas back-extraction recovery values of REEs were above 99% (Shabani et al., 1990). With on-line solvent extraction and back-extraction using a mixture of 35% H$_2$MEHP and 65% HDEHP in heptane, high extraction efficiencies and back-extraction recoveries of REEs could be reached (Shabani and Masuda, 1991). However, problems with blanks and contamination still exist. The operating procedures of these methods are often complex and thus need further improvement.

A recently developed technique is REEs preconcentration in seawater using the chelating ion-exchange resin, Chelex-100. Although this technique has successfully been employed for seawater analysis using INAA, it has also serious drawbacks, e.g. time consumption, and the need to remove calcium and magnesium prior to elution of the REEs. Coprecipitation techniques are not suitable as preconcentration techniques for the determination of REEs in seawater by ICP-MS (Shabani et al., 1992).

1.5.4. Limitations of ICP-MS for the analysis of REEs

The interferences encountered in ICP-MS can be subdivided into two categories: spectroscopic and non-spectroscopic interferences (Evans, 1993).

(i) Spectral interferences

Spectroscopic interferences are caused by atomic or molecular ions having the same nominal mass as the element of interest. Interferences caused by overlapping isotopes of different elements are easy to predict and well documented, and can be overcome by utilizing alternative isotopes or elemental equations for analysis. Molecular or polyatomic-ion interferences are caused by polyatomic ions formed from precursors in the plasma gas, entrained atmospheric gases, water, acids used for dissolution and the sample matrix. The polyatomic ions so formed, may then result in interferences with
elements with the same nominal mass/atomic number (m/z) values (Heuzen and Nibbering, 1993).

Spectral interference from oxides (MO\(^+\)), hydroxide (MOH\(^+\)) and isobaric overlap is of concern in the determination of REEs by ICP-MS. REEs have a strong tendency to form oxides and hydroxides. One of the most significant examples of interference occurs at mass 156, which occurs in the case of \(^{156}\)Gd, \(^{156}\)Dy, \(^{140}\)Ce\(^{16}\)O, and \(^{139}\)La\(^{16}\)O\(^1\)H. For analysis of \(^{156}\)Gd, the spectral interferences from \(^{156}\)Dy, \(^{140}\)Ce\(^{16}\)O, and \(^{139}\)La\(^{16}\)O\(^1\)H should be removed. For another example, the signal intensity of \(^{157}\)Gd and \(^{158}\)Gd can also originate from \(^{141}\)Pr\(^{16}\)O and \(^{142}\)Ce\(^{16}\)O respectively. In both cases, the oxide signal represents ranges of 50 - 70% of the total signal.

The problem of spectral overlap is clearly demonstrated with REEs, since the strong oxide-forming elements are mostly at the lower mass end of the REEs and their oxides overlap the REEs at the upper mass end, as shown in Table 1.4. (Vaughan and Horlick, 1986, Lichte et al., 1987, Vaughan and Horlick, 1990 and de Boer et al., 1995).

Various approaches can reduce the effects of spectral interferences such as (a) separation of light and heavy REEs, (b) optimization of instrumental parameters, (c) mathematical corrections, and (d) the use of high resolution ICP-MS.

Optimization of instrumental parameters to reduce spectral interferences was carried out by Lichte et al. (1987). A second approach is the use of mathematical correction schemes like the classical algebraic approach (Vaughan and Horlick, 1990), and principal component analysis (Vaughan and Horlick, 1990). Spectral interference fitting procedures to reduce the effects of spectral interference in ICP-MS have been described by Van Veen et al. (1994) and De Boer et al. (1995).

High resolution ICP-MS is capable of separating the majority of these spectral interferences. Mathematical correction is an economic and reasonable method of removing interferences. However, a need exists to develop a mathematical model, which can be applied for all concentration levels of REEs and removes the interferences from all REE oxides and hydroxides and isobaric overlap.

(ii) Non-spectroscopic interferences

Unlike spectroscopic interferences, where the analytical signal is enhanced by another element or polyatomic species with the same nominal mass, the non-spectroscopic
interferences are characterized by a reduction or enhancement in the analysis signal due to factors exerting an influence on the sample transport, ionization in the plasma, ion extraction or ion throughput in the resultant ionic ions.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Spectral interference form</th>
<th>Isotope</th>
<th>Spectral interference form</th>
</tr>
</thead>
<tbody>
<tr>
<td>138La</td>
<td>138Ba, 138Ce, 122Sn16O, 122Sb16O</td>
<td>158Gd</td>
<td>158Dy, 142Ce16O, 142Nd16O</td>
</tr>
<tr>
<td>138Ce</td>
<td>138Ba, 138La, 122Sn16O, 122Sb16O</td>
<td>158Dy</td>
<td>158Gd, 142Ce16O, 142Nd16O</td>
</tr>
<tr>
<td>139La</td>
<td>123Sb16O</td>
<td>159Dy</td>
<td>142Nd16O, 142Ce16O10H</td>
</tr>
<tr>
<td>140Ce</td>
<td>124Sn16O</td>
<td>160Gd</td>
<td>160Dy, 144Nd16O, 144Sm16O</td>
</tr>
<tr>
<td>141Pr</td>
<td>125Te16O</td>
<td>160Dy</td>
<td>160Gd, 144Nd16O, 144Sm16O</td>
</tr>
<tr>
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<td>142Nd, 126Te16O</td>
<td>161Dy</td>
<td>142Nd16O</td>
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<tr>
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<td>142Nd, 126Te16O</td>
<td>162Dy</td>
<td>162Er, 146Nd16O</td>
</tr>
<tr>
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<td>126Te16O</td>
<td>162Er</td>
<td>162Dy, 146Nd16O</td>
</tr>
<tr>
<td>144Nd</td>
<td>144Sm, 128Te16O</td>
<td>163Dy</td>
<td>147Sm16O</td>
</tr>
<tr>
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<td>164Dy</td>
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<tr>
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<td>164Er</td>
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<td>165Ho</td>
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<td>166Er</td>
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<tr>
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<td>166Er</td>
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<td>135Ba16N</td>
<td>168Er</td>
<td>152Sm16O</td>
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<td>168Yb</td>
<td>168Er, 152Sm16O</td>
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<td>170Er</td>
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<td>170Yb</td>
<td>170Er, 154Sm16O, 138Ba12S</td>
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<td>155Gd16O</td>
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<td>157Gd16O, 138Ba15Cl</td>
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<td>154Hf, 158Gd16O, 159Ba15Cl</td>
</tr>
<tr>
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<td>139La16O, 138Ba16O10H</td>
<td>175Lu</td>
<td>159Tb16O</td>
</tr>
<tr>
<td>156Gd</td>
<td>156Dy, 140Ce16O, 139La16O10H</td>
<td>176Yb</td>
<td>156Lu, 156Hf, 156Gd16O, 160Dy16O</td>
</tr>
<tr>
<td>156Dy</td>
<td>156Gd, 140Ce16O, 139La16O10H</td>
<td>176Lu</td>
<td>156Yb, 156Hf, 156Gd16O, 160Dy16O</td>
</tr>
<tr>
<td>157Gd</td>
<td>140Pr16O</td>
<td>176Lu</td>
<td>156Yb, 156Hf, 156Gd16O, 160Dy16O</td>
</tr>
</tbody>
</table>
A high salt concentration can lead to two different problems. The first problem is that it can suppress or enhance the signal of the analyzed element (matrix effect). The elements present at high concentrations of salt are called concomitant elements. The matrix effects observed are much larger and occur at lower concentrations. In addition, the effect has been found to depend on the mass of the concomitant element. Several mechanisms related to the sampling interface (such as space charge effects and collision processes) have been suggested to account for the matrix effects. By using matrix standards or standard addition techniques, quantitative analysis is still possible. Secondly, high salt concentrations can lead to deposition at the aperture of the sampling cone. Initially deposition leads to a change in the diameter of the aperture. The ion signal is very sensitive to such a change. The change (decrease) in sensitivity is mainly caused by a change in the ion transmission of the ion optics rather than less plasma being sampled, as the ion signal may be restored to its original value by tuning the electrostatic lenses. However, a stable system is not obtained in such a way. To circumvent this problem, use of an internal standard (chosen and employed with care) and/or ion exchange (see Chapter 4) to reduce the salt loading can be employed. In some cases, extraction of the trace elements from the matrix is also a possibility.

(iii) Sensitivity of ICP-MS

Especially for biological samples, REEs are at ng.g⁻¹ (ppb) or pg.g⁻¹ (ppt) levels. The concentration of heavy REEs is usually close to the instrumental detection limits, thus, a preconcentration is required before analysis.

Cation-exchange resins have been used to remove matrix elements and preconcentrate REEs. Kawabata et al. (1991) developed an ion-exchange chromatographic column for the separation and determination of REEs. High performance liquid chromatography (HPLC) was used to separate the REEs prior to detection by ICP-MS (Braverman, 1992), the results show REE separation achieved under specific conditions. The method was only applied to measure REEs in reference materials. No details are available on environmental samples.
1.6. Objectives and outline of the thesis

The main goal of this research was to develop a cheap, reliable and fast analytical tool based on ICP-MS for all the individual REEs, and to demonstrate applications for these tools in selected compartments of the environment.

(i) Analysis

Chapter 2 describes the development of a partial least-squares regression (PLSR) model which corrects for interferences from REE oxides, hydroxides and isobaric spectral overlap during the analysis of REEs with inductively coupled plasma mass spectrometry (ICP-MS). These interferences are the most common ones in analysis of REEs in environmental samples. This technique of ICP-MS allows rapid simultaneous multi-element analysis.

In Chapter 3 this model is applied to the determination of REE concentrations in different reference materials and environmental matrices \textit{i.e.} soil, sediment, sludge and seawater, where high ratios of Ba/REEs and salt/REEs exist, which are typical problematic analytical interferences.

Chapter 4 describes the preconcentration of ultra-trace levels of REEs in environmental samples with a micro ion-exchange column and determination by ICP-MS. This method was applied for the determination of REEs in raw water, purified water and tap water, as well as in environmental aquatic samples.

With the results of Chapters 2 to 4, it is possible to measure reliably all REEs simultaneously in most types of environmental aqueous samples, as well as in most other environmental sample matrices, at very low concentration.

(ii) Occurrence

In Chapter 5 concentrations of REEs in sediments from specific locations in China are given. Normalized pattern plots and factor analysis were employed to distinguish REE depletion or enrichment in sediments.

In Chapter 6 concentrations of REE in ambient air in The Netherlands are given. Atmospheric particulate matter (APM) was collected on micro-quartz glass-fibre filters. Here ambient air near suspected contamination sources was sampled.
In Chapter 7 concentrations of REEs in the different types of soils from China and The Netherlands are given. REE background values in soil from both countries were compared.

(iii) Leaching

In Chapter 7, a comparison is made between the soluble and total REE fractions in Chinese soil samples.

In Chapter 8, three representative Dutch soil samples (sandy clay, clay and peaty soil) are investigated. REE bioavailability and column leaching tests are described and leaching characteristics of REEs and heavy metals are compared.

Finally, Chapter 9 summarizes and discusses the results of this thesis.

References


Chapter 2

A Partial Least-Squares Regression (PLSR) Model for Rare Earth Elements (REEs) Analysis with ICP-MS

Abstract

A partial least-squares regression (PLSR) model was developed for Rare Earth Element (REE) analysis with inductively coupled plasma-mass spectrometry (ICP-MS), in order to correct interferences from REE oxides, hydroxides and isobaric spectral overlap. The total variance was explained by a 14-factor PLSR model. The square error of prediction was less than 0.005 and the oxide/hydroxide/isobaric interferences were almost completely removed. Nd, Sm, Gd, Dy and Yb played a more significant role in the model compared to the other rare earth elements because they possess multiple isotopes which require repeated calibration. REE concentrations could be accurately predicted despite barium interference, even in samples with high ratios of Ba/REE, when the weights of certain isotopes in the model were set below 0.1. The PLSR model was compared to the Normal Calibration Method (NCM) and the Gauss Elimination Method (GEM). Results indicated that the PLSR model was more accurate than the NCM and exhibited greater flexibility than the GEM.

2.1. Introduction

Principal component analysis (PCA), a technique for studying matrices of data, is one of the most powerful mathematical methods in chemistry and environmental chemistry (Malinowski, 1980, Brereton, 1990, Meloun et al., 1992 and Sjogren et al., 1996), which can be applied whenever a signal can be expressed as a linear sum of product terms. PCA has been applied in areas of chemistry such as spectrophotometry and mass spectrometry, and applications of the technique have been described in detail by many authors (Devaux et al., 1988, Machado and Silva, 1993, Smith and Burford, 1993, Sahota and Khaledi, 1994). Both principal component regression (PCR) and partial
least squares regression (PLSR) are projection methods resulting in principal component models. PLSR algorithms, described in detail by several authors (Geladi and Kowalski, 1986, Helland, 1990, De Jong, 1993, Wang et al., 1995 and Ferre and Rius 1996) are becoming more and more popular in analytical chemistry.

ICP-MS is a multi-element analytical method for the determination of REEs. In the past decade, a lot of publications dealing with the analysis of REEs in geological samples have emerged (Lichte et al., 1987, Jarvis, 1989, Doherty, 1989, Croudace and Marshall 1991 and Balaram, 1995). Likewise, many publications on the determination of REEs in aqueous samples e.g. surface, ground and sea water, have been published (Moller et al., 1992, Stetzenbach et al., 1994, De Boer et al., 1996 and Kreamer et al., 1996).

However, this analytical method suffers from polyatomic ion interference from REE oxides and hydroxides, isobaric spectral overlap and interference from doubly charged ions, which reduces the sensitivity and accuracy of measurements (Tan and Horlick, 1986, Vaughan and Horlick, 1986 and Evans, 1993).

Several correction approaches for the analysis of REEs with ICP-MS have been developed. Longerich et al. (1987) and Dulski (1994) provide a detailed discussion of REE oxide formation and potential interferences during analysis. Lichte et al. (1987) minimized oxide formation by instrumental optimisation and employed an algebraic correction scheme during data processing. Spectral fitting procedures to reduce the effects of spectral interference in ICP-MS have been described in detail by De Boer et al. (1996) and Van Veen et al. (1994). Vaughan and Horlick (1990) proposed principal component-analysis correction procedures for REE analysis with ICP-MS, and reported satisfactory results for specific REEs.

In this study, a PLSR model is developed and aspects of experimental design, model optimisation and model application are addressed. Using this model, the concentration of new unknown samples can be predicted accurately and interference from all REE oxides and hydroxides, isobaric overlap as well as barium interference can be corrected.

2.2. Theory

PLSR performs simultaneous and interdependent principle component analysis (PCA) in both $[X]$ and $[Y]$ matrices, in such a way the information in the $[Y]$ matrix is used directly as a guide for optimal decomposition of the $[X]$ matrix, and subsequently

PCA is a method of extraction of systematic variations in a single data set (also called data decomposition). The general purpose of PCA is to perform data description and interpretation. Original data are decomposed into a model comprising both signal and error (noise) parts. To illustrate how PCA can be applied to REE mass spectra in ICP-MS, a hypothetical data matrix is considered i.e. \( [X] \), comprising the signals of a series of objects/samples of the same measured mass spectral components. For example, suppose the \( [X] \) matrix contains \( i \) rows (objects or mixtures) and \( k \) columns (variables or masses), the matrix can be written as:

\[
[X] = \begin{bmatrix}
  x_{11} & x_{12} & \cdots & x_{1k} \\
  x_{21} & x_{22} & \cdots & x_{2k} \\
  \vdots & \vdots & \ddots & \vdots \\
  x_{(i-1)1} & x_{(i-1)2} & \cdots & x_{(i-1)k} \\
  x_{i1} & x_{i2} & \cdots & x_{ik}
\end{bmatrix}
\]  

(2.1)

Assuming \( m \) factors influence the above data set system, \( s \) (score), is a measure of how much a factor is present in an object; \( l \) (loading), expresses how much each original variable contributes to each factor. The data \( x \) can be written as follows:

\[
x_{ik} = s_{k1} l_{1i} + s_{k2} l_{2i} + \cdots + s_{k(m-1)} l_{(m-1)i} + s_{km} l_{mi}
\]  

(2.2)

From equation (2.2), a score matrix \( [S] \) and a loading matrix \( [L] \) can be established:

\[
[S] = \begin{bmatrix}
  s_{11} & s_{12} & \cdots & s_{1m} \\
  s_{21} & s_{22} & \cdots & s_{2m} \\
  \vdots & \vdots & \ddots & \vdots \\
  s_{(i-1)1} & s_{(i-1)2} & \cdots & s_{(i-1)m} \\
  s_{i1} & s_{i2} & \cdots & s_{im}
\end{bmatrix}
\]  

(2.3)

\[
[L] = \begin{bmatrix}
  l_{11} & l_{12} & \cdots & l_{1k} \\
  l_{21} & l_{22} & \cdots & l_{2k} \\
  \vdots & \vdots & \ddots & \vdots \\
  l_{(m-1)1} & l_{(m-1)2} & \cdots & l_{(m-1)k} \\
  l_{m1} & l_{m2} & \cdots & l_{mk}
\end{bmatrix}
\]  

(2.4)
The \([X]\) matrix can also be expressed in terms of \([S]\) and \([L]\) matrixes
\[
[X] = [S] * [L] + R_{(m)} \tag{2.5}
\]
Here, \(R(m)\) is defined as the residual of the \([X]\) matrix for \(m\) factors, and can be regarded as the model error.

In the same way, the concentration matrix \([Y]\) can be expressed as:
\[
[Y] = [S]' * [L]' + R'_{(m)} \tag{2.6}
\]
Here, \([S]'\) and \([L]'\) are the score and loading matrices, respectively. \(R'_{(m)}\) is the model error in the \([Y]\) matrix for \(m\) factors, and may be calculated by subtracting \([S]' * [L]'\) from \([Y]\).

The PLSR model is based on the non-linear iterative partial least squares (NIPALS) algorithm (Geladi and Kowalski, 1986). The algorithm extracts one factor at a time and each factor is obtained iteratively by repeated regression of \([X]\) on scores \([S]\) to obtain improved loading \([L]\).

In summary, PLSR theory can be used to establish a calibration model based on a representative set of corresponding measurements of both \(X\)-data and \(Y\)-data:

\[
X\text{-data} + Y\text{-data} \Rightarrow \text{Calibration Model}
\]

Once the calibration model is available, the model can be use to predict new \(Y\)-data from the measurement of new \(X\)-data:

\[
\text{New } X\text{-data} + \text{Calibration Model} \Rightarrow \text{New } Y\text{-data}
\]

2.3. Experimental

2.3.1. Reagents and standards

REE solutions were prepared from standard 1000 \(\mu\)g/ml stock solutions (Perkin Elmer). Single element standards were prepared for La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Sm, Yb Lu and Ba, and in all cases indium (\(^{115}\)In) was added as an internal standard. Deionized water (18.2 M\(\Omega\).cm\(^{-1}\)) and super pure HNO\(_3\) (MERCK, Germany) were used
for all dilution and digestion experiments. Reference materials employed in this study comprised marine sediment (MAG-1) and soil (GBW07313) materials, from the US Geological Survey and from the Chinese National Research Centre for Certified Reference Materials (Beijing), respectively.

2.3.2. Instrumentation

Measurements were performed on an ICP-MS (VG Plasmaquad Plus, Fison Instruments, U.K.). $^{115}$In was used for optimisation of the operating parameters and ion lens voltages. Typical ICP-MS operating parameters optimised for the analysis of aqueous REEs are shown in Table 2.1. A microcomputer (Hewlett-Packard, Vectra 50 Mhz, 486-DX) with 8 Mb RAM, mathematical coprocessor and 210 Mb hard disk was employed for the model data library. Software packages used for experimental design, data acquisition, model establishment and data prediction included, Unscrambler, version 4.0 (CAM A/S, Norway) and Statgraphic plus, version 6.0 (Manugistics, Inc., USA).

2.3.3. Experimental design

The multivariate calibration model, which relates to $[Y]$ and $[X]$ variables has to be determined from a set of calibration objects/samples. In order to ensure reliable prediction, the program Statgraphic plus was employed and Factorial Design was chosen for the design of the mixed REEs solutions. Two-level designs were considered in this study. 15 factors were selected, corresponding to the number of RE elements (Pr was omitted) and barium in the model system. 40 mixed samples were recommended as the optimal number for the system employing a Folded Plackett-Burman (Deming and Morgan, 1993) design method. In order to develop the best model and test its applicability, four different concentration ranges were studied: (a) 5 - 30 µg.l$^{-1}$, (b) 50 - 500 µg.l$^{-1}$, (c) 0 - 100 µg.l$^{-1}$ and (d) 0.5 -5 µg.l$^{-1}$. 15 pure element standards were prepared for both the lowest and highest concentration of each range (i.e. 30 standards per concentration range).

All mass spectral data (uncorrected counts measured per second,) from the ICP-MS were corrected by $^{115}$In (internal standard) and further transformed to data matrices. The data matrix files were converted to an acceptable format using Unscrambler. A data matrix set is given in Figure 2.1. The data set consists of a number of objects/samples (rows/lines), each object/sample corresponding to a set of variables/REEs isotopes (columns). The matrix dimensions are 70 lines/samples x 52 columns/isotopes. The matrix consists of 3640 data points.
**Table 2.1.** Typical ICP-MS operating parameters for aqueous REE analysis.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>R. F. power</td>
<td>1.439</td>
</tr>
<tr>
<td>Forward (kW)</td>
<td></td>
</tr>
<tr>
<td>Reflected power (w)</td>
<td>0</td>
</tr>
<tr>
<td>Gas flow rates (L.min⁻¹)</td>
<td></td>
</tr>
<tr>
<td>Inner</td>
<td>1.1</td>
</tr>
<tr>
<td>Intermediate</td>
<td>1.18</td>
</tr>
<tr>
<td>Outer</td>
<td>13.5</td>
</tr>
<tr>
<td>Scanning mode</td>
<td>Elemental</td>
</tr>
<tr>
<td>Measurement mode</td>
<td>Multi-channel</td>
</tr>
<tr>
<td>Measurements per peak</td>
<td>3</td>
</tr>
<tr>
<td>Measurement time (s)</td>
<td>1</td>
</tr>
<tr>
<td>Repeats per integration</td>
<td>6</td>
</tr>
<tr>
<td>Mass range (m/z)</td>
<td>100-180</td>
</tr>
</tbody>
</table>

**Figure 2.1.** A data matrix set for PLSR modelling.
2.4. Results and discussion

2.4.1. The effect of the number of factors on the model

PLSR, the model-calibration method of interest in this study, is characterized by the number of factors required for accurate data prediction. When the correct number of factors is employed, the resulting data matrix should equal the original data matrix, within experimental error. If too few factors are employed in the model, the data will not be reproduced with sufficient accuracy and if too many factors are used, the extra factors will introduce additional model error.

Variance is often expressed as the mean square error of the mean value of residual squares. To assess the effect of the number of factors on the model, Explained Variance is employed. Explained Variance is expressed as a percentage, indicating the accuracy of the model. Each additional new factor explains more variance in the original data set. In general, before model calibration, 0% of the original variance is explained, whereas ca. 100% of the original variance is explained by the model when the optimal number of factors is chosen. Here, the first factor explained about 65% of the total variance, and the first six factors together described about 90% of the total variance; further factors (from 7 to 14) explained only marginally more of the total variance (ca. 1% more total variance per factor). Thus, 14 factors together explained nearly 100% of the total variance. When less than 14 factors were used for data prediction, the results always showed lower concentrations than the reference samples. On the other hand, when more than 14 factors were used, the prediction error increased. Furthermore, a part of the results was considered abnormal, because higher order factors increased the unexplained variance in the model. The effect of the number of factors on different REE concentration ranges i.e. 0.5 - 5 μg.l⁻¹, 0 - 100 μg.l⁻¹ and 0 - 30 μg.l⁻¹ (see Experimental Design) was also investigated. The results are shown in Figure 2.2.. The effect of the number of factors on all the concentration ranges was very similar and nearly 0% total residual variance was obtained with 14 factors for all concentration ranges investigated.

2.4.2. Effect of weights on the model

In order to reduce the effects of different variables and noise in a data set, a priori weights can be placed on the [X] and [Y] variables. The term Relative Deviation (RD) was employed to explain the effect of weights on the model. The formula for RD is as follows:
RD = \frac{(C_{\text{prediction}} - C_{\text{certified}})}{C_{\text{certified}}} \times 100\% \quad (2.7)

Where $C_{\text{prediction}}$ is the concentration calculated by the model and $C_{\text{certified}}$ is the certified (known) concentration.

Figure 2.2. A comparison of the model variance explained for different REE concentration ranges (A: 5 to 30 μg.l$^{-1}$, B: 50 to 500 μg.l$^{-1}$, C: 0 to 100 μg.l$^{-1}$ and D: 0.5 to 5 μg.l$^{-1}$).

Figure 2.3. shows the RD obtained using different weights. The PLSR model was very sensitive to added weights. When the weights for all X and Y variables were set at 1.0, a large error resulted (maximum RD of 60%), due to large differences between variable values. For example, $^{142}\text{Ce}^{160}\text{H}$ interferes with the determination of $^{159}\text{Tb}$, and if the weights of all $[X]$ variables were set at 1.0, the RD in the prediction of $^{159}\text{Tb}$ would be ca. 59%. Setting the weights equal to the inverse of the standard deviation (1/SD) of the absolute noise for all $[X]$ and $[Y]$ variables yielded a RD of ca. 8% for the low REE concentration range (below 1 μg/l) and less than 5% for concentration ranges between 1-100 μg.l$^{-1}$.

From the results of residual variance, it can be seen that the model employing weights equal to 1/SD performed better than the model with weights equal to 1. The noise (residual variance) from ICP-MS depends on the interference level. If 1/SD weights is used for the prediction, (i) the effect of normal noise (interference signal) can be easily
reduced and (ii) the influence from accidental cases (unstable instrumental cases or sample contamination) can also be minimized. $^{136}\text{Ba}$, $^{137}\text{Ba}$ and $^{138}\text{Ba}$ seriously influence REE prediction, especially if high concentration ratios ($C_{\text{Ba}} / C_{\text{REEs}}$) are present. As a result, it is very difficult to accurately predict the concentration of Ce, La and some other isotopes because of strong interference from Ba. However, it was found that barium interference could be overcome by changing the model weights. For example, if the weights set for $^{136}\text{Ce}$, $^{138}\text{Ce}$ and $^{138}\text{La}$ in the $[X]$ matrix were decreased, the RD of prediction was reduced for these isotopes. Moreover, when weights below 0.1 were used for these isotopes, a minimum RD was obtained ($< 5\%$).

![Graph showing RD % vs REEs](image)

**Figure 2.3.** The effect of weights on the PLSR model (RD is the Relative Deviation, $1/\text{SD}$ is the inverse of the Standard Deviation of the absolute noise).

### 2.4.3. Loading and score

Loading expresses the relationship between variables and factors in a model (Table 2.2.). From the loading, the importance of each isotope/variable in each factor can be established. Factor 1 primarily described all the REEs and was the most significant factor in the model. Factors 2-6 were important for the description of REEs which possess multiple isotopes, *i.e.*, Nd, Sm, Er, Dy, Yb and Gd. Factors 7-14 were important for the description of REEs which possess individual isotopes or isotopes in abundance, *i.e.*, Pr, Tb, Ho, Tm and $^{139}\text{La}$, $^{140}\text{Ce}$ and $^{175}\text{Lu}$ (see Table 2.2. for summary).
The term “score” can be used to study variations between objects in the data set and to interpret which properties or characteristics of the objects are important in the model. Score results indicated, that 66% of the calibration variance was described by factor 1, and 6, 5, 5, 4, 4 and 2% were described by factors 2-7, respectively. Factors 8-14 described 1% of the variance, implying that higher order factors influence the model by less than 1%. Factor score plots showed that factor 1 is the most important factor in describing all the samples/objects in the model. If higher concentrations of Nd, Sm, Gd, Dy, Er and Yb were present in the sample/object, the importance of the sample/object in this factor is increased. From factors 2 to 14, most score contribution came from samples/objects containing higher concentrations of the elements Nd, Sm, Gd, Dy. For these important elements each factor in the score plot is closely related to the result of the loading plot. Elements such as Nd, Sm, Gd, Dy and Yb played a more important role in the model because they possess multiple isotopes which require repeated calibration.

Table 2.2. The relationship between variables (REE isotopes) and factors in the PLSR model.

<table>
<thead>
<tr>
<th>Factor number</th>
<th>Description of:</th>
<th>Factor number</th>
<th>Description of:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>All REEs</td>
<td>8</td>
<td>$^{140}$Ce, $^{151}$Eu and $^{153}$Eu</td>
</tr>
<tr>
<td>2</td>
<td>Nd, Sm, Gd, Er, Dy and Yb isotopes</td>
<td>9</td>
<td>$^{139}$La, $^{140}$Ce, $^{159}$Tb, $^{165}$Ho, $^{169}$Tm and $^{175}$Lu</td>
</tr>
<tr>
<td>3</td>
<td>Nd and Sm isotopes</td>
<td>10</td>
<td>$^{139}$La and $^{175}$Lu</td>
</tr>
<tr>
<td>4</td>
<td>Gd and Yb isotopes</td>
<td>11</td>
<td>$^{139}$La, $^{140}$Ce, Tb$^{159}$, $^{165}$Ho, $^{169}$Tm and $^{175}$Lu</td>
</tr>
<tr>
<td>5</td>
<td>Gd, Dy and Yb isotopes</td>
<td>12</td>
<td>$^{141}$Pr</td>
</tr>
<tr>
<td>6</td>
<td>Er, Dy and Yb isotopes</td>
<td>13</td>
<td>$^{165}$Ho and $^{169}$Tm</td>
</tr>
<tr>
<td>7</td>
<td>$^{140}$Ce, $^{159}$Tb, $^{165}$Ho, $^{169}$Tm and $^{175}$Lu</td>
<td>14</td>
<td>$^{159}$Tb, $^{165}$Ho and $^{169}$Tm</td>
</tr>
</tbody>
</table>
2.4.4. Accuracy of the model

*Figure 2.4.(a-d)* compares the concentrations of $^{140}$Ce, $^{152}$Sm, $^{164}$Dy and $^{174}$Yb predicted with the PLSR model with their certified concentrations. The correlation coefficients were 0.9967, 0.9995, 0.9998 and 0.9999, respectively. $^{152}$Sm, $^{164}$Dy and $^{174}$Yb showed good correlation between certified and predicted values. The average correlation coefficient of all 52 REE isotopes was 0.9982. It can be concluded that all variables were well modelled and good correlation existed between predicted and known (certified) values.

2.4.5. Error of the model

In order to define the expected error of future predicted values, the uncertainty limits of the model (prediction error) were estimated. *Figure 2.5.(a-d)* shows the predicted values of Ce at 50 and 500 µg.l$^{-1}$ and the predicted values Sm at 50 and 500 µg.l$^{-1}$, respectively. In *Figure 2.5.(a-d)*, the prediction error is represented as the vertical bars on the graph. The prediction error was higher at the lower (50 µg.l$^{-1}$) concentration level ca. 7 - 10%, for all elements. On the other hand, the prediction error at the higher concentration level (500 µg.l$^{-1}$) was less than 5%, for all elements.

2.4.6. Prediction of REE concentrations using the PLSR model

Prediction of REE concentrations in samples was carried out as follows: the sample mass spectral signals were obtained from the ICP-MS, thereafter the signals were normalized by daily calibration (using standard solutions or reference materials) to ensure the same instrumental sensitivity as the model data set. If a large variation in instrumental sensitivity between model input data and sample input data was found or if the sample matrix differed greatly from the model matrix, the model must be re-calibrated using extra input data from samples with standard additions of all REEs and increasing the model weights of these samples.

The concentration of REEs in a set of standard solutions was predicted with the PLSR model. The solutions contained 10 µg.l$^{-1}$ of each rare earth element and were measured by ICP-MS. Results indicated (*Figure 2.6.*) that different isotopes could be measured with the same accuracy even when their abundance differed by a factor of 1000. The recovery of the REEs ranged from 98 to 103% and standard deviations were less than ±0.41 µg.l$^{-1}$. Both the relative error and RSD were less than 5%.
Figure 2.4.(a-d) Accuracy of the PLSR model: A comparison of predicted and certified concentrations of $^{140}$Ce, $^{152}$Sm, $^{164}$Dy and $^{174}$Yb.
Figure 2.5.(a-d) Predicted concentrations of $^{140}\text{Ce}$ (at 50 & 500 µg.l$^{-1}$) and $^{152}\text{Sm}$ (at 50 & 500 µg.l$^{-1}$).
2.4.7. **Comparison of the PLSR model and the normal calibration method**

A comparison of REE concentrations predicted with the PLSR model and the Normal Calibration Method (NCM), for soil reference materials indicated that the PLSR model was more accurate (*Figure 2.6.(a-b)*). The average RSD of prediction was 4.7 % and 15.2 % for the PLSR model and the NCM, respectively. The relative deviation of prediction was less than 5% in most cases, for the PLSR model. However, in the case of Lu, Tm and Ho the relative deviations were 11%, 10.2 % and 8.9 % respectively. This may be attributed to the fact that their concentrations in the soil reference samples were close to the detection limit.

2.4.8. **Comparison of the PLSR model with the PCA and Gauss elimination methods**

PCA only decomposes the original X data into a model comprising signal and error (noise) parts, whereas the PLSR model simultaneously and interdependently decomposes both the [X] and [Y] matrices so that the information in the [Y] matrix is used directly as a guide for optimal decomposition of the [X] matrix, and then performs regression of [Y]. In this way, the concentration of new unknown samples can be predicted accurately using the PLSR model and interference from all REE oxides and hydroxides, isobaric overlap and Ba interferences can be removed.

The Gauss elimination method (GEM) is a method of algebraically solving $n$ equations in $n$ unknowns; a detailed discussion was presented by Vaughan and Horlick (1990). This method provides a correction scheme for spectral overlap of REEs oxides. The accuracy is comparable to that with the PLSR model. However, it is a complicated and time-consuming method for the correction of REE spectral overlap and oxide/hydroxide interferences. In contrast, the PLSR method is fast, flexible and simple to use.
Figure 2.6.(a-b) A comparison of the PLSR model and the NCM (Prediction was made using GBW07313 soil reference material, diluted 1000 times with HNO₃).
2.5. Conclusions

Employing optimal modelling parameters (e.g. 14 factors, model centre at the origin and model weights equal to 1/SD), almost 0% total residual variance was achieved with the PLSR model. The square error of prediction was less than 0.005 and the oxide/hydroxide/isobaric interferences were almost completely (ca.100%) removed. Nd, Sm, Gd, Dy and Yb played a more significant role in the model because they possess multiple isotopes which require repeated calibration. Barium interference could be overcome by setting the weights of certain isotopes in the model below 0.1. Results indicated that the PLSR model was more accurate than the Normal Calibration Method (NCM) and was simpler and more flexible than the Gauss Elimination Method (GEM).

References


Chapter 3

Application of a PLSR Model for Spectral Correction in ICP-MS Analysis of REEs in Environmental Samples

Abstract

A method is described for the determination of rare earth elements (REEs) in environmental samples using inductively coupled plasma-mass spectrometry (ICP-MS), in combination with a partial least squares regression (PLSR) model for the correction of interferences from REE oxides, hydroxides and isobaric spectral overlap. Interferences from REE oxides and hydroxides were estimated to be 1 and 0.1% respectively. The accuracy and precision (RSD<5%) of the PLSR model was satisfactory for the measurement of REE concentrations in different reference materials and environmental samples i.e. soil, sediment, sludge and seawater, even in samples where high ratios of Ba/REEs and salt/REEs existed. The detection limit ranged from 14 - 34 ng.l⁻¹.

3.1. Introduction

Today, ICP-MS is becoming predominant compared to other techniques because of the (i) full elemental coverage, (ii) the ability to analyze samples of different quality, and (iii) the low detection limits, particularly when using ultrasonic nebulization (Batley, 1991, Jarvis et al., 1992, Evans, 1993 and De Boer et al., 1995). However, spectral interference from oxides (MO⁺), hydroxide (MOH⁺) and polyatomic ions are problems in the determination of REEs by ICP-MS. REEs have a strong tendency to form oxides and hydroxides. One of the most important examples occurs at mass 156, where spectral interference exists from 156Gd, 156Dy, 140Ce16O, and 139La16O1H. For analysis of 156Gd, these spectral interferences should be removed (Vaughan and Horlick, 1986, Vaughan and Horlick, 1990 and Zhu et al., 1997).
Overcoming the problem of polyatomic ion interference has been a prominent feature in several publications in the field of ICP-MS (Lichte et al. 1987, Van Veen et al., 1994 and De Boer et al., 1995). In this context, PLSR modelling is gaining importance in the field of analytical chemistry (Geladi and Kowalski, 1986, Helland, 1990, Meloun et al., 1992 and De Jong, 1993). Vaughan and Horlick (1990) reported principal component analysis correction procedures for REE analysis with ICP-MS and Zhu et al. (1997) developed a PLSR model for spectral correction in ICP-MS for analysis of REEs. The application of the PLSR model for spectral correction in ICP-MS analysis of REEs in environmental samples is addressed here. REEs oxide and hydroxide yields as well as precision, accuracy and detection limits of the technique are estimated and discussed.

3.2. Experimental

3.2.1. Reagents and standards

REE solutions were prepared from standard 1000 μg/ml stock solutions (Perkin-Elmer). Single element standards were prepared for each of the following 14 elements: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. In all cases indium (115In) was used as an internal standard. Purified water (demineralized Milli-Q, 18.2 MΩcm⁻¹ purity) was used throughout. Superpure HNO₃ and HCl were obtained from MERCK, Germany. Reference materials employed for this study comprised marine sediment and two types of soil, received from the US Geological Survey and the Chinese National Research Centre for Certified Reference Materials.

3.2.2. Sample preparation

After drying overnight at 105 °C, 0.2 g of sample was weighed directly into a 100 ml digestion container and 10 ml of HNO₃ (70%) and deionized water were added, respectively. Thereafter, the mixture was digested in a microwave oven (CEM MDS 2000). After cooling, the solution was diluted to 100ml. All samples were diluted with 1% HNO₃ and spiked with In (internal standard) to give a final concentration of 10ppb.

3.2.3. Measurement

The analyses were performed using the "peak jump" mode of data acquisition. The scan conditions are summarised in Table 3.1. The analytical procedure comprised measuring blank and control standards at the beginning and end of the experiment and
after every eight samples. Each sample was measured in triplicate. A 3% v/v HNO₃ solution was used for washing the interment in order to remove any contamination and "memory effect" prior to sample and standard introduction to the ICP-MS.

**Table 3.1.** ICP-MS measurement conditions.

<table>
<thead>
<tr>
<th>Mode of data acquisition:</th>
<th>peak jump</th>
</tr>
</thead>
<tbody>
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<td>Acquisition time (s):</td>
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</tr>
<tr>
<td>Dwell time (ms):</td>
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</tr>
<tr>
<td>Points/peak:</td>
<td>3</td>
</tr>
<tr>
<td>Collector type:</td>
<td>Pulse</td>
</tr>
<tr>
<td>Repeat time/samples:</td>
<td>3</td>
</tr>
</tbody>
</table>

### 3.2.4. Data preparation

All raw mass spectral data (i.e. uncorrected counts measured per second) from the ICP-MS were corrected by ¹¹⁵In (internal standard) and further transformed to data matrices. The data matrix files were converted to an acceptable format by the program Unscrambler. In this study, [X] data and [Y] data matrices represent REE signals and concentrations, respectively. Detailed procedures of the model set-up are given in Chapter 2.

### 3.3. Results and discussion

#### 3.3.1. Interference from REE oxides and hydroxides

The problems of spectroscopic overlap of REE oxides and hydroxides, as well as overlap of their own isotopes with (M⁺) signals were reported by Vaughan and Holick (1990). In order to understand REE oxide and/or hydroxide interference in instrumental systems, the response of elemental oxides and hydroxides was studied with 500 μg.l⁻¹(ppb) standard REE solutions, under similar plasma conditions. In **Figure 3.1.** and **Figure 3.2.**, the percentage oxide and hydroxide concentration in most REEs is presented. Oxide levels between 0.2 and 1.5 % were recorded for Pr, Ce, La, Nd, Tb, Dy, Gd, and Sm. Oxide levels below 0.1% were recorded for Ba and Eu and levels below 0.5% were recorded for the remaining rare earth elements. These results are similar to those reported by Lichti et al. (1987). An understanding of oxide and Ba interference with light REEs is extremely important as the resulting signals overlap with
some of the heavy REEs. For example, the signal intensity of $^{157}$Gd and $^{158}$Gd can also originate from $^{141}$Pr$^{16}$O and $^{142}$Ce$^{16}$O respectively. In both cases, the oxide signal represents ca. 70% of the total REE signal.

**Figure 3.1.** Percentage of REE oxide

**Figure 3.2.** Percentage of REE hydroxide
Tan *et al.* (1986) and Dulski (1994) provide a detailed discussion of oxide and hydroxide formation with REEs. High oxide levels were reported in their studies. They also indicated that the removal of Ba from rock solutions and the separation of REEs into two groups *i.e.* light REEs and heavy REEs, reduced oxide interference and allowed more accurate determination of all REEs. Lichte *et al.* (1987) used instrumental setting to minimize oxide formation and employed an algebraic correction scheme in the data processing step (Zhu *et al.*, 1997). However, this correction method was not very flexible and a more appropriate correction method is still required.

### 3.3.2. The measurement of REE concentrations in references materials using the PLSR model

The performance and reliability of the PLSR model was evaluated by the measurement of REE concentrations in soil and marine sediment reference materials. Reference materials, MAG-1 (marine sediment) and GBW07407 (marine sediment), as well as GBW07313 (soil) were used in this study. The concentration of Ba in these samples was 180, 4400 and 479 mg·kg⁻¹, respectively. Results of the measurement of REE concentrations in these samples are shown in Figure 3.3.(*a-b*), Figure 3.4.(*a-b*) and Figure 3.5.(*a-b*), respectively.

The values measured are in good agreement with the certified values. For most REE isotopes in the samples, the measured values deviated less than 5% from the certified values. In particular, ¹³⁶Ce, ¹³⁸Ce and ¹³⁸La, which are present in very low concentrations due to their limited abundance, can be accurately predicted even with spectral (overlap) interference from Ba. High Ba concentrations appear to have no effect on the accuracy of REE measurement when the PLSR model was employed. Nevertheless, the accuracy decreases if the isotope concentration in the sample is close to the detection limit. As a result, REE concentrations must be considered when measuring their concentrations in environmental samples with the PLSR model because the greatest measured error is always for the element of lowest concentration.
Table 3.2. The interferences from oxides and hydroxides.

<table>
<thead>
<tr>
<th>Oxide or hydroxide</th>
<th>Interference for measurement of</th>
<th>Interference coefficient</th>
<th>Oxide or hydroxide</th>
<th>Interference for measurement of</th>
<th>Interference coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{135}$Ba$^{16}$O</td>
<td>$^{151}$Eu</td>
<td>0.0007</td>
<td>$^{144}$Sm$^{16}$O</td>
<td>$^{165}$Dy</td>
<td>0.033</td>
</tr>
<tr>
<td>$^{136}$Ba$^{16}$O</td>
<td>$^{152}$Sm</td>
<td>0.017</td>
<td>$^{144}$Sm$^{16}$O</td>
<td>$^{165}$Gd</td>
<td>0.0034</td>
</tr>
<tr>
<td>$^{138}$Ba$^{16}$O</td>
<td>$^{152}$Gd</td>
<td>0.00013</td>
<td>$^{145}$Sm$^{16}$O</td>
<td>$^{165}$Dy</td>
<td>0.0025</td>
</tr>
<tr>
<td>$^{137}$Ba$^{16}$O</td>
<td>$^{153}$Eu</td>
<td>0.0013</td>
<td>$^{146}$Sm$^{16}$O</td>
<td>$^{164}$Dy</td>
<td>0.003</td>
</tr>
<tr>
<td>$^{138}$Ba$^{16}$O</td>
<td>$^{154}$Gd</td>
<td>0.00072</td>
<td>$^{148}$Sm$^{16}$O</td>
<td>$^{164}$Er</td>
<td>0.00016</td>
</tr>
<tr>
<td>$^{138}$Ba$^{16}$O</td>
<td>$^{154}$Sm</td>
<td>0.00063</td>
<td>$^{149}$Sm$^{16}$O</td>
<td>$^{165}$Ho</td>
<td>0.0036</td>
</tr>
<tr>
<td>$^{138}$Ba$^{16}$O$^3$H</td>
<td>$^{155}$Gd</td>
<td>0.011</td>
<td>$^{150}$Sm$^{16}$O</td>
<td>$^{166}$Er</td>
<td>0.0072</td>
</tr>
<tr>
<td>$^{139}$La$^{16}$O</td>
<td>$^{155}$Gd</td>
<td>0.0082</td>
<td>$^{151}$Sm$^{16}$O</td>
<td>$^{168}$Er</td>
<td>0.0027</td>
</tr>
<tr>
<td>$^{139}$La$^{16}$O$^3$H</td>
<td>$^{156}$Gd</td>
<td>0.00093</td>
<td>$^{152}$Sm$^{16}$O</td>
<td>$^{170}$Yb</td>
<td>0.076</td>
</tr>
<tr>
<td>$^{139}$La$^{16}$O$^3$H</td>
<td>$^{156}$Dy</td>
<td>0.001</td>
<td>$^{153}$Sm$^{16}$O</td>
<td>$^{170}$Er</td>
<td>0.002</td>
</tr>
<tr>
<td>$^{140}$Ce$^{16}$O</td>
<td>$^{156}$Gd</td>
<td>0.0098</td>
<td>$^{151}$Eu$^{16}$O</td>
<td>$^{167}$Er</td>
<td>0.00041</td>
</tr>
<tr>
<td>$^{140}$Ce$^{16}$O</td>
<td>$^{156}$Dy</td>
<td>0.011</td>
<td>$^{153}$Eu$^{16}$O</td>
<td>$^{169}$Tm</td>
<td>0.00057</td>
</tr>
<tr>
<td>$^{140}$Ce$^{16}$O$^3$H</td>
<td>$^{157}$Gd</td>
<td>0.00083</td>
<td>$^{154}$Gd$^{16}$O</td>
<td>$^{170}$Yb</td>
<td>0.0089</td>
</tr>
<tr>
<td>$^{142}$Ce$^{16}$O</td>
<td>$^{158}$Gd</td>
<td>0.0064</td>
<td>$^{154}$Gd$^{16}$O</td>
<td>$^{170}$Er</td>
<td>0.008</td>
</tr>
<tr>
<td>$^{142}$Ce$^{16}$O$^3$H</td>
<td>$^{159}$Tb</td>
<td>0.0018</td>
<td>$^{155}$Gd$^{16}$O</td>
<td>$^{171}$Yb</td>
<td>0.0049</td>
</tr>
<tr>
<td>$^{141}$Pr$^{16}$O</td>
<td>$^{157}$Gd</td>
<td>0.0112</td>
<td>$^{156}$Gd$^{16}$O</td>
<td>$^{172}$Yb</td>
<td>0.028</td>
</tr>
<tr>
<td>$^{141}$Pr$^{16}$O$^3$H</td>
<td>$^{158}$Gd</td>
<td>0.00056</td>
<td>$^{157}$Gd$^{16}$O</td>
<td>$^{173}$Yb</td>
<td>0.0062</td>
</tr>
<tr>
<td>$^{143}$Nd$^{16}$O</td>
<td>$^{158}$Gd</td>
<td>0.009</td>
<td>$^{158}$Gd$^{16}$O</td>
<td>$^{174}$Yb</td>
<td>0.006</td>
</tr>
<tr>
<td>$^{143}$Nd$^{16}$O</td>
<td>$^{159}$Tb</td>
<td>0.0016</td>
<td>$^{160}$Gd$^{16}$O</td>
<td>$^{176}$Yb</td>
<td>0.0059</td>
</tr>
<tr>
<td>$^{144}$Nd$^{16}$O</td>
<td>$^{160}$Dy</td>
<td>0.0096</td>
<td>$^{160}$Gd$^{16}$O</td>
<td>$^{176}$Lu</td>
<td>0.0083</td>
</tr>
<tr>
<td>$^{144}$Nd$^{16}$O</td>
<td>$^{160}$Gd</td>
<td>0.0091</td>
<td>$^{158}$Tb$^{16}$O</td>
<td>$^{175}$Lu</td>
<td>0.077</td>
</tr>
<tr>
<td>$^{145}$Nd$^{16}$O</td>
<td>$^{161}$Dy</td>
<td>0.011</td>
<td>$^{158}$Tb$^{16}$O$^3$H</td>
<td>$^{176}$Yb</td>
<td>0.0003</td>
</tr>
<tr>
<td>$^{146}$Nd$^{16}$O</td>
<td>$^{162}$Dy</td>
<td>0.011</td>
<td>$^{158}$Tb$^{16}$O$^3$H</td>
<td>$^{176}$Lu</td>
<td>0.00039</td>
</tr>
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<td>$^{148}$Nd$^{16}$O</td>
<td>$^{164}$Dy</td>
<td>0.01</td>
<td>$^{160}$Dy$^{16}$O</td>
<td>$^{176}$Yb</td>
<td>0.001</td>
</tr>
<tr>
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<td>$^{164}$Er</td>
<td>0.01</td>
<td>$^{160}$Dy$^{16}$O</td>
<td>$^{176}$Lu</td>
<td>0.067</td>
</tr>
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<td>$^{150}$Nd$^{16}$O</td>
<td>$^{166}$Er</td>
<td>0.0095</td>
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</table>
Figure 3.3. (a-b) A comparison of the concentrations of certified and measured marine sediment reference material (Mag-1).
Figure 3.4. (a-b) A comparison of the concentrations of certified and measured marine sediment reference material (GBW07407).

Figure 3.5. (a-b) A comparison of the concentrations of certified and measured soil reference material (GBW07313).
3.3.3. The measurement of REE concentrations in environmental samples using the PLSR Model

The PLSR model was used for the measurement of REE concentrations in different environmental samples *i.e.* soil, sludge and sea water samples. The soil sample was taken from Heerewaarden (The Netherlands); the sludge samples were from a drinking water treatment plant (Groningen, The Netherlands) and the sea water sample came from the North Sea coastal area (Den Helder, The Netherlands). The results are presented in Table 3.3. and Table 3.4. The precision of measured REE concentrations,

<table>
<thead>
<tr>
<th>REE</th>
<th>Soil (n=6)</th>
<th></th>
<th>Sea water (n=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C (mg.kg⁻¹)</td>
<td>RSD (%)</td>
<td>Recovery (%)</td>
</tr>
<tr>
<td>La</td>
<td>15.5±1.2</td>
<td>7.9</td>
<td>101.4</td>
</tr>
<tr>
<td>Ce</td>
<td>33.9±2.5</td>
<td>7.3</td>
<td>99.7</td>
</tr>
<tr>
<td>Pr</td>
<td>4.1±0.31</td>
<td>7.7</td>
<td>101.6</td>
</tr>
<tr>
<td>Nd</td>
<td>16.0±0.94</td>
<td>5.9</td>
<td>103.2</td>
</tr>
<tr>
<td>Sm</td>
<td>3.18±0.13</td>
<td>4.1</td>
<td>101.1</td>
</tr>
<tr>
<td>Eu</td>
<td>0.44±0.002</td>
<td>0.5</td>
<td>101.6</td>
</tr>
<tr>
<td>Gd</td>
<td>2.79±0.018</td>
<td>0.6</td>
<td>102.8</td>
</tr>
<tr>
<td>Tb</td>
<td>0.24±0.009</td>
<td>3.8</td>
<td>101.0</td>
</tr>
<tr>
<td>Dy</td>
<td>1.81±0.031</td>
<td>1.7</td>
<td>97.2</td>
</tr>
<tr>
<td>Ho</td>
<td>0.30±0.007</td>
<td>2.3</td>
<td>97.8</td>
</tr>
<tr>
<td>Er</td>
<td>0.81±0.004</td>
<td>0.5</td>
<td>99.4</td>
</tr>
<tr>
<td>Er</td>
<td>0.81±0.004</td>
<td>0.5</td>
<td>99.4</td>
</tr>
<tr>
<td>Yb</td>
<td>0.49±0.14</td>
<td>2.9</td>
<td>99.2</td>
</tr>
<tr>
<td>Lu</td>
<td>0.09±0.008</td>
<td>8.1</td>
<td>95.7</td>
</tr>
</tbody>
</table>

n: number of duplicates.
* The calculated recovery was based on the REE concentration added for the purpose of standard addition.
Table 3.4. REE concentrations in the ground and surface-water-sludge sample measured via the PLSR model.

<table>
<thead>
<tr>
<th>REE</th>
<th>Ground water sludge (n=6)</th>
<th>Surface water sludge (n=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C (mg.kg⁻¹)</td>
<td>RSD (%)</td>
</tr>
<tr>
<td>La</td>
<td>1.03±0.059</td>
<td>5.8</td>
</tr>
<tr>
<td>Ce</td>
<td>2.11±0.10</td>
<td>4.9</td>
</tr>
<tr>
<td>Pr</td>
<td>0.28±0.0035</td>
<td>1.3</td>
</tr>
<tr>
<td>Nd</td>
<td>1.36±0.066</td>
<td>4.8</td>
</tr>
<tr>
<td>Sm</td>
<td>0.83±0.029</td>
<td>3.6</td>
</tr>
<tr>
<td>Gd</td>
<td>1.31±0.043</td>
<td>3.3</td>
</tr>
<tr>
<td>Eu</td>
<td>0.24±0.006</td>
<td>2.6</td>
</tr>
<tr>
<td>Tb</td>
<td>0.09±0.005</td>
<td>6.1</td>
</tr>
<tr>
<td>Dy</td>
<td>0.68±0.023</td>
<td>3.3</td>
</tr>
<tr>
<td>Ho</td>
<td>0.18±0.01</td>
<td>6.5</td>
</tr>
<tr>
<td>Er</td>
<td>0.62±0.031</td>
<td>5</td>
</tr>
<tr>
<td>Tm</td>
<td>0.09±0.0026</td>
<td>2.9</td>
</tr>
<tr>
<td>Yb</td>
<td>0.62±0.0004</td>
<td>0.1</td>
</tr>
<tr>
<td>Yb</td>
<td>0.62±0.0004</td>
<td>0.1</td>
</tr>
<tr>
<td>Lu</td>
<td>0.13±0.003</td>
<td>2.6</td>
</tr>
</tbody>
</table>

n: number of duplicates.
*The calculated recovery was based on the REE concentration added for the purpose of standard addition.

expressed as RSD, in environmental samples ranged from 0.1 to 8%, with ca. 80% of the measured RSD values below 5%. The relatively poor precision for La, Ce and Nd resulted from the measurement procedure (*i.e.* digestion and analysis). The RSD of Lu (soil and sea water samples), Tb (ground water sludge sample) and Ho (ground and surface water sludge samples) were greater than 5%. This phenomenon may be attributed to the fact that the concentrations of these isotopes in the samples (after preparation) were close to their detection limit. The precision of environmental samples measured can be very high if the REE concentration in the sample is at least 5 times greater than the detection limit.
The recovery ranged from 95 to 105% for soil, seawater and ground water samples and from 95 to 110% for the surface water sludge sample. The sea water and ground water sludge samples contained large amounts of NaCl and Fe. However, if the operating conditions of the ICP-MS are optimized and the PLSR model is employed, the concentration of REEs in environmental samples can be measured with high accuracy and precision, despite matrix effects and interferences.

3.3.4. Detection limits

The detection limits were calculated from the threefold of the standard deviations of the blank. All values are based on data collected during multi-element, multi-channel scans using optimal instrument settings and measurement with the PLSR model. The detection limits of all REEs are between 0.014 and 0.034 μg.l⁻¹. Therefore, the REE concentration in most environmental samples, without preconcentration, is high enough to allow precise and accurate determination with ICP-MS when the PLSR model is employed for spectral correction. However, a preconcentration procedure could be useful if the REE concentrations in the sample were below the detection limit.

3.4. Conclusions

The PLSR model is a possible method of spectral correction for REE analysis with ICP-MS. REE oxide and hydroxide levels were estimated to be 1 and 0.1%, but the interference may be substantially larger e.g. 70% for ¹⁵⁷Gd and ¹⁵⁸Gd from ¹⁴¹Pr¹⁶O and ¹⁴²Ce¹⁶O, respectively. The PLSR model was satisfactorily used for the measurement of REE concentrations in different reference materials and environmental samples i.e. soil, sediment, sludge and sea water, with acceptable accuracy and precision (RSD<5%), even in samples where high ratios of Ba/REEs and salt/REEs exist. The detection limit ranged from 14 - 34 ng.l⁻¹.
References


Chapter 4

Preconcentration and Determination of Ultra Trace REEs in Environmental Samples with an Ion Exchange Micro-Column

Abstract

A study was carried out on the preconcentration of ultra trace rare earth elements (REEs) in environmental samples with a micro ion-exchange column and determination by inductively coupled plasma mass spectrometry (ICP-MS). The preconcentration parameters were optimized with synthetic standard solutions and the REE recovery was found to be in the range of 94-98% in the pH range 4 to 6 with an ionic strength (μ) less than 0.18. The ion-exchange column capacity with respect to REEs was estimated as 0.96 mmol/g. The linear response coefficients ranged from 0.995 to 0.997 at the ng.l⁻¹ level. The concentration in the blank could be minimized (0.09 to 3.1 ng.l⁻¹) if the buffer solution and the water were purified. The detection limits ranged from 0.03 to 0.40 ng.l⁻¹, for a preconcentration factor of 100. The precision and accuracy of the method was evaluated on real samples by spiking experiments with synthetic standard solutions. Results indicated that the REE recovery ranged from 88.1% to 100.2% and the RSD from 2.7% to 6.7 % for tap water. Results with comparable accuracy and precision were achieved when this method was applied for the determination of REEs in environmental aquatic samples.

4.1. Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) is widely used for the determination of rare earth elements (REEs) in geological material and environmental samples (Lichte et al., 1987, Jarvis, 1989, Moller et al., 1992, Balaram, 1995, De Boer et al., 1995 and Kreamer et al., 1996). However, the determination of REE ions in aquatic samples usually requires a preconcentration step since most of these elements are present in concentrations close to or below the detection limit of the analytical equipment.
Preconcentration techniques currently used for REE determination in water, include coprecipitation with Fe(OH)$_3$, Al(OH)$_3$, CaC$_2$O$_3$ or CaF$_2$ (Greaves et al., 1989, Honda et al., 1989 and Roychowdhury et al., 1989), ion exchange with Chelex 100, Dowex 50W X12 and AG 50W (De Baar et al., 1985, Zachmann, 1988, Mathermy and Macejko, 1991, Kubova et al., 1994 and Kawabata et al., 1991), liquid-liquid extraction (Deorkar and Khopkar, 1991 and Pandy et al., 1995) and extraction chromatography (Braverman, 1992, Yang et al., 1993 and Yang and Guan, 1993), adsorption onto silica-immobilized 8-hydroxyquinoline (Silica-8HQ) (Esser et al., 1994), or immobilized bacteria (Maquirira et al., 1996).

Complexation with bis-(2-ethylhexyl) hydrogen phosphate/2-ethylhexyl dihydrogen phosphate (HDEHP/H$_2$DEHP) for the preconcentration of REEs was reported by Shabani et al. (1990, 1991 and 1992). The method of coprecipitation with M(OH)$_n$ was developed and used for many years, but suffers from several limitations, including non quantitative recovery and the requirement of additional procedures to remove Mg$^{2+}$, Ca$^{2+}$ and Fe$^{3+}$ (Shabani et al., 1992 and Esser et al., 1994). Chelating resins are presently the most popular preconcentration materials for trace amounts of REE, however, an extra process is also required to remove Ca$^{2+}$ and Mg$^{2+}$, e.g. careful washing with ammonium acetate or cation and anion-exchange chromatography prior to elution of REEs. All these procedures increase sample manipulation and possible contamination of the blank (Shabani et al., 1992). Complexation with HDEHP/H$_2$DEHP and adsorption on a C$_{18}$ cartridge does not require removal of alkaline earth metals, however, the preconcentration procedures are very complicated. The use of 8-hydroxyquinoline immobilized on silica (I-8HQ) for REE preconcentration involves conditioning of the column with 8-hydroxyquinoline, passage of the sample, and elution at low pH. The main problems are the release of trace impurities from the silica gel, where also partial dissolution may occur at pH >8, reducing the recovery.

In the past decades, a number of papers have reported preconcentration of trace metals onto a micro-column based on reverse-phase adsorption of complexed metals or direct adsorption of metal ions (Elsholz and Schulze, 1995). However, limited knowledge is available on the preconcentration of REEs using micro-columns, and in particular, REE behavior on the column.

The aims of this work are to develop a simple and precise preconcentration method for the analysis of ultra trace amounts of REEs in water, using a micro ion-exchange column which can be used without preconditioning, which can be operated under relatively high flow conditions to reduce the time needed for the adsorption step and
which, in principle, can be operated in line with the ICP-MS. To optimize the preconcentration step, the REE behavior on the column was studied under different pH, flow conditions and ionic strength and the final method was applied to the determination of REEs in aquatic environmental samples.

4.2. Experimental

REE solutions were prepared from standard 1000 mg.l⁻¹ stock solutions (Perkin-Elmer). Single element standards were prepared for each of the following 16 elements: Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. Indium (¹¹⁵In) was used as an internal standard.

Acetic acid - ammonium acetate (pH=4.2) buffer solution: 65 ml of high purity glacial acetic acid was added to 800 ml of water and adjusted to pH 4.2 with superpure NH₃·H₂O. Finally, the solution was diluted to 1000 ml with purified water. The buffer solution and water (18.2 MΩ.cm⁻¹) used for this experiment were first passed through a cartridge in order to minimize the blank.

Synthetic ion-strength solution: 81.8g NaCl, 19.22g MgSO₄, 4.6g CaCl₂·2H₂O, 2.24 g KCl and 0.728g Na₂CO₃ were dissolved in 1500 ml of water. The solution was adjusted with HNO₃ to a pH about 4.2 and purified by passing through a cartridge. The ionic strength (μ) of the solution was ca. 1.35. Superpure HNO₃ and NH₃·H₂O were from MERCK, Germany.

Fresh water samples: Drinking water samples were collected from a drinking water plant in Amsterdam. Surface water samples were collected from the harbor of Rotterdam. After collection, the samples were acidified to pH ≤ 2 with HNO₃. The surface water samples were filtered through 0.45μm Supor filters (Gelman Sciences).

Cartridges (Sep Pak Light-CM, Waters Chromatography Company, U.S.A.) were used for this work. The physical and chemical characteristics of these cartridges are as follows. Weight of packing material 130 mg/cartridge. The packing material is an acrylic acid/acrylamide copolymer on Diol silica. The ligand density is 350 mmoles.kg⁻¹ material, surface pH=4, pore size 300 Å, particle size of the material 35-55 μm.

Preconcentration procedures: Sample preparations and preconcentration procedures were performed in a clean laboratory. The preconcentration system consisted of a Gilson peristaltic pump, with Tygon pump tubes connected to a cartridge. The cartridge
was washed with 0.25 M HNO₃ solution and water, respectively, prior to use for the preconcentration. The pH of each sample was adjusted to 3.5 - 4.5 with a few drops of high-purity NH₃.H₂O, then, 5ml acetic acid - ammonium acetate (pH=4.2) buffer solution was added. The sample was passed through a cartridge (3ml/min). When the sample was completely passed through, the cartridge was washed with water for one minute to remove any remaining matrix. REEs in the cartridge were eluted with 10 ml 0.25 M HNO₃ at a flow rate of 2.5 ml.min⁻¹. The outlet solution was collected in a Teflon test tube, and the solution was directly measured by ICP-MS.

Experiments (effect of pH, ionic strength and flow rate were on REE adsorption) were carried out with 100 ml batches of synthetic REE solution. The solutions contained 1 µg.l⁻¹ of each REE.

4.3. Results and discussion

4.3.1. Effect of pH on REE adsorption onto ion exchange micro-column (cartridge)

The effect of pH on the recovery of four different REEs onto a cartridge is illustrated in Figure 4.1. The adsorption/desorption efficiency was ca 98% when the pH of the adsorption solution was between 4-6. The REE recovery decreased slightly if the solution pH exceeded 6.

This phenomenon can be explained by following equations:

When equilibrium is reached,

\[ H₂O + RCOOH_\zeta RCOO^- + H₃O^+ \quad (K_a) \]  \hspace{1cm} (4.1)

\[ REE(H₂O)_{n^{2+}} + zRCOO^- \zeta REE(RCOO)_{z} + nH₂O \quad (K_D) \]  \hspace{1cm} (4.2)

\[ REE(H₂O)_{n^{2+}} + zRCOOH \zeta REE(RCOO)_{z} + (n-z)H₂O + zH₃O^+ \]  \hspace{1cm} (4.3)
Figure 4.1. Effect of pH on recovery of REEs after adsorption/desorption (the experiments were carried out at adsorption flow rate = 3 ml/min and desorption flow rate = 2 ml/min).

From equation (4.1) and (4.2), equation (4.3) can be written as

$$\frac{[\text{REE} (\text{RCOO})_2 [\text{H}_3\text{O}^+]^2]}{[\text{REE} (\text{H}_2\text{O})_n^{2+}] [\text{RCOOH}]^2} = (K_d)^2 K_L$$  \hspace{1cm} (4.4)

$$K_d = \frac{[\text{REE} (\text{RCOO})_2]}{[\text{REE} (\text{H}_2\text{O})_n^{2+}]}$$

$$= (K_a)^2 K_L [\text{RCOOH}]^2/[\text{H}_3\text{O}^+]^2$$  \hspace{1cm} (4.5)

in which:

$K_L =$ REE and ligand stability constant
$K_a =$ acid equilibrium constant
$K_d =$ [REE (RCOO)$_2$]/[REE (H$_2$O)$_n$]$^{2+}$, the ratio of REE concentrations in the resin and in the outlet concentration.
Suppose

\[ [RCOOH] = C_1 \] (constant)

\[ \log K_d = z \log C_1 + z \log K_a + \log K_L + z \cdot pH \quad (4.6) \]

Suppose \( C = z \log C_2 + z \log K_a + \log K_L \)

Then, equation (6) can be written as

\[ \log K_d = C + z \cdot pH \quad (4.7) \]

The total amount of REE adsorbing to the column is dependent on the pH. At pH < 3.5 no adsorption of REE can occur because no carboxylic acid anions are available, but with increasing pH, the carboxylic acid groups in the copolymer will dissociate and the adsorption capacity will increase until complete dissociation at approximately pH = 10. However, the \( pK_a \) (hydrolysis equilibrium constant) of REEs is in the range of 20 to 26 and REE precipitation will occur if the pH exceeds 6, thus, decreasing the adsorption efficiency of REEs.

4.3.2. Effect of ionic strength (\( \mu \)) on adsorption onto an ion exchange micro-column

Ionic strength had a clear effect on the adsorption (see Figure 4.2.). The adsorption efficiencies of all REEs were 95% within an ionic strength range of 0 to 0.18. If \( \mu \) exceeded 0.18, the recovery decreased. This situation can be explained by the following two reasons. Firstly, under high ionic strength the activity of the \( REE^{2+} \) ions decreases as follows:

\[ a_{REE} = [REE^{2+}] f_\alpha \quad (4.8) \]

Where \( a_{REE} \) is the REE activity, \( [REE^{2+}] \) is its molar concentration and \( f_\alpha \) is the activity coefficient. Under high ionic strength (\( \mu = 0.18 \) to 0.70), the \( f_\alpha \) ranges from 0.3 to 0.1, thus, the effective “free” REE concentration available for adsorption is reduced. Secondly, the ionic strength solution contains high concentrations of \( Ca^{2+}, Mg^{2+}, K^+ \) and \( Na^+ \) (represented by \( M^{x+} \)) (concentrations of \( Ca^{2+}, Mg^{2+} \) and \( Na^+ \) are 83, 260, 80, and 2100 mg/L, respectively at \( \mu = 0.18 \)). In principle, these ions can also be adsorbed onto the resin, however, their bonding strength with \( RCOO^- \) is much lower than that of the REEs. Assume the ratio of bonding strengths between
Chapter 4. Preconcentration and Determination of ... 65

REE(RCOO)$_x$ and $M(RCOO)_x$ is $R$ (called the selectivity coefficient). When the ratio of concentration $[M^{x+}] / [REE^{z+}]$ is close to $R$, the amount of REE adsorbed on the resin would be reduced due to competition from $M^{x+}$. Meanwhile, the concentration of REEs and $M$ concentrations in the resin and column effluent would be different.

![Graph](image)

**Figure 4.2.** Effect of ionic strength on the adsorption of REE (the experiments were carried out at pH=4.2, adsorption flow rate = 3 ml/min and desorption flow rate = 2ml/min).

4.3.3. The effect of eluent flow rate on adsorption

The effect of flow rate on adsorption and desorption was investigated. The flow rate was varied from 1 ml/min to 5 ml/min. It was found that the adsorption efficiency of all the REEs was 98%. Even if the flow rate was increased to 8 ml/min, high adsorption efficiency (ca. 90%) was achieved. With a flow rate above 8 ml/min, the adsorption efficiency decreased. This may be due to adsorption kinetics, of which the rate decreases at high flow rates. A flow rate of 2-5 ml/min is recommended for the REE preconcentration step. For the off-line experiment, a minimum of 2-3 ml of eluent solution (0.25M HNO$_3$) is required for complete desorption of the REE from the cartridge, with a desorption flow rate in the range 1-4 ml/min. However, using online preconcentration (combined with ICP-MS), the desorption flow rate is similar to the ICP-MS sampling flow rate and 0.25M HNO$_3$ as the eluent solution is quite satisfactory.
4.3.4. REE behavior in the cartridge

*Figure 4.3.* demonstrates the competition between REEs and the ligands (RCOO\(^-\)) of the cartridge. The adsorption rates of REEs are similar with the exception of Y. After 19 minutes, equilibrium of most REEs was established in the cartridge (close to the absorption capacity). The real equilibrium was reached in the 25-th minute. From *Figure 4.3.*, it can be seen that the stability of light REEs is slightly greater than that of heavy REEs in the cartridge.

4.3.5. Capacity of the cartridge

The capacity of the cartridge was investigated by continuous injection of four different standard solutions (*e.g.* 20 mg.l\(^-1\) of La, Eu, and Lu, respectively, and 30 mg.l\(^-1\) of a REE mixed solution excluding Sc *i.e.*15 elements, 2 mg/L per element). The total amount of REEs adsorbed onto the cartridge was estimated as 10.9 mg, 9.9 mg, 10.1 mg and 9.53 mg for La, Eu, Lu and REEs, respectively. The average capacity was 10.1 ± 1.2 mg at the 95% confidence level. When calculated as mmol of REE absorbed per gram ligand, the capacities were 1.24, 1.03, 0.91 and 0.96 mol.kg\(^-1\) for La, Eu, Lu and REEs, respectively.

It was concluded that the column capacity did not vary much for the different elements, however, light REEs were less strongly bound to the ligands than the heavy REEs. The column could be re-used at least 25 times under normal operation conditions.

4.3.6. Calibration

Off-line preconcentration was carried out with a concentration range of 1 ng.l\(^-1\) to 50 ng.l\(^-1\) using optimal preconcentration parameters (pH=4.2, adsorption step: flow rate 3 ml/min, desorption step: flow rate 2 ml.min\(^-1\), and the preconcentration factor = 100). Results are given in *Figure 4.4. (a-b).* The linear response coefficients ranged from 0.995 to 0.997 for all REEs. In general, the concentration in the samples was higher than 50 ng.l\(^-1\) and could be directly measured by ICP-MS without preconcentration. However, this preconcentration method can also be applied for samples above 50 ng.l\(^-1\).
Figure 4.3. Competition of REEs in the micro ion-exchange column (2 mg.l⁻¹ concentration of each element, pH= 4.2, adsorption flow rate = 1.8 ml/min).

4.3.7. Blanks and detection limits

The mean of the blanks of individual REEs which comprised 1000 ml superpure water and 5 ml buffer solution (both solutions were already purified before the experiments) were 0.98, 0.89, 2.73, 0.42, 0.96, 0.93, 0.22, 3.1, 0.08, 0.34, 0.12, 0.45, 0.19, 0.66, 0.09 ng for Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, respectively (5 replicates were taken). They were calculated as concentrations in the solution, the results are shown in Table 4.1. Relatively high blanks were found for Ce and Gd i.e. 2.73 ng.l⁻¹ and 3.1 ng.l⁻¹, respectively. All others were lower than 1 ng.l⁻¹.
Figure 4.4. (a-b). Relationship between ICP-MS signal and REE concentrations (off-line preconcentration) (the experiments were carried out at adsorption flow rate = 3 ml/min and desorption flow rate = 2 ml/min).
Detection limits (DL), based on three times the standard deviation of the blank observed for the preconcentration of 1000 ml superpure water (eluted with 10 ml 0.25 M HNO₃) are given in Table 4.1. The detection limit DLₐ and DL represent the values calculated with and without preconcentration, respectively. DL is considered the instrument detection limit which varies between 3.0 to 40.4 pg.ml⁻¹ for REEs and DLₐ is the estimated detection limit, with a preconcentration factor of 100 (0.03 to 0.4 ng.l⁻¹). The concentration of REEs in fresh water in most case ranges between 100 to 0.1 μg.l⁻¹, thus, a 10 to 100 fold preconcentration would give good accuracy for REE analysis with ICP-MS.

4.3.8. Precision and accuracy

The precision and accuracy were determined by the analysis of a standard solution spiked with a tap water sample with a known REE concentration. 20 ng of each element was added to 1000 ml of tap water (added concentration was 20 ng.l⁻¹), and the samples were subsequently preconcentrated and measured. The experiment was repeated 5 times with the same procedure. The results of the recovery, relative standard deviation (RSD) are listed in Table 4.2. The recoveries of all REEs ranged from 88.1% to 100.2%. The recovery of most elements was ca. 95%. Only Yb, Er and Ho had recoveries slightly lower than 90%. The results indicated that the RSD of most elements was better than 5%.

4.3.9. Application to environmental samples

(i) Preconcentration of Dutch drinking water

The method was used to determine the REE concentration of raw water, purified water and tap water. A preconcentration factor of 100 was used for all samples (Raw water is before purification and purified water is water, which has gone through a purification process, while tap water was sampled from tap in the distribution system. The results are presented in Table 4.3. REE concentrations in raw water ranged from 0.49 ng.l⁻¹ (Tb) to 17.65 ng.l⁻¹ (Ce). REE concentrations in purified water ranged from 5.84 ng.l⁻¹ (Gd) to 0.16 ng.l⁻¹ (Tb). From the results, it can be seen that the REE concentration in the raw water was much higher (ca. 2 to 14 times) than in the purified water. The REE concentration in the tap water ranged from 5.45 ng.l⁻¹ (Y) to 0.20 ng.l⁻¹ (Tb). The REE concentration level in purified water is comparable to that in the tap water for most elements. The precision of these sample preconcentrations and analysis were quite satisfactory at such low REE (from 0.1 to 10 ng.l⁻¹) levels.
Table 4.1. The detection limits and blanks of REEs with cartridge preconcentration and determination by ICP-MS (ng.l⁻¹).

<table>
<thead>
<tr>
<th></th>
<th>DL</th>
<th>DLᵃ</th>
<th>Cᵇ blank (n=5)</th>
<th></th>
<th>DL</th>
<th>DLᵃ</th>
<th>Cᵇ blank (n=5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>15.2</td>
<td>0.15</td>
<td>0.98 ± 0.10</td>
<td>Tb</td>
<td>3.0</td>
<td>0.03</td>
<td>0.08 ± 0.02</td>
</tr>
<tr>
<td>La</td>
<td>11.8</td>
<td>0.12</td>
<td>0.89 ± 0.08</td>
<td>Dy</td>
<td>16.8</td>
<td>0.17</td>
<td>0.34 ± 0.11</td>
</tr>
<tr>
<td>Ce</td>
<td>18.4</td>
<td>0.18</td>
<td>2.73 ± 0.12</td>
<td>Ho</td>
<td>8.2</td>
<td>0.08</td>
<td>0.12 ± 0.06</td>
</tr>
<tr>
<td>Pr</td>
<td>21.6</td>
<td>0.22</td>
<td>0.42 ± 0.15</td>
<td>Er</td>
<td>40.4</td>
<td>0.40</td>
<td>0.45 ± 0.27</td>
</tr>
<tr>
<td>Nd</td>
<td>15.8</td>
<td>0.16</td>
<td>0.96 ± 0.11</td>
<td>Tm</td>
<td>14.6</td>
<td>0.15</td>
<td>0.19 ± 0.10</td>
</tr>
<tr>
<td>Sm</td>
<td>33.1</td>
<td>0.33</td>
<td>0.93 ± 0.23</td>
<td>Yb</td>
<td>37.0</td>
<td>0.37</td>
<td>0.66 ± 0.25</td>
</tr>
<tr>
<td>Eu</td>
<td>9.4</td>
<td>0.09</td>
<td>0.22 ± 0.06</td>
<td>Lu</td>
<td>4.5</td>
<td>0.04</td>
<td>0.09 ± 0.03</td>
</tr>
<tr>
<td>Gd</td>
<td>27.2</td>
<td>0.27</td>
<td>3.10 ± 0.19</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ᵃ DLᵃ = DL/100 for a preconcentration factor = 100
ᵇ blank values ± 2sd

Table 4.2. The recovery (R) and RSD for the preconcentration of REE.

<table>
<thead>
<tr>
<th></th>
<th>Added (ng.l⁻¹)</th>
<th>Found (ng.l⁻¹)</th>
<th>R (%) (n=5)</th>
<th>RSD(%) (n=5)</th>
<th>Added (ng.l⁻¹)</th>
<th>Found (ng.l⁻¹)</th>
<th>R (%) (n=5)</th>
<th>RSD(%) (n=5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>20.0</td>
<td>18.88</td>
<td>94.4</td>
<td>6.7</td>
<td>Tb</td>
<td>20.0</td>
<td>18.53</td>
<td>92.7</td>
</tr>
<tr>
<td>La</td>
<td>20.0</td>
<td>20.05</td>
<td>100.2</td>
<td>1.8</td>
<td>Dy</td>
<td>20.0</td>
<td>18.57</td>
<td>92.8</td>
</tr>
<tr>
<td>Ce</td>
<td>20.0</td>
<td>19.93</td>
<td>99.6</td>
<td>6.8</td>
<td>Ho</td>
<td>20.0</td>
<td>17.99</td>
<td>89.9</td>
</tr>
<tr>
<td>Pr</td>
<td>20.0</td>
<td>19.26</td>
<td>96.3</td>
<td>3.4</td>
<td>Er</td>
<td>20.0</td>
<td>17.63</td>
<td>88.1</td>
</tr>
<tr>
<td>Nd</td>
<td>20.0</td>
<td>19.09</td>
<td>95.4</td>
<td>2.7</td>
<td>Tm</td>
<td>20.0</td>
<td>18.61</td>
<td>93.0</td>
</tr>
<tr>
<td>Sm</td>
<td>20.0</td>
<td>18.77</td>
<td>93.8</td>
<td>3.5</td>
<td>Yb</td>
<td>20.0</td>
<td>17.89</td>
<td>89.4</td>
</tr>
<tr>
<td>Eu</td>
<td>20.0</td>
<td>18.70</td>
<td>93.5</td>
<td>4.7</td>
<td>Lu</td>
<td>20.0</td>
<td>18.85</td>
<td>94.2</td>
</tr>
<tr>
<td>Gd</td>
<td>20.0</td>
<td>18.81</td>
<td>94.1</td>
<td>4.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4.3. REE concentrations in raw, purified and tap water measured by ICP-MS with an ion-exchange resin preconcentration (ng.l⁻¹).

<table>
<thead>
<tr>
<th>Sample 1 (raw water)</th>
<th>Sample 2 (purified water)</th>
<th>Sample 3 (tap water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean (n=2)</td>
<td>Mean (n=2)</td>
<td>Mean (n=2)</td>
</tr>
<tr>
<td>SD (n=2)</td>
<td>SD (n=2)</td>
<td>SD (n=2)</td>
</tr>
<tr>
<td>Y</td>
<td>9.59</td>
<td>0.63</td>
</tr>
<tr>
<td>La</td>
<td>4.89</td>
<td>0.56</td>
</tr>
<tr>
<td>Ce</td>
<td>17.65</td>
<td>1.17</td>
</tr>
<tr>
<td>Pr</td>
<td>1.55</td>
<td>0.63</td>
</tr>
<tr>
<td>Nd</td>
<td>5.10</td>
<td>0.90</td>
</tr>
<tr>
<td>Sm</td>
<td>3.04</td>
<td>1.63</td>
</tr>
<tr>
<td>Eu</td>
<td>0.91</td>
<td>0.42</td>
</tr>
<tr>
<td>Gd</td>
<td>8.29</td>
<td>5.84</td>
</tr>
<tr>
<td>Tb</td>
<td>0.49</td>
<td>0.16</td>
</tr>
<tr>
<td>Dy</td>
<td>2.48</td>
<td>0.67</td>
</tr>
<tr>
<td>Ho</td>
<td>0.66</td>
<td>0.23</td>
</tr>
<tr>
<td>Er</td>
<td>2.65</td>
<td>0.74</td>
</tr>
<tr>
<td>Tm</td>
<td>0.68</td>
<td>0.38</td>
</tr>
<tr>
<td>Yb</td>
<td>3.28</td>
<td>1.41</td>
</tr>
<tr>
<td>Lu</td>
<td>0.59</td>
<td>0.16</td>
</tr>
</tbody>
</table>

(ii) Preconcentration of environmental samples

Three water samples were collected from Rotterdam harbor and measured by ICP-MS with and without preconcentration. Ten fold preconcentration was employed (preconcentration of 100 ml sample to 10 ml). The results are given in Table 4.4. Comparing the results with and without preconcentration indicated that the results are in good agreement although the data originating from the preconcentration are a few % less on average than the corresponding data resulting from direct determination. This implies an average value of 95% for the recovery after preconcentration. However, there are two advantages of using a preconcentration procedure. The first is that some elements such as Eu, Ho, Tb, Er, Yb, Lu cannot be accurately measured by ICP-MS because their concentration is low or close to the detection limit. The second reason is that if AAS or ICP-AES is used to measure REE concentrations,
preconcentration is a prerequisite for aqueous samples in any case. Thus, a simple preconcentration step is necessary for the determination of REE in water samples with high accuracy and precision.

For strongly contaminated waters with high concentrations of suspended solids, high humic acid concentrations, etc., the method may not give correct results after direct preconcentration because of incomplete adsorption. In such cases sample digestion may be needed, which was, however, not investigated in this study.

Table 4.4. Comparison of the results with and without preconcentration (ng.l⁻¹).

<table>
<thead>
<tr>
<th></th>
<th>Concentration measured directly by ICP-MS</th>
<th>Concentration measured by ICP-MS after 10 fold preconcentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 4</td>
<td>Sample 5</td>
</tr>
<tr>
<td>Y</td>
<td>916</td>
<td>417</td>
</tr>
<tr>
<td>La</td>
<td>1094</td>
<td>478</td>
</tr>
<tr>
<td>Ce</td>
<td>1678</td>
<td>741</td>
</tr>
<tr>
<td>Pr</td>
<td>251</td>
<td>118</td>
</tr>
<tr>
<td>Nd</td>
<td>1005</td>
<td>447</td>
</tr>
<tr>
<td>Sm</td>
<td>197</td>
<td>108</td>
</tr>
<tr>
<td>Gd</td>
<td>216</td>
<td>118</td>
</tr>
<tr>
<td>Dy</td>
<td>159</td>
<td>85</td>
</tr>
</tbody>
</table>

4.4. Conclusions

Preconcentration of ultra trace REEs with a micro ion-exchange column and analysis with ICP-MS, appears to be a relatively simple method, which produces accurate and precise results. The optimal preconcentration parameters are (i) pH range of 4 to 6, and (ii) ionic strength (μ) less than 0.18. No special procedure is required for the separation of high concentration of Mg²⁺, Ca²⁺ and Ba²⁺ for normal surface waters. The ion-exchange column capacity with respect to REEs was estimated as 0.96 mol.kg⁻¹. The linear response coefficients ranged from 0.995 to 0.997 at the ng.l⁻¹ level.
The blank is one of the most important problems for ultra trace analysis, however, the concentration in the blank could be minimized (0.09 to 3.1 ng.l⁻¹) if the buffer solution and the water are purified prior to use. The detection limits ranged from 0.03 to 0.40 ng.l⁻¹ for a preconcentration factor of 100. The precision and accuracy of the method was evaluated with real samples and standard addition experiments. The results indicated that the average recovery was ca 95%, and the RSD ranged from 2.7% to 6.7 %. Comparable precision and accuracy with respect to the recovery, was achieved when this method was applied for the determination of REEs in environmental aquatic samples.

References


Chapter 5

Occurrence of REEs in Chinese River Sediments

Abstract

59 sediment samples were collected from the major rivers of China and analysed using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The total REEs, light-REEs (LREEs), heavy-REEs (HREEs) concentrations and the ratio of LREEs to HREEs ranged from 44.5 to 315.8, 38.1 to 264.6, 6.36 to 51.2 (mg.kg\(^{-1}\)) and 5.2 to 14.4, respectively in Chinese river sediment. The samples showed HREE depletion. Strong Gd enrichment was found in the sediment. No significant variation in average REE sediment concentration was found. Variation in REE sediment concentration in individual samples may have been caused by the different geological origin of, or REE adsorption onto different fractions of the sediment.

Factor analysis indicated that REE concentrations in sediments were mainly described by two factors. Factor score plots could be employed to indentify anomalous sediment samples (element depletion or enrichment). Based on the inter-correlation of REEs in the sediment samples, a data-base estimation method was applied for the estimation of REE concentrations in sediment samples, which were reported in literature and a good agreement between literature and calculated values was found.

5.1. Introduction

In the past decades, many publications dealing with distribution, accumulation, transportation as well as ecological effects of trace elements in river sediment have emerged (Kersten and Forstner, 1989 and Zdenek, 1996). A large body of literature is available concerning the distribution and abundance of REEs from the geochemical and mineralogical stand point (Henderson, 1984, Bhatia, 1985, Taylor and
Mclennan, 1988, Wronkiewitz and Condie, 1990, Mclennan et al., 1990, Scott, 1990, Liu et al., 1993 and Braun and Pagel, 1994). However, in recent years, more attention has been paid to REE behavior in sediments, and in particular to aquatic environmental aspects of REEs (Bhatia, 1985, Goldstein and Jacobsen, 1988, Wood, 1990, Markert et al., 1989, Paul et al., 1994; Denchev et al., 1994, Cullers, 1994, Jarvis et al., 1994, Albarede and Sembhi, 1995, Ross et al., 1995, Wang et al. 1995 and Kreamer, et al., 1996). This is important because, under different environmental conditions sediments can act as efficient sinks for metals released into aquatic environments or as a source thereof.

REEs have great economic value, which is the best illustrated by their increased usage in recent years, in particular, for industrial and agricultural purposes. Compounds of Sm, Pr and Ce are applied as magnetic materials and La and Yb are applied in the preparation of high-temperature super conductors. Some REEs are used as catalysts for chemical reactions or are necessary for the production of laser crystals. Human activities such as mining, extraction of metal from ores and minerals and metal refining, release trace amounts into the biosphere at increasing rates, augmented by the worldwide use of metal-bearing fossil fuels as a source of energy. Moreover, millions of tons of fertilizers containing REEs are used worldwide for increasing agricultural productivity (Bremmer, 1994, Yu and Chen, 1995, Diatloff et al., 1995 and Xu, 1995).

China has the largest REE reserves in the world (80%) and is a major producer of REEs for the world market. Since 1990, REE enriched fertilizer has been widely used in more than 20 Chinese provinces (Yu and Chen, 1995, Xu, 1995 and Wu and Guo, 1995). REE enriched fertilizers intended for agriculture production were predicted to cover over 16-20 × 10^6 ha of Chinese agricultural land in 1995 (Tu et al., 1994 and Zhong and Min, 1995). A study of background levels of REEs in the water and sediment of the Yangtze River was carried out by Zhong and Min (1995). This study focused on the characteristics of REEs in suspended matter, sediment and the aqueous phase. A report of the geochemical characteristics of REEs in the Wuhan section of the Yangtze River was published by Wang et al. (1995), indicating the REE content of the suspended fraction of the river. Results indicated that speciation characteristics of REEs in both sediment and suspended matter were quite similar. However, in general, information on background REE levels in sediments throughout China is very sparse.

Factor analysis is a technique suitable for simplifying large and complex data sets in such a way that it may create a limited number of factors, each representing a cluster of interrelated variables within a data set. In recent years, the technique has been
frequently applied in environmental pollution studies with the aim of identifying possible sources of pollution and determining the elemental composition of these sources as well as the contribution of each source to the total pollution level (Alpert and Hopke, 1980, Hopke, 1988, Sloof, 1993 and Kuik et al., 1993). This technique has also been applied widely in the field of chemistry (e.g. spectral chemistry and analytical chemistry) (Malinowski, 1980, Geladi and Kowalski, 1986, Brereton, 1990, Helland, 1990, Vaughan and Horlick, 1990, Meloun et al., 1992, De Jong, 1993, Diatloff et al., 1993 and Wang et al., 1995).

The aims of the present work are to (i) determine the occurrence of REEs in selected Chinese river sediments and the correlation between individual REEs, (ii) develop a data-base based on these internal correlations, to extrapolate total and individual REE concentrations in river sediments, and (iii) use the results of crust-normalized ratios and factor analysis to identify anomalous samples.

5.2. REEs in soil and aquatic environments in China

There are seven major rivers in China i.e Yangtze river, Yellow river, Sunhuanjing river, Pearl river, Haihe river, Huaihe river and Liaohe river. Their river basins cover an area of ca 4.3 million km². Some hydrological data for these rivers are presented in Table 5.1.

No systematic data are available with respect to REE background levels in the earth’s crust around China. However, in the past twenty years, some progress has been achieved with aspect to background levels of REEs in Chinese soil (Zhong and Min, 1995). The concentration of REEs reported in Chinese soil is similar to that reported worldwide (Bowen, 1979 and Wang et al., 1995). The average total REE concentration in Chinese soil is 177 mg.kg⁻¹ (Wang et al., 1995), which is a little higher (13%) than the average world concentration (156 mg.kg⁻¹) although it is likely that this difference is not significant. Large variations in REE concentrations were reported for different areas of China. The highest concentrations were recorded in the areas of Guangzhou, Heilin (Pearl River basin) and Hunan (Yangtze River basin) and the lowest concentrations were recorded in the areas of Xingjiang. The ratio of light REEs to heavy REEs (LREE/HREE) in Southern China (Pearl River basin and part of Yangtze River basin) was higher than that of other areas in China. Light REE enrichment in the soil, relative to the earth’s crust, was reported in most areas of China (Zhong and Min, 1995).
Table 5.1. Hydrological data of seven major Chinese rivers.

<table>
<thead>
<tr>
<th>Rivers</th>
<th>Length (km)</th>
<th>Basin area (10^3 km^2)</th>
<th>Total discharge/year (10^8 m^3)</th>
<th>Sediment transportation/year (10^6 tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yangtze</td>
<td>6300</td>
<td>1808</td>
<td>9512</td>
<td>510</td>
</tr>
<tr>
<td>Yellow</td>
<td>5464</td>
<td>752</td>
<td>662</td>
<td>1600</td>
</tr>
<tr>
<td>Sunhuajing</td>
<td>2308</td>
<td>557</td>
<td>762</td>
<td>14</td>
</tr>
<tr>
<td>Pearl</td>
<td>2214</td>
<td>442</td>
<td>3360</td>
<td>86</td>
</tr>
<tr>
<td>Haihe</td>
<td>1090</td>
<td>308</td>
<td>283</td>
<td>170</td>
</tr>
<tr>
<td>Huaihe</td>
<td>1000</td>
<td>269</td>
<td>741</td>
<td>27</td>
</tr>
<tr>
<td>Liao</td>
<td>1390</td>
<td>192</td>
<td>148</td>
<td>80</td>
</tr>
</tbody>
</table>

Data on REE background levels in aquatic environments is limited for China. Reported REE concentrations in fresh water (rivers and lakes) were in the range 10^{-3} to 10^{-2} μg.l^{-1}. Concentrations of REEs in Chinese sediments ranged between 9~200, 5~651, 7~246, 1.4~42, 0.1~3.6, 0.12~6.2, 0.5~13.6 and 0.1~1.95 (mg.kg^{-1}) for La, Ce, Nd, Sm, Eu, Tb, Yb and Lu, respectively (Zhong and Min, 1995). Insufficient data is available to make a sediment mass balance because the literature sources are not specific enough about granulometry, mineral composition, sampling procedure, sediment adsorption capacity etc..

5.3. Experimental

5.3.1. Sampling

Random grab samples were collected and because of logistical reasons it was not possible to separate the fine and coarse material. 59 sampling sites, covering the major rivers of China were selected. The sites were far away from industrial areas and municipal wastewater outlets, so, can be considered to represent “natural” conditions. Samples were collected in the basins of the Yangtze river (n=30), Pearl river (n=12) and the Yellow, Sunhuajing, Haihe, Huaihe and Liao river basins (n=17). Approximately 2 kg of sediment per sample was collected at a depth ca. 10-20 cm below the surface sediment layer. At least 5 subsite samples were taken for each site and homogenized. The samples were stored in polyethylene bags. The wet samples were air-dried at room temperature and sieved to remove large particles. Subsequently, the debris was passed through a 2 mm sieve.
5.3.2. Analytical procedure

The samples were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) (VG Plasmaquad Plus, Fison Instruments, U.K.). Prior to analysis, the samples were dried for 24 hr at 105 °C. 0.5 g of the sample was weighed and transferred into a vessel liner and 5 ml of H₂O and 10 ml HNO₃ were added. The mixture was digested by Microwave (MDS-2000, CEM, U.S.A.) for 90 minutes at 700 kPa and full power (650 Watts). All data are expressed on a dry weight basis.

5.4. Results and discussion

5.4.1. Occurrence of REEs in sediments

A partial least-squares regression (PLSR) model (described in Chapter 2) was used to process the analytical data from the ICP-MS. In order to control the quality of sample digestion and analysis, a marine sediment reference material (GBW-07313, from the National Research Centre for Certified Reference Materials, Beijing, China) was analyzed in the same run as the 10 different river sediment samples. In Figure 5.1(a-b), results of analysis of the marine reference material are compared to their certified values; the mean ± 2σ is represented by the bar. The average REE recovery was 93.6 % (n=10). In particular, the light REEs showed good recovery (ca. 95%), while the recoveries of the heavy REEs ranged from 83 % to 97 %.

Table 5.2. shows the average REE content of the sediment samples (n=59). REE concentrations reported by Henderson (1984) in the earth’s crust are used for data normalization and are also presented in Table 5.2. The average total REE concentration for the 59 samples was 65 to 289 mg.kg⁻¹. The concentration of REEs in Chinese river sediments was as follows: Ce > La > Nd > Y > Sc > Gd > Pr > Sm > Dy > Er > Yb > Eu > Tb, Ho, Tm and Lu, which is normal order expected for sediment samples (Wang et al., 1995 and Zhong and Min, 1995).

A comparison of the average REE concentration between Chinese river sediments and average REE concentration in the earth’s crust, crust-normalized REE ratios of Chinese river sediment are plotted in Figure 5.2(a-b). Heavy REEs are significantly depleted in Chinese sediments, with the exception of Gd and Dy. On the contrary, the light REEs showed no significant enrichment/depletion in river sediment. Strong Gd enrichment (positive Gd anomaly) was found in the river sediments. This phenomenon has been
reported by Tricca et al. (1999) for the river Rhine. No significant enrichment/depletion of Dy was found in any of the sediments.

Table 5.2. The maximum, median, minimum and average REE content (mg.kg⁻¹) of 59 Chinese sediment samples (L/H: LREEs/HREEs. L/H*: LREEs/HREEs, without Sc & Y).

<table>
<thead>
<tr>
<th></th>
<th>Max</th>
<th>Median</th>
<th>Min</th>
<th>Average</th>
<th>Crust</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>23.1</td>
<td>11.63</td>
<td>13.2</td>
<td>11.11</td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>57.3</td>
<td>31.14</td>
<td>7.6</td>
<td>30.8</td>
<td>30</td>
</tr>
<tr>
<td>Ce</td>
<td>122.6</td>
<td>65.3</td>
<td>16.5</td>
<td>64.4</td>
<td>60</td>
</tr>
<tr>
<td>Pr</td>
<td>14.35</td>
<td>7.57</td>
<td>1.6</td>
<td>7.3</td>
<td>8.2</td>
</tr>
<tr>
<td>Nd</td>
<td>58.5</td>
<td>29.31</td>
<td>5.6</td>
<td>27.8</td>
<td>28</td>
</tr>
<tr>
<td>Sm</td>
<td>10.98</td>
<td>5.33</td>
<td>1.1</td>
<td>5.1</td>
<td>6.0</td>
</tr>
<tr>
<td>Eu</td>
<td>1.72</td>
<td>0.87</td>
<td>0.05</td>
<td>0.85</td>
<td>1.2</td>
</tr>
<tr>
<td>Gd</td>
<td>16.81</td>
<td>8.86</td>
<td>1.64</td>
<td>8.9</td>
<td>5.4</td>
</tr>
<tr>
<td>Tb</td>
<td>1.16</td>
<td>0.65</td>
<td>0.12</td>
<td>0.62</td>
<td>0.9</td>
</tr>
<tr>
<td>Dy</td>
<td>4.96</td>
<td>3.20</td>
<td>0.53</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Ho</td>
<td>0.99</td>
<td>0.57</td>
<td>0.09</td>
<td>0.55</td>
<td>1.2</td>
</tr>
<tr>
<td>Er</td>
<td>2.44</td>
<td>1.40</td>
<td>0.26</td>
<td>1.4</td>
<td>2.8</td>
</tr>
<tr>
<td>Tm</td>
<td>0.38</td>
<td>0.18</td>
<td>0.06</td>
<td>0.19</td>
<td>0.48</td>
</tr>
<tr>
<td>Yb</td>
<td>2.89</td>
<td>0.96</td>
<td>0.22</td>
<td>1.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Lu</td>
<td>0.42</td>
<td>0.15</td>
<td>&lt;0.02</td>
<td>0.16</td>
<td>0.5</td>
</tr>
<tr>
<td>Y</td>
<td>24.8</td>
<td>14.6</td>
<td>3.31</td>
<td>13.70</td>
<td></td>
</tr>
<tr>
<td>REEs</td>
<td>315.8</td>
<td>185.1</td>
<td>44.5</td>
<td>1769</td>
<td></td>
</tr>
<tr>
<td>L/H</td>
<td>7.67</td>
<td>5.02</td>
<td>3.7</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>L/H*</td>
<td>14.4</td>
<td>8.8</td>
<td>5.2</td>
<td>9.0</td>
<td>72</td>
</tr>
</tbody>
</table>

5.4.2. Variation of REE concentrations in the major Chinese rivers

The average total REE concentration in the Chinese rivers investigated was: Pearl river (196.3 mg.kg⁻¹) > Haihe river (185 mg.kg⁻¹) > Song Liao River (179.5 mg.kg⁻¹) > Yangtze river (175.6 mg.kg⁻¹) > Yellow river (173.3 mg.kg⁻¹). The differences between average concentrations, were not greater than 25 mg.kg⁻¹ and are not statistically significant. The results are consistent with the average concentration of REEs in the earth’s crust (Henderson, 1984). The concentrations of La, Ce and Nd are comparable with those reported by van Dijk and Montizaan (1986) in the North Sea, indicating that these sediments have typical REE features of sedimentary rock laid down by shell and soil erosion. However, the concentrations reported in this study are
20 - 30% lower than reported by Wang (Wang et al., 1995). These differences may be partly explained on the basis of variations in different materials. In this work, the samples were passed through a 2 mm sieve. Wang, however, sieved his samples through a 20 mesh sieve, and subsequently the samples were ground and sieved through a 100 mesh sieve. It has been reported that the REE content of sediments is dependent on the size of the sediment fraction analyzed (Zhang et al., 1995). Generally, finer fractions have higher levels of REEs (Zhang et al., 1998), which may account for the discrepancies between this work and that of Wang (1995).

**Figure 5.1.(a-b)** A comparison of the certified and analyzed (ICP-MS) concentrations of the marine sediment reference material (GBW-07313).
Figure 5.2.(a-b) (a) Comparison of average REE concentrations in Chinese river sediments (59 sampling locations) and average REE concentrations in the earth’s crust, and (b) Crust-normalized REE ratios of Chinese river sediments (59 sampling locations)

The total REE concentration in the various river sediments showed little variation between the upper and lower reaches of the rivers. Statistical analysis could not be applied to quantify the variation in REE concentration along the length of each river because limited samples were taken for each river, covering a distance of thousands of kilometres.

The crust-normalized REE ratios for sediments in the main Chinese rivers are shown in Figure 5.3. From this figure it is apparent that these rivers have a similar crust-normalized ratio. Four rivers showed depletion of heavy REEs, with the exception of Gd and Dy. A negative Yb anomaly was found in the Liao river. A positive Gd anomaly was found in four rivers, in particular in the Yellow and Yangtze rivers. This phenomenon was also reported by (Zhang et al., 1998). Eu depletion clearly existed in the Yangtze river.
Figure 5.3. Comparison of crust-normalized REE patterns in major Chinese rivers (Pearl river: n=12, Liao River: n=4, Yangtze river: n=15 and Yellow river: n=7).

In Figure 5.4 (a-b), the variation in the total REE concentration and crust-normalized La and Gd ratios in the Yangtze river are presented. Samples were taken over a total length of 1200 km. The first sampling point is referred to as 0 km while the last is 1200 km downstream. The average REE concentration measured along the length of the 1200 km was 191 mg.kg$^{-1}$.

Both figures exhibit similar trends. The decrease in the total REE concentration at the sampling point (B) at 700 km may be due to the mixing of Jiujiang river sediment, which may have a different REE composition (net concentration dilution), with the Yangtze river at this location. The increase in the total REE concentration at sampling point A and E is attributed to Gd enrichment. For sampling points C and D, the REE concentration increased towards the end of the stretch, which was sampled. This may be attributed to Gd and light REE enrichment. This situation may be due to geological variation or possibly non-point pollution sources. Other deviations from the mean are probably due to sediment dilution by small rivers or variation in geological composition. However, because only 13 samples were taken over a distance of 1200 km, the more serious deviations from the mean should be addressed in a more detailed study.

In Table 5.3., the correlation coefficients between the REEs are presented. The correlation can be divided into two groups: a light group (La, Ce, Pr, Nd, and Sm) and a heavy group (Tb, Dy, Ho, Er, Tm, Yb and Lu). Good correlation exists within each group e.g. the correlation coefficient between La and Ce (both light) is 0.99 and
between Yb and Lu (both heavy) is 0.94. In general, the coefficients were greater than 0.85. However, the coefficients between elements in different groups i.e. heavy versus light, range between 0.4 and 0.8. Element Eu and Gd lie between the light and heavy group and no clear distinction exists between their correlation with heavy and light elements. Poor correlation was found between Sc and Y and the other REEs. Correlation between three light and heavy elements is also presented in Figure 5.5.(a-b), respectively.

**Figure 5.4.a.** Yangtze river from Three Gorges to Nanjing (upper reaches to lower) (km)

**Figure 5.4.b.** The variation of the REE concentration in the Yangtze river and (b) the variation of crust-normalized La and Gd ratio in the Yangtze river (13 sampling locations, from the Three Gorges to Nanjing, covering a total distance of ca. 1200 km, A, B, C and D refer to the locations Yeyang, Jujiang, Moanshang and Nanjing, respectively).
Chapter 5. Occurrence of REEs in Chinese River Sediments

Table 5.3. Correlation coefficients between all the REEs.

<table>
<thead>
<tr>
<th></th>
<th>Sc</th>
<th>Y</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>0.75</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>0.51</td>
<td>0.82</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
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<td>Ce</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Pr</td>
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<td>0.84</td>
<td>0.98</td>
<td>0.98</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd</td>
<td>0.52</td>
<td>0.82</td>
<td>0.95</td>
<td>0.95</td>
<td>0.99</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sm</td>
<td>0.47</td>
<td>0.77</td>
<td>0.87</td>
<td>0.88</td>
<td>0.92</td>
<td>0.96</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Eu</td>
<td>0.76</td>
<td>0.71</td>
<td>0.65</td>
<td>0.68</td>
<td>0.73</td>
<td>0.75</td>
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<tr>
<td>Gd</td>
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<td>0.73</td>
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<td>0.77</td>
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<td></td>
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</tr>
<tr>
<td>Tb</td>
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<td>0.86</td>
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<td>0.84</td>
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<td></td>
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<tr>
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<td>0.76</td>
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<td>0.83</td>
<td>0.84</td>
<td>0.80</td>
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<td>0.91</td>
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<td>0.77</td>
<td>0.79</td>
<td>0.81</td>
<td>0.81</td>
<td>0.73</td>
<td>0.74</td>
<td>0.93</td>
<td>0.94</td>
<td></td>
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<tr>
<td>Tm</td>
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<td>0.71</td>
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<td>0.67</td>
<td>0.74</td>
<td>0.88</td>
<td>0.86</td>
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<td>0.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yb</td>
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<td>0.66</td>
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<td>0.67</td>
<td>0.84</td>
<td>0.81</td>
<td>0.88</td>
<td>0.91</td>
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<td></td>
</tr>
<tr>
<td>Lu</td>
<td>0.21</td>
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<td>0.63</td>
<td>0.64</td>
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<td>0.61</td>
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<td>0.47</td>
<td>0.58</td>
<td>0.81</td>
<td>0.76</td>
<td>0.88</td>
<td>0.87</td>
<td>0.90</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Figure 5.5.(a-b) Correlation between three light REEs (La, Ce and Nd) and correlation between three heavy REEs (Lu, Yb and Ho).
5.4.3. Factor analysis

(a) Number of factors required to describe the river sediment data set

In order to extract the most important parameters influencing REE sediment concentration, factor analysis, which is described in detail in the Chapter 2, was employed to study 59 Chinese river sediment samples. A sharp increase in the explained variance was observed when two factors were used. However, increasing the number of factors above 2 had little effect on the explained variance. Ca. 87% of the variance could be explained by factors 1 and 2. Factors 3 to 5 explained ca. 10% of the variance, while factors 6 to 16 only explained about 3% of the variance. It can be concluded that REE concentrations (16 elements) in the sediments analyzed are mainly described by factors 1 to 2.

(b) Which factors describe heavy and light REEs in the river sediment data set?

(i) Factor loadings
Loading expresses the relationship between variables and factors in a model. It can be seen which rare earth elements (variables) are important for each factor. In Figure 5.6.a, the loadings of factor 1 are presented as a function of the loadings of factor 2, for all elements. Factor 1 describes all REE elements with a loading range of 0.59 to 0.97. Loadings in excess of 0.9 were recorded for Ce, Dy Er, Ho, La, Nd, Pr, Sm, Gd and Tm. Loadings between 0.8 to 0.9 were recorded for Eu, Gd, Lu, Y, and Yb. Only Sc, with a loading of 0.59 did not fall within this loading range.

Factor 2 also describes the REEs and loadings of 0.31 to -0.54 were recorded. However, as can be seen from Figure 5.6.a., factor 2 exhibited negative loading for heavy REEs (e.g. Lu, Yb, Tm, Ho, Dy, Er and Tb) while positive loadings were found for light REEs (Eu, Y, Gd, Sm, La, Pr, Ce, Nd) (0.13 to 0.30, except Sc: 0.62). Increasing the atomic weight of the REEs (from Sc to Lu) decreased the factor 2 loadings (Figure 5.6.b.), however, no clear relationship could be found between atomic weight and the loadings of factor 1.

From Figure 5.6.b., it can be seen that the element loadings of factor 3 and 4 are approximately the same (i.e. -0.26 to 0.29 and -0.04 to 0.3, for factors 3 and 4, respectively) illustrated by the circle on Figure 5.6.b.. However, as mentioned previously, factor 3 and 4 only explain ca. 8% of the variance. From Figure 5.6.b., Y
and Sc are far removed from the main bulk of element loadings. This may be due to the fact that their atomic weights are considerably lower than the other REE.

Figure 5.6.(a-b) Plot of loadings on factor 1 to 2 and on factor 3 to 4.

(ii) Identification of anomalous samples using factor score plots
The relationship between samples (objects) and factors is expressed as score. A score plot can be used to look for outliers. The total REE concentration of the samples was mainly described (87%) by the scores of factor 1 and 2. From Figure 5.7.a., it can be seen that sample scores of factor 1 and 2 are mostly located in the circle (i.e. -20 to 20 and -3 to 3 for factor 1 and 2, respectively), which divides the score data. Ca. 8 of
the 59 samples are located outside the circle (i.e. sample number: S7, S25, S38, S45, S49, S50 and S55). Factor scores which clearly lie outside the constructed circle in Figure 5.7.a. have either very high or low total REE concentrations. For example, in Figure 5.7.a., sample 7 (S7), 49 (S49) and 50 (S50) lay outside the circle because the total REE concentration is very low (68 mg.kg⁻¹) in the samples compared to the concentration of most samples in the circle is ca.3 times higher. Furthermore, sample 38 (S38) and 55(S55) have total REE concentration ca. twice as high as the average.

Score plots of factor 1 and 2 do not give any information on the nature or specific element(s) causing contamination. For this detailed information, scores of factor 3 and 4 are needed. These are presented in Figure 5.6.b. Most of the sample scores are inside the constructed circle (i.e. -1.2 to 1.2 and -0.5 to 0.7 for factor 3 and 4, respectively). Sample numbers S4, S25, S38, S52 and S56 are clearly outside the circle. Samples which lie outside the circle, e.g. in sample 4 (S4), the concentration of La, Ce, Pr, and Nd, is twice the average LREE concentration. The concentration of Sc and Dy in sample S52 is ca. 1.5 and 2 times the average, respectively. Other samples e.g. S25 and S38 have high levels of HREEs while S56 has a high level of LREEs. Score plots of factor 3 and 4 are useful for identifying the exact element(s) involved in the anomaly (enriched or depleted).

(c) Estimation of REE concentrations in river sediment

The correlation coefficients between the REEs (Table 5.3) can be used to estimate total and individual REE concentrations when the concentration of one or more REEs is known. Based on the inter-correlation coefficients established in Table 5.3, the following equation was obtained:

\[ Y_n = a_n X_n + C_n \quad (5.1) \]

\( Y_n \) is the unknown concentration to be calculated.
\( X_n \) is a known input concentration.

\( X_n \) or \( Y_n \) can be any individual REE concentration, or the total REE or the total HREE or the total LREE concentration. Slope (\( a_n \)) and intercept (\( c_n \)) are calibration coefficients established from the calibration data set.
Figure 5.7 (a-b) Plot of scores on factor 1 to 2 and on factor 3 to 4.

This concept can be used in combination with ICP-AES, which is limited for the measurement of individual heavy REEs in environmental samples below a concentration of ca. 100 ppb. ICP-AES can be used to measure the individual concentration of the light REEs and some heavy REEs, and with the help of the inter-
correlation coefficients presented in Table 5.3, the concentration of each individual heavy REE can be estimated. Another possible application for this concept is in conjunction with classical colorimetric methods, which can only be used to measure the total REE concentration and the concentration of the heavy and light REEs in environment samples. When used in combination with the inter-correlation coefficients in Table 5.3, the concentration of each individual heavy and light REE can be estimated.

The use of inter-correlation coefficients to estimate the total REE concentration, when the concentration of only one or more REE is known, was tested using the measured concentration of La and Yb (Table 5.2.) as input data. Thereafter, the average total REE concentration was estimated for all the sediment samples using equation (5.1). The error in using inter-correlation coefficients to estimate the total REE concentration when the concentration of only two individual were known REEs (one heavy and one light REE) was between 6 and 10%, when outliers (12 in total) were excluded. The choice of input data will also affect the accuracy of the estimated individual REE concentrations. For example, if the concentration of an individual light REEs is required, the estimation will be more accurate if the concentration of one or more of the light REEs or the total concentration of the light REEs is used as input data, and vice versa for the heavy REEs.

(d) Use of inter-correlation coefficients to estimate REE concentrations

In order to assess the applicability of using inter-correlation coefficients to estimate the concentration of REEs, literature data on the Yangtze river sediment reported by Zhong and Min (1995) was used. The total REE concentration, the light REE concentration and the heavy REE concentration were measured as well as La, Ce, Nd, Sm, Eu, Tb, Yb and Lu by NAA. The input data for the estimation was the heavy REE and the light REE concentration. The error in calculating the total and individual concentrations of the aforementioned eight elements was between 10 - 15%. The accuracy was best for La, Ce, Sm, Nd and total REE, HREE and LREE and poor for Eu, Tb, Yb and Lu. The accuracy of the estimation method with respect to the calculation of individual REE concentrations can be seen in Figure 5.8.(a-b). The discrepancies between the results reported by Zhong and Min (1995) and that estimated using the inter-correlation coefficients established in Table 5.3 may be due to the fact that number of samples used in the estimation of the inter-correlation coefficients was limited (n=59) and cannot accurately represent the entire Yangtze river.
Figure 5.8 (a-b) Comparison of REE concentrations in Yangtze river between reported (Zhong and Min, 1995) and calculated by estimation method.

The use of inter-correlation coefficients to estimate the concentration of individual and total REEs, when the concentration of one or more REEs is known, is restricted to Chinese sediments because the coefficients are based on background REE levels measured in Chinese river sediments.

5.5. Conclusions

(i) The total REE, light-REE (LREE), heavy-REE (HREE) concentrations and the ratio of LREE to HREE ranged from 44.5 to 315.8, 38.1 to 264.6, 6.36 to 51.2 (mg.kg$^{-1}$) and 5.2 to 14.4, respectively in Chinese river sediment. The samples showed
HREE depletion. Strong Gd enrichment was found in the sediment. No significant variation in average REE sediment concentration was found.

(ii) No significant variation in average REE sediment concentration was found. Variation in REE sediment concentration in individual samples may have been caused by the different geological origin of, or REE adsorption onto different fractions of the sediment.

(iii) Factor analysis indicated that REE concentrations in sediments were mainly described by two factors. Factor score plots could be employed to identify anomalous sediment samples (element depletion or enrichment).

(iv) Based on the inter-correlation of REEs in the sediment samples, a data-base estimation method was established and was also applied for the calculation of REE concentrations in sediment samples, which were reported in literature and good agreement between literature and calculated values was found.

References


Chapter 6

REE and Metal Concentrations in Atmospheric Particulate Matter in Delft, The Netherlands

Abstract

Atmospheric particulate matter (APM) was collected on micro-quartz glass fibre filters from July to September 1997, using a Sierra High Volume Air Sampler. The concentration of rare earth elements (REE) and 9 other metals (Cd, Pb, Fe, V, Ti, Mg, Ca, Na and Al) in the APM was determined by ICP-MS and ICP-AES. Average concentrations of Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu in the samples (ng/m³) were 0.12, 0.29, 0.50, 0.59, 0.11, 0.35, 0.064, 0.018, 0.070, 0.0084, 0.046, 0.0086, 0.023, 0.003, 0.024, 0.0027, respectively. The total REE (REEs) concentration, light-REE (LREEs) concentration, and heavy-REE (HREEs) concentration was 0.22-33.0; 0.21-30.68; and 0.01-2.32 ng/m³, respectively. The ratio of LREEs to HREEs ranged from 6.37 to 33.58; the ratio of LREEs to REEs was 0.86-0.97, the average being 0.90; and the ratio of HREEs to REEs was 0.03-0.14, (average was 0.10). The La to Ce, and La to Sm ratio varied considerably i.e. 0.5-4.38 and 4.33-71.42 respectively, and could be used as a tracer for the source of REEs. The concentrations of other metals (ng/m³) were: Cd, 0.458; Pb, 16.64; Mg, 221.9; Al, 396.2; Na, 765.1; Ca, 1234; V, 8.14; Fe, 533.9; Ti, 12. The variation in concentration observed depended upon the wind direction and consequently on prevailing meteorological conditions and anthropogenic activity.

6.1. Introduction

Air pollution in urban areas arises from a multitude of sources and anthropogenic activity is a major contributor. The concentrations of carbon monoxide, oxides of nitrogen, sulphur dioxide, ozone, volatile organic compounds (VOC), smoke and metals (such as lead) in the atmosphere have been widely studied (Harrop, 1988;
Werner and Meckel, 1989, Leleveld, 1989). They all exhibit adverse effects on man and nature. However, the content of Rare Earth Elements (REEs) in air has not been widely researched. Along with the world wide use of REE, their emissions into the atmosphere have been increasing. Therefore, it is of importance to determine the concentration levels of REE in air. This work focused on the determination of REEs in atmospheric particulate matter near Delft in the western part of the Netherlands, which is rather heavily urbanised and industrialised. For source recognition, the concentration of Cd, Pb, Fe, V, Ti, Mg, Ca, Na and Al, which were used as tracer elements, were determined as well. The influence of wind direction on the concentration of REE and metals was taken into account.

6.2. Materials and methods

6.2.1. Sampling

Atmospheric particulate matter (APM) was collected, from July to September 1997, on micro-quartz glass fibre filter paper (8in×10in, 25pcs, Chemical Sciences, Inc. Ann Arbor, Michigan 48106) using a Sierra High Volume Air Sampler (Sierra Instruments, Inc. Carmel Valley, California; air flow: 1m³.min⁻¹). Samples were taken from two sites referred to as A and B (see Figure 6.1). Location A was in Delft, The Netherlands. The number of samples taken was 31. Location B was within a distance of 10 meters from the highway between Delft and Rotterdam, The Netherlands. The number of samples taken was 6. Before and after each sampling period, the filters were conditioned for 24 hours at constant relative humidity (60%±5%) and temperature (20±2°C) and weighed to determine the concentration of particulate matter.

As explained in Chapter 1, there is evidence that REEs enter the environment via fuels that have passed refining and petroleum cracking processes. Therefore, in this study one site was selected next to a main highway on the north-south transport axis in The Netherlands, and a second site was chosen outside the direct influence of that highway but with otherwise similar atmospheric characteristics. Sampling was avoided during rainy conditions, which could cause washout. Except for the traffic and the petrochemical complex in Rotterdam (14-20 km south west of Delft, no other source is expected to emit REEs into the atmosphere in the study area. Points A and B are approximately 3km apart (Figure 6.2).
Figure 6.1. Sampling location A and B (A: Delft; B: highway between Delft and Rotterdam).
6.2.2. Analysis of rare earth elements and other metals

The whole filter sample was used for extraction of the REEs and the other metals. The filter paper was cut into small pieces (1×3cm) using plastic scissors and subsequently leached for 4 hours with 45ml, 43% of HNO₃ (super pure, Merck, Germany). The leaching solution was filtered and transferred to a volumetric flask and diluted to 100ml with milli-pore water (18.2 MΩ.cm⁻¹). The concentration of REEs, Cd and Pb was determined by ICP-MS. Concentrations of the other 7 metals (Fe, V, Ti, Mg, Ca, Na and Al) were determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES).

6.3. Results and discussion

Table 6.1. shows the maximum, median, minimum and mean concentration of REEs and the other 9 metals in the APM collected from July to September, 1997, at site A (N= 31). The relative concentration levels of the REEs was as follow: Ce > La > Nd > Y > Sc > Pr > Gd > Sm > Dy > Yb, Er > Eu > Ho, Tb > Tm, Lu. This concentration sequence is similar to that of REE found in a number of soil, sediment (see Chapter 5 and Chapter 7), animal, plant, and other environmental and geological samples (Wang et. al., 1995; Zhong and Min, 1995). From the minimum and maximum values in Table 6.1., it can be concluded that the concentration of REEs, light REEs (LREEs), heavy REEs (HREEs), total REEs (REEs), and the other 9 elements in the APM vary by two orders of magnitude. Even the ratio of LREE/HREE, La/Ce and La/Sm may differ from day to day by a factor of 5-10.

High La/Sm ratios in aerosols are one of the most reliable indicators of refinery emissions (Kitto et al., 1992). A La/Sm ratio of 27±7 was measured in the stack of an oil-fired power plant (Morz, 1976). The background ratio due to windborne material such as soil derived from the crust of the Earth is about 4.8. Also Olmez and Gordon (1985) have shown that the ratio of La to other REEs in emissions from petroleum-refining and oil-burning sources could be used to distinguish them from other sources. For atmospheric emissions from a refinery and a coal and an oil-fired power plant, La/Sm ratios reported by Olmez and Gordon (1985) were 20, 5.2, and 28, respectively. The average ratios of La/Ce, 1.1 (0.5-4.4) and La/Sm, 12.6 (4.3-71.6) reported in this study (Table 6.1.) were higher than the “crustal ratio” of 0.5 and 4.8, respectively (Kitto, 1992). This may suggest that REEs measured in this study may be partly due to refining and oil burning.
Table 6.1. The maximum, median, minimum and mean content of REEs and metals as atmospheric particulate matter in air samples (ng m\(^{-3}\)) in Delft (site A), The Netherlands (n=31).

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<tr>
<td>Sc</td>
<td>0.73</td>
<td>0.08</td>
<td>0.0031</td>
<td>0.12</td>
<td>LREE</td>
<td>30.7</td>
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<tr>
<td>Y</td>
<td>2.05</td>
<td>0.17</td>
<td>0.0068</td>
<td>0.29</td>
<td>HREE</td>
<td>2.3</td>
<td>0.14</td>
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<td>La</td>
<td>1.72</td>
<td>0.45</td>
<td>0.042</td>
<td>0.50</td>
<td>REEs</td>
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<td>Ce</td>
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<td>0.41</td>
<td>0.047</td>
<td>0.59</td>
<td>L/H</td>
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<td>8.7</td>
<td>6.4</td>
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<td>Pr</td>
<td>0.41</td>
<td>0.10</td>
<td>0.0072</td>
<td>0.11</td>
<td>La/Ce</td>
<td>4.4</td>
<td>0.7</td>
<td>0.5</td>
</tr>
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<td>Nd</td>
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<td>0.26</td>
<td>0.0178</td>
<td>0.35</td>
<td>La/Sm</td>
<td>30.3</td>
<td>6.6</td>
<td>4.3</td>
</tr>
<tr>
<td>Sm</td>
<td>0.35</td>
<td>0.043</td>
<td>0.0072</td>
<td>0.064</td>
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<tr>
<td>Eu</td>
<td>0.09</td>
<td>0.012</td>
<td>0.0019</td>
<td>0.018</td>
<td>Cd</td>
<td>3.3</td>
<td>0.2</td>
<td>0.1</td>
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<tr>
<td>Gd</td>
<td>0.34</td>
<td>0.050</td>
<td>0.0061</td>
<td>0.070</td>
<td>Pb</td>
<td>60.7</td>
<td>12.6</td>
<td>3.1</td>
</tr>
<tr>
<td>Tb</td>
<td>0.04</td>
<td>0.006</td>
<td>0.0003</td>
<td>0.008</td>
<td>Mg</td>
<td>818</td>
<td>216</td>
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<tr>
<td>Dy</td>
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<td>0.032</td>
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<td>Al</td>
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<tr>
<td>Ho</td>
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<td>0.0005</td>
<td>0.009</td>
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<td>1995</td>
<td>659</td>
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<td>Er</td>
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<td>0.017</td>
<td>0.0010</td>
<td>0.023</td>
<td>Ca</td>
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<tr>
<td>Tm</td>
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<td>0.002</td>
<td>0.0004</td>
<td>0.003</td>
<td>V</td>
<td>23</td>
<td>8</td>
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<tr>
<td>Yb</td>
<td>0.097</td>
<td>0.019</td>
<td>0.0093</td>
<td>0.024</td>
<td>Fe</td>
<td>1425</td>
<td>425</td>
<td>78</td>
</tr>
<tr>
<td>Lu</td>
<td>0.014</td>
<td>0.002</td>
<td>0.0004</td>
<td>0.003</td>
<td>Ti</td>
<td>58</td>
<td>9</td>
<td>2</td>
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</tbody>
</table>

Figure 6.2. shows the variations in the La/Sm ratio as a function of the wind direction for the samples taken at the sampling site (A) in Delft. From Figure 6.2, it can be seen that for wind directions roughly between 140° and 270° the ratio was much higher than for all other wind directions. This phenomenon is attributed to the fact that the heavily industrialised “Rijnmond” area situation near the port of Rotterdam lies in that direction. For the other wind directions the La/Sm ratio resembles that of the “natural background”.
Figure 6.2. Ratio of La to Sm in 31 24-hour air dust samples collected in Delft (Site A), The Netherlands, from July 11 to September 25, 1997.
Comparing the concentrations of REEs and the other 9 elements as a function of the wind direction (Figure 6.3.(a-d)), it can be seen that a close relationship exists between element concentration and wind direction. The sampling site near Delft (site A) is situated in the western part of the Netherlands, 14 kilometres from the industrialised area near Rotterdam (south). The North Sea is situated to the west, about 20 kilometres away. Towards the north and east, traffic is the dominant source of pollution. Due to the location of the sampling site, aerosols reaching the site from the north-west (NW) are influenced by the sea and by traffic, those from the south-west (SW) mainly by industrial activity and to a lesser degree also by the sea, those from the north-east (NE) mainly by traffic emissions and those from the south-east (SE) by a mixture of industry and traffic.

From Figure 6.3.(a-d), it can be observed that the relative concentration of REEs, Ti, Fe, Mg and Al increase in the order: SE > NE > SW > NW. It has been reported (Kainuma et al., 1989) that elements such as Al, Sc, Ti, Fe, and Mg can be used as tracers for suspended soil material. The results obtained indicated that for the wind coming from the SE direction, traffic, industry and suspended soil particles were the main contributors to REEs.

Most airborne Pb in urban areas originates from combustion of leaded gasoline (Olmez and Gordon, 1985), while industrial processes mainly emit Cd. In this study, the source of Pb and Cd appeared to be mainly industry and traffic. The relative concentration level for the various wind directions was: SW > SE > NE > NW. For Na, a tracer for sea salt, in this case originating from the North Sea, the relative concentration level for the various wind direction was: NW, SW > NE > SE. Finally for Ca, which is considered to be a tracer for soil and cement manufacturing, aerosols from the SW direction had higher Ca concentration than those from the NW.

The relative concentration levels of REEs in the samples collected at site B, which is located 10 meters away from a very busy highway between Delft and Rotterdam, were similar to those of site A (see Figure 6.4.(a-d)). Only the Pb concentration was markedly higher for wind directions from the NE, which may be attributed to Pb emissions by traffic from the highway, which is located NE of the sampling site. During sampling at this site, only two wind directions prevailed, i.e. from the NE and SW. Furthermore, at this site only two sources were dominant; traffic to the NE and industry to the SW. Although concentration levels are dependent on the strength of the source and atmospheric stability, the following conclusions may be drawn.
Traffic is an important source of Pb, as a result of combustion of leaded gasoline and Ce and Nd due to the widespread use of three-way catalysts in automobiles. For Cd, V, Ca, and La emission, industry seems to be an important source.

The results of this study were compared with results from a study of concentration of REEs and metals in Delft in 1973 and with measurements performed elsewhere in the Netherlands in 1995 (see Table 6.2). Concentrations are not only dependent on source strength (emissions) but also on prevailing meteorological conditions during the respective sampling periods (1973 and 1997). Enrichment factors are given in Table 6.2. These factors are determined relative to the occurrence of elements in soil derived air particulate matter, based on data given by Parker (1967).

From Table 6.2., it can be seen that concentrations measured in 1997 are lower (mostly up to a factor 8) than those measured in 1973. Pb levels are lower by a factor of 70, which is very probably due to the introduction of lead-free petrol in most of the countries in Western Europe. This can also be seen from the enrichment factors (EF). The EF for Na is about five times higher, thus, it may be concluded that wind from the west occurred more frequently during sampling in 1997 compared to 1973. Western winds in this part of the country are accompanied by unstable meteorological conditions and higher wind velocities which, possibly also for Pb, are partly responsible for the lower concentrations which were measured for most of the elements. From Table 6.2., it also follows that the REEs and metals measured in 1997 near Delft are of the same order of magnitude as those measured elsewhere.

A good correlation between the REE concentration and the wind direction (NE and SW) was found for sampling sites A and B (Figure 6.5). The concentration of individual REE elements was lower in both sampling sites when the wind direction was from the SW compared with the NE, with the exception of La and Pr. In the case of the aforementioned elements higher concentrations were measured from the SW, for both sampling sites. This phenomenon may be attributed to the presence of the petrochemical industry to the south west of sampling points A and B.
Figure 6.3.(a-d) The influence of wind direction on the concentration (ng.m⁻³) of metals as APM in air (6.3a: individual REE; 6.3b: REEs, LREEs and HREEs; 6.3c: Pb, Cd, V and Ti, and 6.3d: Mg, Al, Na, Ca and Fe).
Figure 6.4.(a-d). A comparison of the concentration of metals as APM in air (ng.m⁻³). Samples were collected at site B (see Figure 6.1.), 19-27, August 1997. (6.4a: individual REEs; 6.4b: the total REEs, LREEs and HREEs; 6.4c: Pb, Cd, V and Ti; and 6.4d: Mg, Al, Na, Ca and Fe).

Figure 6.5. Comparison of the influence of sampling location on the concentration (ng.m⁻³) of metals as APM in air (sampling location A: NE_A and SW_A and sampling location B: NE_B and SW_B).
Table 6.2. Comparison of the metal concentration as APM in air in The Netherlands (ng/m$^3$), and enrichment factors related to Ti

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<td>ng/m$^3$</td>
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<td>ng/m$^3$</td>
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<td>ng/m$^3$</td>
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<td>0.7</td>
<td>1.2</td>
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<td>1.3</td>
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<td>La</td>
<td>3.0</td>
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<td>2.1</td>
<td>0.8</td>
<td>0.3</td>
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<tr>
<td>Cd</td>
<td>4.0</td>
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<td>846</td>
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<tr>
<td>Pb</td>
<td>1150</td>
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<td>16.6</td>
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<td>Al</td>
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<tr>
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<td></td>
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</tr>
<tr>
<td>Ca</td>
<td>2590</td>
<td>5.4</td>
<td>1235</td>
<td>16</td>
<td>150</td>
<td>220</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>45</td>
<td>9.1</td>
<td>8.1</td>
<td>10</td>
<td>17</td>
<td>20</td>
<td>13</td>
</tr>
<tr>
<td>Fe</td>
<td>2555</td>
<td>1.7</td>
<td>534</td>
<td>2.2</td>
<td>490</td>
<td>760</td>
<td>804</td>
</tr>
<tr>
<td>Ti</td>
<td>77</td>
<td>1.00</td>
<td>12.5</td>
<td>1.00</td>
<td>15.1</td>
<td>8</td>
<td>10.9</td>
</tr>
</tbody>
</table>

- For determining EF data was normalized to Ti.
- EF: Enrichment Factors

6.4. Conclusions

The total REE ($\Sigma$REE), light-REE (LREE), and heavy-REE (HREE) concentrations were 0.22-33.0; 0.21-30.7; and 0.01-2.3 ng/m$^3$, respectively. The ratio of LREE to HREE ranged from 6.4 to 33.6; the ratio of LREEs to REEs was 0.86-0.97 (the average ca. 0.90); and the ratio of HREEs to REEs was 0.03-0.14, (average ca. 0.1). The La to Ce, and La to Sm ratio varied considerably i.e. 0.5-4.4 and 4.3-71.4 respectively, and could be used as a tracer for the REE source. Traffic was an important source of Pb, as result of combustion of leaded gasoline and Ce and Nd,
due to the widespread use of three-way catalysts in automobiles. For Cd, V, Ca, La and Pr, industrial emission seems to be the important source. Traffic, industry and suspended soil particles were the main contributors to the concentrations of REE.

References


Chapter 7

Occurrence of REEs in Chinese and Dutch Soils

Abstract

Randomly collected soil samples from Guangdong Province (China) and selected samples from The Netherlands were analysed for REEs. Twenty five soil samples were collected from 13 sites in The Netherlands, and 27 samples from 12 sites in Guangdong Province. Some Dutch samples originated from sites that were suspected of contamination. Guangdong soils had large differences in the concentrations per individual REE. These soils were depleted with respect to heavy REEs, but the ratios and concentrations for light REEs were comparable to those in the earth’s crust. Higher sample to crust ratios were observed for Ce and Dy, however, and these geological anomalies are believed to be particular for the soils in this region. The Dutch soils had a slight depletion for the heavy REEs but no enrichment or depletion was observed for the light REEs. The soluble REE fraction ranged 0.7 – 15.6% of the total REE concentration. Heavy REEs were easier to extract. Crust-normalized REE ratios were compared. The ratio between the individual REEs is quite different between the two sample sets. In both countries the concentrations for the individual elements could vary 20 – 250% among the samples. In Dutch soil samples taken from a site where polluted sludge was known to have been dumped, enrichment of most REEs was found, especially of Gd, Nd, Dy and Ce. Soils near a major highway revealed no significant difference, however.

7.1. Introduction

In recent years, more attention has been paid to rare earth element (REE) behaviour in soil (Markert, 1987, Yasuda, et al., 1990, Volokh et al., 1990 and Ichihashi, et al., 1992). Under different environmental conditions soil can act as an efficient sink for REEs. China has the largest REE reserves in the world (80%) and is a major producer of REEs for the world market. Since 1990, REE fertilizer has been widely used in
more than 20 Chinese provinces (Wu and Guo, 1990, Yu and Chen, 1995 and Xu, 1995). REE fertilizer intended for agricultural use was predicted to cover over 16-20 x 10^6 ha of agricultural land in 1995 in China (Tu et al., 1994 and Yu and Chen, 1995). In particular, in some areas of Guangdong province, the REE concentration in the soil was 2-3 times higher than in other areas of China (Zhu et al., 1988 and Wu and Guo, 1990). The aims of this study are (i) to determine the occurrence of REEs in soils of different origin and (ii) to investigate the correlation between the total and soluble REE fractions in soil.

7.2. Materials and methods

7.2.1. Sampling

27 soil samples (from Guangdong province, China) were collected from 12 different sampling sites. The samples were collected at a depth of 10-20 cm below the soil surface. The general area where the soil samples were collected is characterised by intensive agriculture.

25 soil samples (from The Netherlands) were collected from 11 different sampling sites. 19 natural soil samples were collected: from Haren experimental farm (s1), Lovinkhoeve experimental farm (s2), Zegveld experimental farm (s3), Delft recreational park (s4), Eendenkooi 't Broek (s5), Spelderholt (s6), Korenburgerveen (s7), Harense Wildernis (s8) and Wierde Wetsinge (s9). Another 6 soil samples (from The Netherlands) were collected near the A13 highway between Delft and Rotterdam (see Figure 6.1., site B). S10 and s11 represent the samples taken at a distance of 10m and 600m from the highway, respectively. Furthermore samples were taken from the Hoge Nespolder, located between Heerjansdam and Zwijndrecht (s12 and s13).

At least 5 sub-samples (ca. 2 kg in total) were taken for each site and homogenized. The samples were stored in polyethylene bags. The wet samples were air-dried at room temperature and sieved to remove large particles. Subsequently, the debris was passed through a 2 mm sieve.

7.2.2. Extraction & digestion

For the soluble fraction (soil samples from Guangdong province, China), 1g of sample was weighed and extracted with 25 ml 0.1 M acetic acid - ammonium acetate (pH=4.2)
for 24 hours. In order to determine the total REE content, 0.5 g of the sample was weighed and transferred into a vessel and digested with HNO₃ by Microwave. REEs in the digested solutions were analysed by ICP-MS. The results are given on dry weight basis.

### 7.3. Results and discussion

#### 7.3.1. Occurrence of REEs in Chinese and Dutch natural soil samples

In Table 7.1. and 7.2., the distribution of the maximum, median, minimum and average REE concentration (mg kg⁻¹) of Dutch (n=19) and Chinese (n=27) natural soil samples are presented.

The average REE concentration in Guangdong soil samples was as follows: Ce > La > Nd > Y > Pr > Sc > Sm > Gd > Dy > Er > Yb > Eu > Tb, Ho, Tm and Lu. The total rare earth element concentration (REEs), the total light rare earth element concentration (LREEs) and the total heavy rare earth element concentration (HREEs) ranged from 88.9 to 469.0, 76.2 to 447.7 and 9.2 to 55.2 (mg kg⁻¹), respectively. The ratio of LREEs to HREEs ranged from 14 to 18.2. Large differences in concentration (3 to 15 times) were found for individual REEs in different soil samples. These differences may be attributed to the different soil types in Guangdong province.

A comparison of average REE concentrations in Guangdong soils (GD-soils) and average REE concentrations in the earth’s crust (Henderson, 1984) and crust-normalized REE abundance for Guangdong soils are shown in Figure 7.1a. and Figure 7.1c., respectively. In Figure 7.1a, significant depletion of heavy REEs in Guangdong soils can be observed, with the exception of Dy. The ratio of light REEs in Guangdong soil samples to that of the earth’s crust (Figure 7.1c.) was constant, which suggests that the concentrations of light REEs in the soil samples were comparable to those of the earth’s crust. The higher sample/crust ratios observed for Ce and Dy in Figure 7.1c. are believed to be geological anomalies. The average REE crust-normalized ratio for (La/Yb)ₙ and (La/Sm)ₙ was 3.5 ± 1.6 and 1.3 ± 0.2, respectively in Guangdong soils.

The average REE concentration (Cₙₐ) of the Dutch soil samples followed the same order as the Guangdong soil samples. The total REEs, LREEs and HREEs ranged from 26.09 to 186.51, 22.06 to 154.32 and 4.03 to 35.31 mg kg⁻¹, respectively. The ratio of LREEs to HREEs ranged from 8.40 to 13.80. It was also found that these results are comparable to these reported by Edelman (1983).
Table 7.1. The maximum, median, minimum and average total REE content (mg.kg⁻¹) of 27 soil samples collected in Guangdong province, China.

<table>
<thead>
<tr>
<th></th>
<th>Max</th>
<th>Median</th>
<th>Min</th>
<th>Average</th>
<th>Max</th>
<th>Median</th>
<th>Min</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>10.65</td>
<td>7.89</td>
<td>3.80</td>
<td>7.62</td>
<td>Er</td>
<td>3.43</td>
<td>1.31</td>
<td>0.53</td>
</tr>
<tr>
<td>La</td>
<td>71.23</td>
<td>35.97</td>
<td>14.03</td>
<td>35.22</td>
<td>Tm</td>
<td>0.49</td>
<td>0.18</td>
<td>0.07</td>
</tr>
<tr>
<td>Ce</td>
<td>351.11</td>
<td>86.39</td>
<td>33.38</td>
<td>97.35</td>
<td>Yb</td>
<td>3.17</td>
<td>1.04</td>
<td>0.41</td>
</tr>
<tr>
<td>Pr</td>
<td>18.05</td>
<td>8.73</td>
<td>3.15</td>
<td>8.44</td>
<td>Lu</td>
<td>0.45</td>
<td>0.16</td>
<td>0.03</td>
</tr>
<tr>
<td>Nd</td>
<td>61.88</td>
<td>30.03</td>
<td>10.63</td>
<td>29.24</td>
<td>Y</td>
<td>28.91</td>
<td>12.46</td>
<td>4.86</td>
</tr>
<tr>
<td>Sm</td>
<td>12.34</td>
<td>5.48</td>
<td>1.87</td>
<td>5.49</td>
<td>REEs</td>
<td>469.0</td>
<td>212.3</td>
<td>88.9</td>
</tr>
<tr>
<td>Eu</td>
<td>1.51</td>
<td>0.89</td>
<td>0.23</td>
<td>0.83</td>
<td>LREEs</td>
<td>447.7</td>
<td>186.0</td>
<td>76.2</td>
</tr>
<tr>
<td>Gd</td>
<td>9.69</td>
<td>4.71</td>
<td>1.81</td>
<td>4.78</td>
<td>HREEs</td>
<td>55.2</td>
<td>23.0</td>
<td>9.2</td>
</tr>
<tr>
<td>Tb</td>
<td>1.27</td>
<td>0.56</td>
<td>0.20</td>
<td>0.58</td>
<td>L/H</td>
<td>21.0</td>
<td>7.3</td>
<td>5.3</td>
</tr>
<tr>
<td>Dy</td>
<td>6.95</td>
<td>2.72</td>
<td>1.00</td>
<td>2.89</td>
<td>*L/H</td>
<td>18.2</td>
<td>13.8</td>
<td>14</td>
</tr>
<tr>
<td>Ho</td>
<td>1.24</td>
<td>0.47</td>
<td>0.19</td>
<td>0.51</td>
<td>*without Sc and Y</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7.2. The maximum, median, minimum and average total REE content (mg.kg⁻¹) of 19 natural soil samples (9 sampling locations) collected in The Netherlands.

<table>
<thead>
<tr>
<th></th>
<th>Max</th>
<th>Median</th>
<th>Min</th>
<th>Average</th>
<th>Max</th>
<th>Median</th>
<th>Min</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>18.09</td>
<td>3.07</td>
<td>0.88</td>
<td>6.02</td>
<td>Er</td>
<td>1.89</td>
<td>0.55</td>
<td>0.21</td>
</tr>
<tr>
<td>La</td>
<td>31.46</td>
<td>11.65</td>
<td>4.89</td>
<td>17.13</td>
<td>Tm</td>
<td>0.30</td>
<td>0.08</td>
<td>0.03</td>
</tr>
<tr>
<td>Ce</td>
<td>69.55</td>
<td>24.11</td>
<td>10.34</td>
<td>36.18</td>
<td>Yb</td>
<td>1.50</td>
<td>0.46</td>
<td>0.18</td>
</tr>
<tr>
<td>Pr</td>
<td>7.93</td>
<td>2.76</td>
<td>1.10</td>
<td>4.20</td>
<td>Lu</td>
<td>0.25</td>
<td>0.08</td>
<td>0.03</td>
</tr>
<tr>
<td>Nd</td>
<td>30.05</td>
<td>10.79</td>
<td>4.08</td>
<td>16.13</td>
<td>Y</td>
<td>19.03</td>
<td>6.82</td>
<td>2.19</td>
</tr>
<tr>
<td>Sm</td>
<td>6.34</td>
<td>2.14</td>
<td>0.76</td>
<td>3.32</td>
<td>REEs</td>
<td>186.51</td>
<td>66.67</td>
<td>26.09</td>
</tr>
<tr>
<td>Eu</td>
<td>1.48</td>
<td>0.38</td>
<td>0.12</td>
<td>0.65</td>
<td>LREEs</td>
<td>154.32</td>
<td>54.93</td>
<td>22.06</td>
</tr>
<tr>
<td>Gd</td>
<td>6.10</td>
<td>1.78</td>
<td>0.67</td>
<td>3.00</td>
<td>HREEs</td>
<td>35.31</td>
<td>11.74</td>
<td>4.03</td>
</tr>
<tr>
<td>Tb</td>
<td>0.85</td>
<td>0.24</td>
<td>0.08</td>
<td>0.40</td>
<td>L/H</td>
<td>6.41</td>
<td>5.02</td>
<td>3.81</td>
</tr>
<tr>
<td>Dy</td>
<td>3.94</td>
<td>0.90</td>
<td>0.10</td>
<td>1.17</td>
<td>*L/H</td>
<td>13.80</td>
<td>10.58</td>
<td>8.40</td>
</tr>
<tr>
<td>Ho</td>
<td>0.77</td>
<td>0.21</td>
<td>0.08</td>
<td>0.36</td>
<td>*without Sc and Y</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
From *Figure 7.1.b* and *Figure 7.1.c*), slight depletion of the heavy REEs was found for the Dutch soil samples (NL-soils). No significant enrichment or depletion was observed for the light REEs in Dutch soil samples. The average REE crust-normalized ratio for $(\text{La/Yb})_N$ and $(\text{La/Sm})_N$ was $3.6 \pm 0.46$ and $2.1 \pm 0.11$, respectively in Dutch soil samples.

*Figure 7.1.(a-c).* (a) comparison of REE occurrences between GD-soil and crust (27 soils); (b) comparison of REE occurrences between NL-soil and crust (9 soils) and
7.3.2. Comparison of the total and soluble fractions in Guangdong soil samples

In Figure 7.2a., the relationship between the LREEs and HREEs in the total content fraction is presented and in Figure 7.2b., the relationship between the soluble LREEs and HREEs is presented. A better linear relationship existed between the LREEs and HREEs in the total fraction (Figure 7.2d.). This phenomenon may be due to the soil origin (geological composition, humic acid etc.). However, in Figure 7.2 (a-b) samples G18 and G19 clearly did not follow the linear relationship which existed for the other samples. This phenomenon is due to a high normalized Ce concentration in both samples. The origin of the high Ce levels is not clear and may be attributed to excessive use of Ce-enriched fertilizer, as this area is characterised by intensive agricultural activity.

From the crust-normalized REE ratio, it was found that the (La/Yb)_N and (La/Sm)_N in the soluble fraction of Guangdong soil (n=27) was 3.1 ± 1.6 and 0.87 ± 0.2, respectively. The crust-normalized ratio of (La/Sm)_N in the soluble fraction was lower (0.87) than in the total fraction (1.1) and may be attributed to the fact that the HREEs were easier to extract from the soluble fraction. This phenomenon is discussed in more detail in Chapter 8 of this thesis.

The soluble REE fraction ranged from 0.7 to 15.6 % of the total REE concentration (see Figure 7.3.) Changes in the concentration of the soluble REE fraction may be a more reliable index than changes in the total REE concentration, for the potential release of REEs from soil. The (total) REE soluble fraction was divided into five levels by Zhu and Liu (1988) (level 1: < 5 mg.kg⁻¹, level 2: 5-10 mg.kg⁻¹, level 3: 11-15 mg.kg⁻¹, level 4:16-20 mg.kg⁻¹ and level 5:≥20 mg.kg⁻¹). Results of the soil samples analyzed in this study indicated that 18.5, 22.2, 14.8 and 22.2% corresponded to levels 1, 2, 3, 4 and 5, respectively. The proportion of the samples, which corresponded to levels 4 and 5 were high compared to other areas of China (Zhong and Min, 1995).
Figure 7.2a. The relationship between LREEs and HREEs in the total fraction of Guangdong soil samples (n=27).

Figure 7.2b. The relationship between the soluble LREEs and HREEs in Guangdong soil samples (n=27).
Figure 7.3. The soluble REE content expressed as percentage of the total REE content.

7.3.3. Comparison of the average REE concentration in Dutch and Chinese soil samples

In Figure 7.1c., a comparison of the crust-normalized REE ratio in Guangdong (n=27) and Dutch soil samples (n=19) is presented. The ratio between the individual REEs is quite different in both areas. In both countries, concentrations for each individual element could vary 20-250%. Light REEs, Gd and Dy were responsible for the variation in the total REE concentration in Guangdong soil samples. This may be due to geological differences between sampling sites in Guangdong and The Netherlands and the limited number of samples collected and analysed for such a large area.

7.3.4. REE concentration in Dutch soil samples suspected of being contaminated

From Figure 7.4., it can be observed that a large difference in REE concentration (up to a factor 2) existed between natural Dutch soil samples and soil samples suspected of being contaminated. The soil samples suspected of being contaminated were taken from two different sampling sites in the Hoge Nespolder (Rotterdam), which has remained undisturbed since the dumping of sludge spoils.

A comparison of the crust-normalized REE ratio in natural soil and soil samples suspected of contamination (from the Hoge Nespolder, Rotterdam) is given in Figure 7.4.. Enrichment of most REEs was observed in the soil samples taken from the Hoge
Nespolder in Rotterdam. In particular, strong enrichment was observed for Gd, Nd, Dy and Ce compared to the natural soil. The concentration of Pb and Cd was also measured and found to be in the following range (Pb: 205 – 2355 ppm, and Cd: 92 – 99 ppm) in this area. It cannot be concluded that this area is contaminated despite the higher than average concentration of REEs; since the contaminated soil is composed of sediment with a high specific area. The increase in Gd may indicate contamination; however Gd enrichment is also reported in uncontaminated areas (see Chapter 5).

![Graph of Crust-normalized REE patterns in NL-soil and soil samples suspected of being contaminated from Hoge Nespolder.](image)

**Figure 7.4.** Crust-normalized REE patterns in NL-soil and soil samples suspected of being contaminated from Hoge Nespolder.

Analysis of the soil samples collected close (10-600m) to the highway between Delft and Rotterdam revealed no significant difference compared with natural soil samples. A small variation in concentration (ca. 20%) was observed between soil samples collected 10m and 600m from the highway, and may be attributed to geological differences between the two sampling points. However, a more detailed study is required to determine the impact of traffic on the concentration of REEs in areas surrounding the highway.

### 7.4. Conclusions

Randomly collected soil samples from Guangdong Province (China) and selected samples from The Netherlands were analysed for REEs.
Guangdong soils had large differences in the concentrations per individual REE. These soils were depleted with respect to heavy REEs, but the ratios and concentrations for light REEs were comparable to those in the earth’s crust. Higher sample to crust ratios were observed for Ce and Dy, however, and these geological anomalies are believed to be particular for the soils in this region. The Dutch soils had a slight depletion for the heavy REE abundance but no enrichment or depletion was observed for the light REEs.

The soluble REE fraction ranged 0.7 – 15.6% of the total REE concentration. Heavy REEs were easier to extract.

Crust-normalized REE ratios were compared. The ratio between the individual REEs is quite different between the two sample sets. In both countries the concentrations for the individual elements could vary 20 – 250% among the samples.

In Dutch soil samples taken from a site suspected of being polluted, enrichment of most REEs was found, especially of Gd, Nd, Dy and Ce. However, the origin of this enrichment is unknown. Soils near a major highway revealed no significant difference.

References


Chapter 8

Leaching Behaviour of Rare Earth Elements in Dutch Soil

Abstract

Rare earth elements (REEs) are a new type of potential pollutant in groundwater in areas where the rain water percolating through the top-soil layers is highly acidic. Therefore, three different types of soil samples (sandy clay, clay and peaty soil) were collected in The Netherlands. Availability tests and column leaching tests were carried out to study the behaviour of REEs under acid rain conditions in different soil types.

Availability tests indicated that the fraction of REE that is available for leaching (expressed as CMR) was always less than 0.8% of the total concentration in the soil. Heavy REEs leached at pH ≈ 4 to a greater extent than light REEs. Individual REEs showed similar behaviour in the soil leaching (except Sc). Heavy metals showed higher release capacity (maximum capacity of Zn was 22%) than REEs and a different leaching behaviour in comparison to REEs. The acid buffering capacity and the original pH of the soil played an important role in determining soil leaching. The leachability of REEs in column leaching tests was not similar to that of the availability tests. The cumulative released REE concentration (CCR) ranged from 20 to 60% of the CMR.

8.1. Introduction

During the last decade numerous investigations on trace and toxic metals in soil have been conducted in order to assess micronutrient availability, or to assess the continuing soil pollution by heavy metals. Both in urban and agricultural areas, soil has accumulated heavy metals (Sposito, 1991, Ross, 1993 and Selim and Amacher, 1994). These heavy metals may adversely affect soil ecology, agricultural production or product quality, and surface and ground water quality. These effects are closely
related to both the biological availability and the mobility of metals, which in turn are controlled by the chemical speciation of these metals (Ross, 1993, Onken and Hossner, 1995 and Romkens et al., 1996).

Soil consists of a heterogeneous mixture of different organic and mineral substances, such as clay minerals, oxides of iron, aluminium, and manganese, and other solid components as well as a variety of soluble organic substances such as humic and fulvic acid (Sposito, 1991). The binding mechanisms for heavy metals in soil vary with the composition of the soils, the soil reaction, and redox conditions. Thus, a metal may form different species depending on the soil compounds it is bound to, the soil surface reaction and whether it is bound to external or internal binding sites, which have different binding energies (Brummer, 1983).

The mobility of Zn, Mn, Cd and other metals has been reported to increase with soil acidity (Brummer, 1983 and Grinsven et al., 1992). Even a minor decrease in pH has been shown to increase the leaching of Zn, Cd, Ni and Mn significantly from both metal polluted and unpolluted soil layers (Brummer, 1983 and Wilkens and Loch, 1997). The concentration of heavy metals in the soluble phase is of major importance for all ecological considerations, because plants can take up the available metal ion from the soil solution (Hunter and Hans, 1991 and Castilho and Chardon, 1995).

On the one hand, REEs enriched fertilizer has been widely used in the world for increasing crop productivity (Yu and Chen, 1995 and Zhong and Min, 1995). On the other hand, REEs are known to exhibit toxicity to living organisms (Gerritsen and Bowmer, 1992 and Hooftman et al., 1992). In recent years, more attention has been paid to rare earth element (REEs) behaviour in soil (Bosman et al., 1996 and Zhu et al., 1997). It is important to understand the leaching behaviour of REEs in soil in order to assess the potential transport of Rees from soil to groundwater and their possible release into the aquatic environment.

Compared with other chemicals or elements such as pesticides and heavy metals, little is known about the leaching behaviour of REEs in soil. There are several reports describing the factors which influence the mobility of REEs in soil or solution (Coughtry and Thorne, 1983, Diatloff et al., 1995, Diatloff et al., 1996 and De Boer et al., 1997). pH is a major factor. At low pH, the concentration of REEs in soil solution increases. Goldstein and Jacobsen (1988) also reported that pH is an important factor in controlling both the absolute abundance of the light REEs in river water and suspended materials. It was reported that about 10% of the total content of REEs existed in REE soluble fraction in soil (Zhu et al., 1997). It was suggested that
the concentration of REEs in surface water should be less than 1 mg.l⁻¹ (Tang and Liu, 1987).

However, data on the availability and leaching of REEs in soil are very scarce. The aims of the present work are to (i) determine the availability of REEs in representative soil and assess the mobilisation of REEs that results from the weathering of soil and (ii) to understand REE behaviour in soil solution that dictates the concentrations of REEs in the leachate, and investigate leaching characteristics of REEs and compare it with that of heavy metals. Based on the hypothesis that the soil behaviour of REEs could be similar to that of heavy metals, availability and column leaching tests were carried out and pH was considered as the most important variable.

8.2. Fate of heavy metals in soil

8.2.1. Mobility of heavy metals in soil

The relative mobility of the different metals can be roughly expressed by the ratio of the dissolved to bound amounts of each metal or by the percentage of the total content of each metal which is dissolved at pH values below 6 (Brummer, 1983). According to this interpretation and in close agreement with the concept of metal-ion hydrolysis, the mobility of heavy metals in acidic soil decreases in the order Cd > Zn > Ni > Mn > Cu > Pb > Hg (Brummer, 1983 and Sposito, 1991).

In general, the capacity of inorganic soil to retain bound metal ions increases and the mobility of the cations decreases with increasing pH. Herbert and Sticher (1991) reported that the relative mobility of some trace elements was strongly influenced by pH:

\[
\begin{align*}
\text{pH 4.2 to 6.6:} & \quad \text{Cd, Hg, Ni and Zn: relatively mobile} \\
& \quad \text{As, Be and Cr: moderately mobile} \\
& \quad \text{Cu, Pb and Se: slowly mobile} \\
\text{pH 6.7 to 8.8:} & \quad \text{As and Cr: relatively mobile} \\
& \quad \text{Be, Cd, Hg and Zn: moderately mobile} \\
& \quad \text{Cu, Pb and Ni: slowly mobile}
\end{align*}
\]
There are several indications that considerable proportions of Pb and Cu are bound by solid organic substances even at pH around 3, and of Cd still at pH between 3 and 4, whereas solid metal-organic complexes of Zn are not stable below pH 5 (Herbert and Sticher, 1991). Thus, soil samples with a relatively high content of organic matter are characterised at pH 3 to 5 by lower solution concentrations of Cd, Cu and Pb than soil samples with a low content of organic matter and a high content of clay minerals and iron oxides.

Retention and release reactions in soils include adsorption, desorption, precipitation and ion exchange reactions (Amacher et al., 1986). Retention and release are influenced by a number of soil properties including texture, bulk density, pH, organic matter content, and the type and amount of clay minerals. For instance, the concentration of Zn and Cd in the equilibrium solution of three soil samples containing different amounts of heavy metals were determined in relation to adjusted pH values between 3 to 8. The concentration of Zn and Cd in the equilibrium solutions strongly increased with decreasing pH and increasing total content of these metals in the soils (Herms and Brummer, 1984).

8.3. Experimental

8.3.1. Materials and methods

REE solutions and heavy metals were prepared from standard 1000 mg.l⁻¹ stock solutions (Perkin-Elmer). Single element standards were prepared for each of the following elements: Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Cu, Zn, Pb and In.

Three different representative types of soil (sandy-clay, clay and peaty soil) were collected from three different sampling sites in The Netherlands. Approximately 4 kg of soil (per sample) was taken from each site and homogenized (at a depth of ca. 10 cm and at least consisting of 5 sub-site samples). The samples were stored in polyethylene bags. Firstly, the sample was crushed to pass through a 4mm sieve and mixed thoroughly. The sample was homogenized and sub-divided into four sub-samples, one sub-sample was directly used for a column leaching test, and another one was sub-divided into eight sub-samples. For the availability test, the sample was dried for 24 hours at 40 °C and crushed to pass through a 125 μm sieve and mixed thoroughly. For analysis of the total REE and heavy metal content, the dried sample (for 24 hours at 105 °C) was used. The moisture content was determined for each
sample before performing the column leaching and availability tests. Moisture content was analysed by drying at 105 °C for 24 hours.

pH: 5 g air dry soil was mixed with 25 ml of 1 mol 1\textsuperscript{-1} KCl solution. 24 hours later, the soil KCl mixture was re-suspended and the pH of the suspension was measured.

Total organic carbon (TOC): 0.3 g of ground soil was placed in a 100 ml erlenmeyer flask. 20 ml of dichromate sulphuric acid-solution (13.072 g K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}, 550 ml H\textsubscript{2}SO\textsubscript{4} brought to 1 l with water) was added. The suspension was boiled for 0.5 hour under reflux. A few drops of indicator was added and the solution titrated with Mohr's salt solution (78.390 g (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}FeSO\textsubscript{4}.6H\textsubscript{2}O, 25 ml H\textsubscript{2}SO\textsubscript{4} made up to 1000 ml with water) until the indicator (o-phenanthroline solution) turned from green to brown-red.

Particle size: after eliminating organic matter with 30 % H\textsubscript{2}O\textsubscript{2} and elimination of carbonate with diluted HCl (for non acidic soils) and addition of a peptisation agent, an aliquot was brought into the top of a water filled cylinder. The particle size fractions are calculated according to differences in falling velocities (Stokes law).

Availability tests were carried out on a crushed sample with particles reduced to less than 125 μm. Two extractions were carried out in series in discontinuous batches, each at a 50:1 liquid to solid ratio (L/S), using distilled water. The pH was set at pH 7±0.05 during the first extraction and at pH 4±0.05 during the second extraction, using an automatic pH controller, which delivers dilute nitric acid. Both extractions were carried out with continuous stirring to maintain the pH at 7±0.05 and 4±0.05, respectively, for three hours by adding nitric acid (1 mol.l\textsuperscript{-1}). The conductivity of the extracted solutions (pH 4 and pH 7) was immediately measured. Thereafter, the solutions were acidified with nitric acid to pH 2.

Column leaching tests were intended to simulate the continuous percolation of (acid) rainwater through the soil. The sample was placed in a column with a diameter of 5 cm and height of 20 cm, and acidified demineralized water (pH=4) was then passed upwards through it. The leachate was collected in seven fractions at a liquid/solid ratio (L/S) of 0.1, 0.2, 0.5, 1, 3, 5, and 10, respectively. pH and conductivity of the eluate were measured. The pH was not controlled, so the soil was allowed to dictate the chemical conditions in the pore solution. Figure 8.1. a schematic of the column leaching test is presented.
The samples (total analysis of REEs and heavy metals, availability ests, leaching tests) were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) (VG Plasmaquad Plus, Fisson Instruments, U.K.).

All experiments mentioned above (availability and column leaching tests) were carried out in duplicate (n=2) and at a temperature of 20 ± 2 °C.

8.3.2. Analytical Procedure

For analysis of the total REE and heavy metal content, the samples were dried at 105 °C for 24 hours. 0.5 g of the sample was weighted and transferred into a vessel liner and 5 ml of H2O and 10 ml HNO3 were added. The mixture was digested by Microwave (MDS-2000, CEM, U.S.A.) for 90 minutes at 100 psi and full power (650 Watts).
8.4. Results and discussion

A partial least-squares regression (PLSR) model (described in Chapter 2) was used to process the analytical data from the ICP-MS. Results indicated that the repeatability of availability and column leaching tests is better than 93.5% and 98%, respectively. The precision of ICP-MS analysis (relative standard deviation: RSD) is better than 2.5%, 3.7% and 4.8% for light REEs, heavy REEs and heavy metals, respectively. The accuracy was determined by the standard addition method (with nearly the same amount of sample concentration added). The average recovery was 96.6% (n=12), 94.5% (n=12) and 93.2% (n=12) for light REEs, heavy REEs and heavy metals, respectively.

In order to discuss the experimental results mentioned below, the terms $C_{TOT}$, $C_{MR}$ and $C_{CR}$ are used:

$C_{TOT}$: total concentration of the element in the soil sample (mg.kg$^{-1}$).

$C_{MR}$: the maximum fraction of the element (availability) that can be released at pH =4 (μg.kg$^{-1}$).

$C_{CR}$: cumulative released (μg.kg$^{-1}$).

8.4.1. Properties of soil samples

The pH of both the sandy-clay and peaty samples was less than 7.0, while the pH of the clay sample was higher than 7.0. pH values depended on the total organic carbon and clay content of the soil samples. The total organic carbon (TOC) content of these samples was different: sandy-clay and clay soils had a lower TOC while peaty soil showed a high concentration of TOC (ca. 35.5%). Both clay and peaty soil samples had very high clay contents (particle size < 16 μm). Details of pH, clay-content and TOC of the samples are given in Table 8.1.

The concentration of the total REEs, light REEs and heavy REEs were 52.0, 45.0 and 7.0 in the sandy soil; 180.8, 154.1 and 26.6 in the clay and 186.64, 154.3 and 32.2 mg.kg$^{-1}$ in the peaty soil, respectively (Table 8.2.). The total REE content of the clay and peaty soil was similar and three times higher, respectively, than that of the sandy soil. Table 8.1. and Table 8.2. also indicated that in these soil samples the REE concentration correlated positively with the clay content (particle size < 16 μm). In the clay fraction of soil, (hydr)oxides of Fe and Al are common. The reactivity of hydroxide coatings on soil particles may be considerably higher than the reactivity of free hydroxides, especially with respect to heavy metal adsorption. It has been suggested that clay Al-hydroxide and clay Fe-hydroxide generally exhibit a high
degree of heavy metal adsorption (Bolt et al., 1990). The clay-soil and peaty soil had high concentrations of Zn, Cu and REEs in comparison to the sandy soil (Table 8.2). High concentrations of Pb (223.2 mg.kg\(^{-1}\)) were found in the peaty soil and was attributed to atmospheric deposition and direct anthropogenic inputs (manure and fertilizer application, etc.), which are common in The Netherlands (Romkens et al., 1996). It may be concluded that the effect of the clay content of soil correlated in a similar way with the adsorption of REEs and heavy metals. On the other hand, the concentration of Pb was positively correlated with TOC. No correlation between the total content of REEs, pH and TOC was found.

Table 8.1. Properties of the soil samples.

<table>
<thead>
<tr>
<th>Soil</th>
<th>pH</th>
<th>Size fraction &lt; 16 μm (% of total weight)</th>
<th>Size fraction &lt; 2μm (% of total weight)</th>
<th>TOC (% of total weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sandy-clay</td>
<td>4.85</td>
<td>6.7</td>
<td>4.0</td>
<td>4.5</td>
</tr>
<tr>
<td>clay</td>
<td>7.33</td>
<td>32.4</td>
<td>18.7</td>
<td>2.0</td>
</tr>
<tr>
<td>peaty-soil</td>
<td>5.00</td>
<td>38.1</td>
<td>28.5</td>
<td>35.5</td>
</tr>
</tbody>
</table>

Table 8.2. REE and heavy metal content of the soil samples (mg.kg\(^{-1}\)), including Sc and Y.

<table>
<thead>
<tr>
<th></th>
<th>Sandy-clay</th>
<th>Clay</th>
<th>Peaty</th>
<th>Sandy-clay</th>
<th>Clay</th>
<th>Peaty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>8.3</td>
<td>26.4</td>
<td>89.4</td>
<td>0.18</td>
<td>0.73</td>
<td>0.85</td>
</tr>
<tr>
<td>Zn</td>
<td>13.4</td>
<td>89.0</td>
<td>175.8</td>
<td>0.10</td>
<td>0.38</td>
<td>0.47</td>
</tr>
<tr>
<td>Pb</td>
<td>22.7</td>
<td>29.0</td>
<td>223.2</td>
<td>0.17</td>
<td>0.63</td>
<td>0.77</td>
</tr>
<tr>
<td>Np</td>
<td>Er</td>
<td>0.46</td>
<td>1.5</td>
<td>1.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sc</td>
<td>2.7</td>
<td>9.0</td>
<td>18.1</td>
<td>0.08</td>
<td>0.23</td>
<td>0.30</td>
</tr>
<tr>
<td>La</td>
<td>9.9</td>
<td>31.5</td>
<td>29.9</td>
<td>0.40</td>
<td>1.3</td>
<td>1.4</td>
</tr>
<tr>
<td>Ce</td>
<td>20.3</td>
<td>69.6</td>
<td>63.1</td>
<td>0.07</td>
<td>0.19</td>
<td>0.25</td>
</tr>
<tr>
<td>Pr</td>
<td>2.3</td>
<td>7.9</td>
<td>7.6</td>
<td>4.0</td>
<td>15.2</td>
<td>18.6</td>
</tr>
<tr>
<td>Eu</td>
<td>0.24</td>
<td>1.1</td>
<td>1.5</td>
<td>REEs</td>
<td>52.0</td>
<td>180.8</td>
</tr>
<tr>
<td>Gd</td>
<td>1.4</td>
<td>5.4</td>
<td>6.1</td>
<td>LREEs</td>
<td>45.0</td>
<td>154.1</td>
</tr>
<tr>
<td>Nd</td>
<td>8.2</td>
<td>30.1</td>
<td>29.2</td>
<td>HREEs</td>
<td>7.0</td>
<td>26.6</td>
</tr>
<tr>
<td>Sm</td>
<td>1.6</td>
<td>6.1</td>
<td>6.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
8.4.2. Availability for leaching of REEs and heavy metals in soil samples at pH 7 and pH 4

The availability tests were performed to assess the maximum amount of REEs and heavy metals or species thereof which could be leached at pH 7 and pH 4 under an assumed “worst case” environmental scenario (Table 8.3.). The two extraction steps required a total of about 0.50, 3.45 and 26.44 mmol acid for 16g sandy-clay, clay and peaty soils, respectively. The acid buffering capacity of sandy-clay, clay and peaty soils was 0.031, 1.65 and 0.216 mmol/g, respectively. No acid was consumed in step 1 for sandy-clay and peaty soils since the pH of both original samples was lower than 7 (4.85 and 5.00, respectively). The large acid buffer helped to keep the trace elements in the solid phase.

From Table 8.3., it follows that the maximum REE fraction released (C_MR) was less than 0.5 mg/kg in the soil samples. If expressed as a percentage of the total initial content (C_TOT) (Figure 8.2. and Figure 8.3.), the following conclusions can be made:

(i) Less than 0.8 % of the C_TOT was leached (with the exception of Sc in clay soil).
(ii) The amount of heavy REEs leached (0.4%) was ca. twice that of the light REEs (0.2%).
(iii) Higher leaching was observed for heavy metals in comparison to the REEs (the largest was Zn with 22%).

The LREEs/HREEs ratio in C_TOT and C_MR fractions was completely different (Figure 8.4.). Heavy REEs were more easily released at pH 4.

The release in step 1 (at pH ≤ 7) of the individual heavy metals, and of total REEs, HREEs and LREEs, ranged from 64% to 95% (except Zn), 58% to 82% (except Zn) and 0.7 % to 5.4% (except Cu and Sc) of C_MR for sandy, peaty and clay soils, respectively (Figure 8.5.). In step 2 (at pH = 4), the ranges were 5% to 36% (except Zn), 18% to 42% (except Zn) and 94.6 % to 99.3% (except Cu and Sc) for sandy, peaty and clay soils, respectively. Both sandy and peaty soil samples exhibited similar behaviour in the availability tests: the major part of the concentration that could maximally be released became available in the first step. The clay sample showed a different release behaviour with the major contribution released during the second step. Which extraction fractions (steps) played an important role depended on the original pH of the soil.
Table 8.3. The leachable of REE and heavy metal fraction released (μg.kg⁻¹) at pH=7 and 4 and acid consumption (mmol/16g), including Sc and Y.

<table>
<thead>
<tr>
<th></th>
<th>Sandy-clay</th>
<th>Clay</th>
<th>Peaty soil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>step1 (pH=7)</td>
<td>step2 (pH=4)</td>
<td>Σstep (1+2)</td>
</tr>
<tr>
<td>HNO₃ (mmol)</td>
<td>0</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Cu</td>
<td>189</td>
<td>59</td>
<td>247</td>
</tr>
<tr>
<td>Zn</td>
<td>693</td>
<td>2267</td>
<td>2960</td>
</tr>
<tr>
<td>Pb</td>
<td>214</td>
<td>119</td>
<td>333</td>
</tr>
<tr>
<td>Sc</td>
<td>5.4</td>
<td>0.71</td>
<td>6.1</td>
</tr>
<tr>
<td>La</td>
<td>13.3</td>
<td>2.7</td>
<td>16.1</td>
</tr>
<tr>
<td>Ce</td>
<td>23.2</td>
<td>5.9</td>
<td>29.1</td>
</tr>
<tr>
<td>Pr</td>
<td>2.4</td>
<td>0.47</td>
<td>2.9</td>
</tr>
<tr>
<td>Nd</td>
<td>10.4</td>
<td>3.1</td>
<td>13.5</td>
</tr>
<tr>
<td>Sm</td>
<td>2.1</td>
<td>0.29</td>
<td>2.4</td>
</tr>
<tr>
<td>Eu</td>
<td>0.55</td>
<td>0.30</td>
<td>0.85</td>
</tr>
<tr>
<td>Gd</td>
<td>2.2</td>
<td>0.25</td>
<td>2.4</td>
</tr>
<tr>
<td>Tb</td>
<td>0.33</td>
<td>0.05</td>
<td>0.38</td>
</tr>
<tr>
<td>Dy</td>
<td>0.17</td>
<td>0.01</td>
<td>0.18</td>
</tr>
<tr>
<td>Ho</td>
<td>0.36</td>
<td>0.08</td>
<td>0.44</td>
</tr>
<tr>
<td>Er</td>
<td>1.11</td>
<td>0.32</td>
<td>1.4</td>
</tr>
<tr>
<td>Tm</td>
<td>0.14</td>
<td>0.01</td>
<td>0.16</td>
</tr>
<tr>
<td>Yb</td>
<td>1.1</td>
<td>0.29</td>
<td>1.4</td>
</tr>
<tr>
<td>Lu</td>
<td>0.17</td>
<td>0.02</td>
<td>0.19</td>
</tr>
<tr>
<td>Y</td>
<td>12.1</td>
<td>3.9</td>
<td>15.9</td>
</tr>
<tr>
<td>REEs</td>
<td>75.1</td>
<td>18.4</td>
<td>93.5</td>
</tr>
<tr>
<td>LREEs</td>
<td>56.9</td>
<td>13.2</td>
<td>70.1</td>
</tr>
<tr>
<td>HREEs</td>
<td>18.2</td>
<td>5.2</td>
<td>23.4</td>
</tr>
</tbody>
</table>
The behaviour of REEs and heavy metals in sandy and peaty soils was similar. About 75% of REEs of the C_MR could be extracted in the step1 for the sandy, clay and peaty soils, respectively. Thus, the water-soluble fraction of REEs may be the main source of REEs. A significant difference was observed for Zn; only about 25% of C_MR became available in a neutral solution. Cu and Pb behaved in a similar manner to the REEs with respect to the pH sensitivity of their release.
Chapter 8. Leaching Behaviour of REEs in Dutch Soil

![Graph showing LREEs/HREEs ratios in CTOT and CMR.](image)

**Figure 8.4.** LREEs/HREEs ratios in CTOT and CMR.

![Graph showing distribution of CMR in first and second extractions.](image)

**Figure 8.5.** Distribution of CMR in the first and second extractions (step 1: pH=7, and step 2: pH=4).

8.4.3. REEs and heavy metals leaching in column tests

(i) Variation of pH and conductivity in leachates

The pH and conductivity in leachate was measured as a function of throughput (*Figure 8.6.* and *Figure 8.7.*); throughput was expressed in terms of liquid to solid ratio (L/S). No significant variation of pH was observed in the leachate of the clay and peaty soils (*Figure 8.6.*). A slight pH increase was observed in initial leachate from the sandy soil after which the pH decreased, slightly by the end of the test.
Conductivity fluctuated considerably (Figure 8.7.). The conductivity of leachate of the peaty soil column was higher than those of sandy-clay soil and clay soil. The results are in good agreement with the results of the availability tests. Conductivity decreased as the \( \ln[L/S] \) increased. When \( \ln [L/S] > 0.6 \) (i.e. \( L/S > 2 \)), conductivity showed only minor fluctuation since most soluble minerals in the column had been leached out. Conductivity fluctuation in the leachate of both sandy-clay soil and peaty soil columns were quite similar.

**Figure 8.6.** pH in leachate of column leaching tests as a function of throughput (L/S is the Liquid to Solid ratio).

**Figure 8.7.** Conductivity in leachate of column leaching tests as a function of throughput (L/S is the Liquid to Solid ratio).
(ii) Behaviour of REEs and heavy metals in the column leaching tests

Figure 8.8(a)-(h) shows typical curves for leachate concentration as a function of the $\ln [L/S]$ for dynamic tests. The following behaviour was observed:

(a) A peak was observed in the REE concentration in the column leachate. Sandy-clay and peaty soils showed sharper peaks than clay soil. This phenomenon can be explained by the pH of the soil. A lower pH (5.0 and 4.75) existed in sandy-clay and peaty soils. After the acidic leachant (pH=4 solution) neutralised the excess alkalinity, the pH in the column dropped comparatively fast and the elements were desorbed. In the clay soil, where a pH of 7.33 existed, the acidic leachant could not completely neutralise the excess alkalinity, causing delayed desorption. The concentration of REEs in the leachate seemed to be controlled by the original soil pH. On the other hand, the depletion of major components (such as Ca, Al, Fe and organic matter) of the soil may also have contributed to the peak REE concentration.

(b) REEs were leached more rapidly from sandy-clay soil than from peaty soils. The acidic buffering capacity may play an important role in soil leaching where the original pH of the soil was similar. The acidic buffering capacity of peaty soil (0.216 mol.kg$^{-1}$) was higher than that of sandy-clay soil (0.031 mol.kg$^{-1}$), therefore, a peak REE concentration was observed with sandy-clay soil prior to peaty soil. At L/S=0.5 and L/S=5, a peak REE concentration was observed in the leachates of sandy-clay and peaty soils, respectively. The peak concentration of REEs released was less than 35 $\mu$g.kg$^{-1}$ (ppb) in all tests. However, there are many areas in The Netherlands consisting largely of sandy soils with low clay content and a low buffering capacity. More attention needs to be paid to the leaching of sandy soil.

(c) REEs and heavy metals showed a different leaching behaviour. Individual REE showed a similar leaching behaviour (except Sc) in all the tests. But Pb, Cu, and Zn (in clay soil), Cu and Zn (in peaty soil) and Zn (in sandy-clay soil) had a different response than REEs in the leaching tests. It was reported that Zn is relatively mobile at pH< 6.6 and moderately mobile at pH<8.8, which Cu an Pb are moderately mobile at pH > 4.2 (Herbert and Sticher, 1989).
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Figure 8.8.(a-h). Concentration of REEs, LREEs, HREEs and heavy metals in the leachates vs. L/S.
The leachability of REEs in the column leaching tests was different compared with the earlier availability tests. A comparison of the $C_{TOT}$ (see availability test paragraph), $C_{MR}$ and the cumulative released $C_{CR}$ in the column tests is presented in Table 8.4. It was found that only about 0.1%, 0.067% and 0.2% of total original content of REEs can be released in the sandy-clay, clay and peaty soils, respectively. HREEs show a higher leachability than that of LREEs. It was also found that less than 2% of Cu, Zn and Pb were released in the leaching tests. But heavy metals were more easily released to the environment in comparison to REEs. During the dynamic column tests, about 20%-60% of the maximally available amount of REEs ($C_{MR}$) could be leached at $L/S = 10$.

Table 8.4. Total concentration ($C_{TOT}$), maximum released ($C_{MR}$) and cumulative released ($C_{CR}$) in the column leaching tests (including Sc and Y).

<table>
<thead>
<tr>
<th></th>
<th>$C_{CR}$ (as % of $C_{TOT}$)</th>
<th></th>
<th>$C_{CR}$ (as % of $C_{MR}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sandy Clay Peaty oil</td>
<td>Sandy Clay Peaty soil</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>1.69 0.387 0.48</td>
<td>56.7 30.9 32.5</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>1.46 0.188 0.57</td>
<td>6.6 2.6 11.7</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.32 0.070 0.08</td>
<td>21.6 81.6 21.6</td>
<td></td>
</tr>
<tr>
<td>REEs</td>
<td>0.10 0.057 0.16</td>
<td>54.6 24.6 60.1</td>
<td></td>
</tr>
<tr>
<td>LREEs</td>
<td>0.08 0.060 0.13</td>
<td>53.5 29.8 59.0</td>
<td></td>
</tr>
<tr>
<td>HREEs</td>
<td>0.19 0.042 0.30</td>
<td>57.8 10.2 62.7</td>
<td></td>
</tr>
</tbody>
</table>

8.5. Conclusions

The availability tests indicated that the maximum equivalent concentration of REE that could be released ($C_{MR}$) was less than 0.8% of total REE content in sandy clay, clay or peaty soil. Heavy REEs leached to a greater extent than light REEs at $pH \approx 4$. Heavy metals exhibited a higher release capacity compared with REEs (maximum release capacity of Zn was 22% of the total Zn concentration).

The dynamic column experiments on leaching behaviour of REEs as a function of simulated acidic rain was not similar to the availability tests. The REE cumulative
concentration released (CCR) ranged from 20% to 60% of the C_{MR}. The maximum released concentration of REEs was less than 35 \mu g.kg^{-1} (ppb) in all the tests.

The acidic buffering capacity and the pH of the original soil origin played an important role in leaching. REEs are more easily leached out of soil with acidity and low buffering capacity, such as sandy-clay soil. However, the bioavailable amounts are likely to be very limited.

References


Chapter 9

General Conclusions and Recommendations

9.1. Analytical aspects

A mathematical procedure and an ion-exchange preconcentration technique were employed in this work to reduce the effects of spectral interferences and to improve the detection limits in the determination of REEs by inductively coupled plasma mass spectrometry (ICP-MS). In Chapters 2, 3 and 4, improvement of the accuracy, and precision and detection limits of the analytical technique with respect to the determination of REEs in environmental samples are emphasized.

One of the major problems in the simultaneous determination of all REE’s with ICP-MS is that many spectral interferences from light REE oxides and hydroxides are possible in the determination of the heavy REE, while the determination of the light REE is hampered by interferences from isobaric ions and barium oxides and hydroxides. Since the concentration of the low mass REE is typically 10-100 times higher than the concentration of the high mass REE, the interfering signal from a low mass REE oxide may be up to two times higher than the signal from a high mass REE. A partial least-squares regression (PLSR) model for REE analysis with ICP-MS was developed, which provided a convenient method to correct interferences from REE oxides, hydroxides and isobaric spectral overlap. REE concentrations could be accurately measured despite barium interferences, even in samples with high ratios of Ba/REE, when the weights of certain isotopes in the model were set below 0.1. Accuracy was demonstrated by analysing several certified reference materials from different soils and sediments. The measured values differed not more than 5% from the certified values. The precision of the PLSR model was satisfactory (RSD <5%) for the measurement of REE concentrations in different reference materials and environmental matrices i.e. soil, sediment, sludge, fresh water and seawater, even in samples where high ratios of Ba/REEs and salt/REEs existed.
A relatively simple method for the preconcentration of REEs in aqueous samples, with a micro ion-exchange column and subsequent determination by ICP-MS, was developed for concentrations in the ng/L and pg/L range and for ionic strengths up to 0.18. The results indicated that the average recovery was approximately 95%, while the RSD ranged from 3 to 7%. The detection limits ranged from 0.03 to 0.40 ng.l\(^{-1}\), for a preconcentration factor of 100.

The ICP-MS analysis in combination with the PLSR model and the ion exchange preconcentration method offers a fast multi-element analysis technique with high precision and accuracy and detection limits below 1 ng/L. Satisfactory results were achieved when these methods were applied for the determination of REEs in water, soil, sediment and air as well as in other environmental samples. The use of both the PLSR model and ion exchange preconcentration allowed detailed analysis of REEs in samples from selected compartments of the environment (Chapters 5, 6, 7 and 8).

### 9.2. Environmental aspects

REE occurrence in the environment was studied by measuring REE levels in river sediments, soils and air particulate matter in several areas in The Netherlands and China. The distribution of light and heavy REE in the Yangtze river was described as a function of the distance from the Three Gorges to Nanjing and the variation in REE crust-normalised ratios was discussed. The transport of REE in air through air particulate matter as a function of wind direction was studied in Delft - The Netherlands with the intention to obtain information on the emission of REE from industry and traffic. The high concentrations of REE in ground water as found in The Netherlands (Stuyfzand, 1991 and 1992 and De Boer et al., 1996) prompted us to investigate the REE concentration in Dutch and Chinese soils and the possibility of REEs leaching from soil into ground water under the influence of acid rain.

For the reconnaissance of REE emission sources in air, it was found that the variation of REE concentrations in air was strongly dependent on the wind direction with respect to the emission source. The REE concentrations in Delft ranged from 0.22 to 33.0 ng/m\(^3\) in air. The La to Ce and the La to Sm ratio varied considerably with the direction of the wind and could be used as tracers for the REE source. Suspended soil particles are the major source for the background concentration of REE in air. However, traffic was an important source of Ce and Nd due to the widespread use of three-way catalysts in automobiles and industry from the Rijnmond area was a source for La.
Factor analysis indicated that REE concentrations in Chinese sediments were mainly described by two factors. Factor score plots and crust-normalised ratios could be employed to identify anomalous sediment samples (element depletion or enrichment). Based on the inter-correlation of REEs in sediment samples, a data-base estimation method was applied for the estimation of individual REE concentrations in sediment samples reported in literature, and good agreement between literature and calculated values was found. In general, Chinese river sediments showed depletion of heavy REEs except for Gd for which element a strong enrichment was found. No significant variation in the average REE sediment concentration was found. Any variation in REE sediment concentration in individual samples was believed to be caused by the different geological origin of the samples or REE adsorption onto different fractions of the sediment.

Large differences in the concentrations of individual REEs were found in Guangdong soils. These soils were depleted with respect to heavy REEs, but the ratios and concentrations of light REEs were comparable to those in the earth’s crust. Higher crust-normalised ratios were observed for Ce and Dy. However, these geological anomalies are believed to be typical for the soils in this region. The Dutch soils also showed slight depletion with respect to the heavy REEs but no enrichment or depletion was observed for the light REEs. In Dutch soil samples taken from a particular site enrichment of most REEs was found, especially Gd, Nd, Dy and Ce. However, soils near a major highway revealed no significant difference.

Zhang et al. (1996) described the binding of REE to Chinese soils and distinguished five forms for all the REEs. In order of importance they are described as residual >> bound to organic matter > bound to Fe-Mn oxides > bound to carbonates >> exchangeable and water soluble. The exchangeable and water soluble fraction in Chinese soils was found in this thesis to be approximately ten times larger than in Dutch soils. Possibly this difference can be explained by the different sample characteristics and geological origin.

Availability tests and column leaching tests indicated that the maximum amount of REEs released was less than 0.8% of the total REE content of the soil samples. Heavy metals, on the other hand, showed a higher release capacity in comparison to REEs. The acidic buffering capacity and the original pH of the soil played an important role in leaching. It seems that REE leaching is unlikely to influence groundwater quality in areas with alkaline soil or soil with a high acid buffering capacity. However, more attention should be given to acidic sandy soil as the leaching potential is higher for this soil type.

In conclusion, in addition to geological processes, REEs are sometimes noticeably disseminated in different environmental compartments (air, water and soil) typically as a
by-product of industrial activity (fuel production and use, agriculture, etc.) and acid rain leaching.

Figure 9.1. reviews the emission sources, pathways and “sinks” of the REEs. It is partly based on the results of this research, which explored (i) selected critical deposition pathways, (ii) the role of soil, sludge and river sediment as sinks, and (iii) the extent to which REEs (and heavy metals) can be leached from various types of soils. Further insights were obtained from literature. Soil and other solid surfaces (sludge and sediment) seem to act as more effective concentration sinks for REEs than for heavy metals, thus removing REEs from the water phase. REEs are much more difficult to leach from soil, than heavy metals. This suggests that in many instances REEs are less likely than heavy metals to enter the food chain and pose a danger to public health.

9.3. Recommendations

To further improve REE analytical capacity high resolution-ICP-MS as well as sample laser ablation should be further developed and applied. A comparison study of ICP-MS on the one hand, and NAA and IDMS could give a better insight into the accuracy of ICP-MS based techniques.

Better preconcentration methods should be developed. On-line ion chromatography-ICP-MS is suggested for this purpose. More systematic studies after the effects of sample destruction methods will also contribute to more consistent analysis results.

With respect to REE environmental aspects, the following priority issues are recommended for further investigation:

- To quantify more precisely the emission of REEs into the environment, more samples from representative point and non-point sources should be collected. An REE environmental database should be set up.
- To further investigate REE leaching properties, more fundamental research should be carried out, e.g. by using a broader set of soil types in column leaching tests, studying the effect of humic acid and clay content on the leaching, etc. It is also important to quantify the degree to which soils and sediments act as “absolute” sink for REEs. If solids act as “absolute” sinks, then REEs are probably available for biological uptake in very small amounts only.
- The distribution and bioavailability of REE in soil and sediment samples as a function of particle size should be studied, in order to get a better insight in the transport behaviour of REE.
- To derive environmental quality standards based on further study of REE toxicology and eco-toxicology.
Figure 9.1. Key emission sources, pathways of distribution, and sinks in the environment, for REEs.
References


Summary

The Rare Earth Elements (REEs), (La..Lu), Y and Sc, show similarities in chemical behavior. They find increasing application in industry, and are also applied in agriculture. Their name is misleading, since they were formed in huge quantities during nucleosynthesis in the universe system. Ever since then, their similarity made them stay mostly together, and the ratios of their individual concentrations in for instance soil samples still largely reflect their primary ratios. However, due to geological, biological and industrial processes and mining not only their total concentrations differ, but the individual element ratios often exhibit strong deviations from their primary ratios. Knowing not only total REE concentrations, but also these deviations is the key to understanding these processes, and is also necessary to assess for instance the environmental effects of REEs.

The fractionation of the REEs can only be determined when analytical tools are available which are fast, cheap, reliable and sensitive as well as provide individual element concentration data, and are suitable for the relevant sample types (soil, airborne particles, (sea) water). For control of industrial separation and purification of REEs, such analytical tools are also required. Among the techniques available, inductively coupled plasma mass spectrometry (ICP-MS) is an excellent candidate provided that certain drawbacks are minimized. Among these are spectral overlap, matrix effects and too high detection limits.

The aim of this work was to develop auxiliary techniques to overcome some of the current major drawbacks, and to investigate whether the improved ICP-MS allows conclusions to be drawn on REE fractionation in environmental samples.

Chapter 1 of the thesis gives an introduction to the chemical and physical properties of REEs, their abundance, industrial and agricultural application, environmental behaviour, and in particular, the analytical technique (ICP-MS) which is used for REE analysis. A literature study indicated that information on REE behaviour in the environment is limited, due to the lack of knowledge on the effects of REEs on human health and sensitive analytical techniques to estimate trace levels of these elements.
Chapter 2 describes a new auxiliary technique which corrects interferences from REE oxides, hydroxides and isobaric spectral overlap by a dedicated partial least-squares regression (PLSR) model. The model parameters were optimized and the oxide / hydroxide / isobaric interferences were almost completely removed. Nd, Sm, Gd, Dy and Yb played a more significant role in the model compared to the other rare earth elements because they possess multiple isotopes which require repeated calibration. REE concentrations could be accurately determined despite barium interference, even in samples with high ratios of Ba/REE, when the weights of certain isotopes in the model were set below 0.1.

In Chapter 3, the PLSR model was tested on real environmental samples i.e. soil, sediment, water, etc. Interferences from REE oxides and hydroxides were estimated to be 1% and 0.1% respectively by the model. The accuracy and precision of the PLSR model was satisfactory (RSD<5%) for the calculation of REE concentrations in different reference materials and environmental samples i.e. soil, sediment, sludge and seawater, even in samples where high ratios of Ba/REEs and salt/REEs existed. The detection limit ranged from 14 to 34 ng.l⁻¹.

Chapter 4, describes an auxiliary technique for the preconcentration of ultratrace rare earth elements (REEs) in environmental samples with a micro ion-exchange column. The REE recovery was 94-98% in the pH range 4 to 6 with an ionic strength less than 0.18. The ion-exchange column capacity with respect to REEs was 0.96 mmol/g. The linear response coefficients ranged from 0.995 to 0.997 at the ng.l⁻¹ level. The detection limits ranged from 0.03 to 0.40 ng.l⁻¹, for a preconcentration factor of 100. The precision and accuracy of the method was evaluated on real samples by spiking experiments with synthetic standard solutions. Results indicated that the REE recovery ranged from 88.1% to 100.2% and the RSD from 2.7% to 6.7 % for tap water.

In Chapter 5, distributions of REEs in the sediment are given. The total REEs, light-REEs (LREEs), heavy-REEs (HREEs) concentrations and the ratio of LREEs to HREEs ranged from 45 to 315, 38 to 265, 6.4 to 51 (mg.kg⁻¹) and 5.2 to 14.4, respectively in Chinese river sediment. The samples showed HREE depletion. Strong Gd enrichment was found in the sediment. No significant variation in average REE sediment concentration was found. Variation in REE sediment concentration in individual samples may have been caused by the different geological origin of the sample, or REE adsorption onto different fractions of the sediment. Factor analysis indicated that REE concentrations in sediments were mainly described by two factors. Factor score plots could be employed to identify anomalous sediment samples (element depletion or enrichment).
In Chapter 6, distributions of REEs in air particulate matter (APM) are described. The total REE (REEs) concentration, light-REE (LREEs) concentration, and heavy-REE (HREEs) concentration was 0.22-33; 0.21-31; and 0.01-2.32 ng/m$^3$, respectively. The ratio of LREEs to HREEs ranged from 6.4 to 33.6; The La to Ce, and La to Sm ratio varied considerably i.e. 0.5-4.4 and 4.3-71 respectively, and could be used as a tracer for the source of REEs. The variation in concentration observed depended upon the wind direction and consequently on prevailing meteorological conditions and anthropogenic activity.

In Chapter 7, randomly collected soil samples from Guangdong Province (China) and selected samples from The Netherlands were analysed for REEs. Guangdong soils had large differences in the concentrations per individual REE. These soils were depleted with respect to heavy REEs, but the ratios and concentrations of light REEs were comparable to those in the earth’s crust. Higher sample to crust ratios were observed for Ce and Dy, however, these geological anomalies are believed to be typical for the soils in this region. The Dutch soils had a slight depletion for the heavy REEs but no enrichment or depletion was observed for the light REEs. The soluble REE fraction ranged 0.7 – 15.6% of the total REE concentration. Heavy REEs were easier to extract. In both countries the concentrations for the individual elements could vary 20 – 250% among the samples. In Dutch soil samples taken from a site where sludge was known to have been dumped, enrichment of most REEs was found, especially of Gd, Nd, Dy and Ce.

In Chapter 8, three different types of Dutch soil (sandy clay, clay and peaty soils) were subjected to batch and column leaching tests. The amount of REE available for leaching (expressed as $C_{MR}$) was always less than 0.8% of the total concentration in the soil. Heavy REEs leached at pH $\approx$ 4 to a greater extent than light REEs. Individual REEs showed a similar behaviour in the soil leaching (except Sc). Heavy metals showed a larger release capacity than REEs. The acid buffering capacity and the original pH of the soil played an important role in the leachability.

Chapter 9 summarises and discusses the main conclusions and recommendations.
Publications resulting from this work


Acknowledgement

The work presented in this thesis was carried out at The Netherlands Organization for Applied Scientific Research (TNO), in Delft (IMW) and Apeldoorn (MEP-TNO).

This thesis could not have been realized without the help of many people. Firstly, I want to thank Dr. Ed de Leer (NMI) and Dr. Maria Kennedy (IHE) for their constant guidance, support, optimism and encouragement throughout this work.

Secondly, I would like to thank the staff and management of the Laboratory for Process Equipment (API), Technical University of Delft for their strong support and contribution in the later stages of my thesis.

My special thanks go to Prof. Jeroen de Goeij (TUD), who despite being involved only as a committee member in the very last stage and for a very brief period, managed to help to significantly improve the thesis with his valuable suggestions and discussions.

Prof. Wim Harder, Dr. Rob Guicherit, Drs. Ron Bosman, Dr. Michel van Son, Ir. Evert Mulder, Ing. Jan Timmner and Ing. Jaap Spijk are acknowledged for their technical guidance and support before and after the reorganization of MEP-TNO. Technical assistance is also acknowledged from Ing. Edith de Haan, Ing. John Stigter, Ing. Elly Stofberg, Ing. Renze Zijlstra and Ing. Marc Houtzager. Finally, Mrs. Flora Utomo is also acknowledged for her kindness during my work in the Department of Analytical Chemistry, MEP-TNO. Sincere thanks also goes to Drs. Pierre del Castilho (AB-DLO) for his help and technical advice.

Sincere thanks is also extended to all the staff of IHE, who have helped and encouraged me throughout my study period in IHE. In particular, Dr. Peter Kelderman, Drs. Ton Jacobs, Ir. Jan Herman Koster and Dr. Henk Lubberding for their encouragement and technical advice throughout. Special thanks are also extended to Ms. Wendy Sturrok for all her help with the English language.

Prof. Guangtao Zhong, Zhongshan University, China and Prof. Huaidong Zhou of
Water Quality Research Center of China (WQRCC) are acknowledged for their help in collecting the environmental samples in various parts of China. Dr. Cunxia Wang, Chinese Academy of Science (CAS) is acknowledged for her contribution to Chapter 6 of this thesis.

I am also grateful to Fransje de Meijere, Sandra Mohlmann and Rik Wolff from TNO, who helped to collect technical information and to Ing. Alex van Renesse van Duivenbode for his computer support during this research.

I owe many thanks to Prof. Gerda van Rosmalen, Drs. Paul Althuis and Ir. Cees Timmers from Technical University of Delft, for their support and encouragement in the later stages of this work.

These acknowledgments would not be complete without expressing my appreciation to MEP-TNO and API-TUD for providing a first class working environment, and to all my friends and colleagues from these two institutions.

Last but not least, I thank my wife, Yanling, for her love, support, understanding, and endless patience over these years.
Biography

Wangzhao Zhu was born in Fujian, China in 1963. He received his B.Sc. in Analytical Chemistry from Fuzhou University, China, in 1983. From September 1983 to November 1984, he worked as an assistant engineer on the field of environmental impact assessment in the Beijing Institute of Hydroelectric Investigation and Design, Ministry of Water Resources and Electronic Power, China. From November 1984 to August 1989, he worked at the Water Quality Research Center of China, the Ministry of Water Resources, Beijing, as an engineer on analytical and environmental chemistry. From August 1989 to October 1990, he assisted in co-ordinating, policy making and planning in the National Water Resources and Soil Conservation Office in Beijing, China.


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