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Maximum Permissible Concentrations and Negligible Concentrations for Rare Earth Elements (REEs)

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Abstract

In this report maximum permissible concentrations (MPCs) and negligible concentrations (NCs) are derived for Rare Earth Elements (REEs), which are also known as lanthanides. The REEs selected for derivation of environmental risk limits in this report are Yttrium (Y), Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), Samarium (Sm), Gadolinium (Gd), and Dysprosium (Dy). Since REEs are natural compounds, the added risk approach is used to derive MPC values. The total amount of toxicity studies for freshwater and saltwater organisms to base the MPA upon is limited, often an assessment factor of 1000 had to be used. Background concentrations were derived from data on environmental occurence in relative pristine areas, a limited data-set was available for this end. For surface waters, environmental concentrations were below detection limits and the detection limits were taken as background concentrations. For fresh surface water, the derived MPCs range from 1.8 µg/L for Nd to 22.1 µg/L for Ce. For salt surface water the derived MPCs are much lower, from 0.28 µg/L for Ce to 3.8 µg/L for Dy. MPC values for fresh water sediments are also higher than those for salt water sediments. Dutch water and sediment concentrations do not exceed the MPCs of the different REEs. Occasionally, environmental concentrations of REEs exceed the NC-levels.

Preface

Thanks are due to dr. M. van der Weiden, who was contact person at the ministry of housing, spatial planning and the environment (VROM-DGM/SVS), and to dr. D. Sijm who co-ordinates the project 'Setting Integrated Environmental Quality Standards' at the National Institute of Public Health and the Environment.

The results as presented in this report are discussed by the members of the 'Setting Integrated Environmental Quality Standards Advisory Group', who are acknowledged for their contribution. The members are drs. J. Appelman (The Board for the Authorization of Pesticides), dr. T. Brock (Institute for Forestry and Nature Research), dr. T. Crommentuijn (Ministry of Housing, Spatial Planning and the Environment), drs. S. Dogger (Health Council of the Netherlands), dr. J. Faber (Institute for Forestry and Nature Research), dr. K. den Haan (Shell International Chemical BV), drs. J. Pijnenburg (National Institute for Coastal and Marine Management), drs. M. Koene (Foundation for Nature and Environment), dr. D. Sijm (National Institute of Public Health and the Environment), dr. E. Sneller (National Institute of Inland Water Management and Waste Water Treatment), dr. J. Struijs (National Institute of Public Health and the Environment), dr. W. van Tilborg (VTBC), dr. M. van der Weiden (Ministry of Housing, Spatial Planning and the Environment), and dr. J. van Wensem (Technical Soil Protection Committee).

Contents

Samenvatting

In dit rapport worden maximaal toelaatbare risiconiveaus (MTR) afgeleid voor zeldzame aardmetalen (ZAM), ook wel bekend als lanthaniden. MTRs worden afgeleid met gebruik van ecotoxicologische en milieuchemische data, en representeren het potentiële risico van stoffen voor een ecosysteem. Het verwaarloosbaar risiconiveau (VR) wordt afgeleid door het MTR door een factor 100 te delen. De ZAMs die zijn geselecteerd om een MTR voor af te leiden zijn Yttrium (Y), Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), Samarium (Sm), Gadolinium (Gd), en Dysprosium (Dy). Deze selectie is gebaseerd op het relatieve voorkomen in het milieu en de beschikbaarheid van toxiciteitsdata.

Omdat ZAMs van nature voorkomende stoffen zijn, is de toegevoegd risico benadering (Crommentuijn et al., 1997a) gevolgd om tot een MTR te komen. Hierbij is het MTR de som van de maximaal toelaatbare toevoeging (MTT), welke berekend wordt uit de beschikbare toxiciteitsdata, en de achtergrondconcentratie. Voor herberekening van bodemconcentraties van ZAMs naar een 'standaardbodem' met vaststaande percentages lutum en organisch koolstof, zijn tot noch toe geen vergelijkingen ontwikkeld. Uitgebreide data-sets zouden nodig zijn voor deze ontwikkeling, en deze zijn voor de Nederlandse situatie nog niet beschikbaar.

Het totale aantal toxiciteitstudies voor zoet- en zoutwater organismen dat beschikbaar is om een MTT op te baseren is beperkt. Vanwege de lage oplosbaarheidproducten van ZAM -carbonaten, -fosfaten en -fluoriden, is het uitvoeren van toxiciteitstudies moeilijk. Neerslagen ontwikkelen zich voor en tijdens het testen, en initiële concentraties kunnen dalen tot minder dan één tiende binnen 24 uur. Daarom worden slechts die testen waarin gemeten concentraties zijn weergegeven geschikt geacht als basis voor risicobeoordeling.

Om de MTTs voor zoet en zout water af te leiden (Tabel I), was vaak een assessment factor van 1000 benodigd. Hoewel het aantal gegevens klein is, lijken mariene organismen gevoeliger voor ZAMs dan zoetwater organismen. Voor andere ZAMs dan weergegeven in de Tabellen I en II, waren geen data beschikbaar om een MTR op te baseren. Gezien het werkingsmechanisme van de ZAMs, verwachten we dat de concentraties die gerelateerd zijn aan ecotoxicologische effecten voor de andere ZAMs in dezelfde orde van grootte liggen.

Omdat toxiciteitsdata voor bodem- en sediment- organismen ontbreken, zijn MTTs voor bodem en sediment afgeleid met gebruik van de equilibrium partitie theorie. Hiervoor werden bodem/water en sediment/poriewater partitie-coëfficiënten gebruikt die zijn afgeleid uit velddata (Tabel 4.2.).

Om de mogelijkheid van doorvergiftiging van de ZAMs in de voedselketen in te schatten, werden gegevens over bioaccumulatiefactoren verzameld. Het aantal gegevens is beperkt, en dikwijls tegenstrijdig. Dit rapport gaat niet verder in op de toxiciteit vanwege doorvergiftiging.

De achtergrondconcentratie van bodem en sediment is gedefinieerd als de 90^{th}-percentielwaarde van de concentraties in relatief onbelaste gebieden. Concentraties in zoet oppervlaktewater liggen beneden de detectielimiet. Detectie-limieten van de ZAMs zijn

genomen als achtergrondconcentratie voor zowel zoet als zout oppervlaktewater, tenzij een tweede studie andere gemeten concentraties voor zout oppervlaktewater rapporteerde. De werkelijke achtergrondconcentraties kunnen lager zijn dan de detectielimiet, wat een lagere MTR tot gevolg zou hebben. Omdat analytisch-chemische technieken gevoeliger zullen zijn geworden sinds het begin van de vroege jaren negentig toen de metingen zijn uitgevoerd, is het aanbevolen nadere metingen te doen naar de achtergrondconcentraties van ZAMs in oppervlaktewater. Gerapporteerde achtergrondconcentratiesn van ZAMs in het grondwater laten een grote spreiding zien. Om deze reden is er geen generieke achtergrondconcentratie voorgesteld voor het compartiment grondwater, en als consequentie hiervan is er ook geen MTR afgeleid voor dit compartiment.

Tabel I geeft de afgeleide MTTs, achtergrondwaarden en resulterende MTRs weer voor oppervlaktewater (opgelost), sediment en bodem. Voor zoet oppervlaktewater ligt de MTR tussen 1,8 µg/l voor Nd en 22,1 µg/l voor Ce. Voor zout oppervlaktewater zijn de afgeleide MTRs veel lager, variërend van 0,28 µg/l voor Ce tot 3,8 µg/l voor Dy. MTRs voor zoete sedimenten liggen eveneens hoger dan voor zoute sedimenten, hoewel de achtergrondconcentraties slechts marginaal hoger liggen voor de zoute sedimenten.
Voor bodem is slechts één partitiecoëfficiënt aanwezig (Ce), waardoor het afleiden van MTRs voor andere ZAMs niet mogelijk is. Tabel II laat de corresponderende VRs zien.
Nederlandse waterconcentraties uit het Rijn-estuarium, waar de grootste emissie plaatsvindt, overschrijden niet de MTRs voor de verschillende ZAMs. Hetzelfde geldt voor de sedimentconcentraties. Af en toe overschrijden de milieuconcentraties het VR. Hoewel er een beperkte databeschikbaarheid is, concluderen we dat de ZAMs niet een acute bedreiging van het Nederlandse ecosysteem opleveren. Echter, de water- en sedimentkwaliteit heeft nog niet overal het gewenste niveau (VR) bereikt.

Tabel I. MTT, achtergrondconcentratie (Cb) en MTR voor oppervlaktewater (opgelost), sediment, en bodem

Element	**oppervlaktewater (µg/L)**						**sediment (g/kg d.s.)**						**bodem (mg/kg d.s.)**		
	zoet			**zout**			**zoet**			**zout**					
	MTT	C*b*	MTR	MTT	C*b*	MTR	MTT	C*b*	MTR	MTT	C*b*	MTR	MTT	C*b*	MTR
Y	6.2	0.22[a]	6.4	0.72	0.22[a]	0.94	1.4	0.017	1.4	0.16	0.019	0.18			
La	10.0	0.08[a]	10.1	1.0	0.012	1.01	4.7	0.039	4.7	0.47	0.044	0.51			
Ce	22.0	0.13[a]	22.1	0.15	0.13[a]	0.28	18.7	0.069	18.8	0.13	0.093	0.22	44	9.0	53
Pr	9	0.08[a]	9.1	0.92	0.08	1.00	5.8	0.008	5.8	0.60	0.011	0.61			
Nd	1.4	0.39[a]	1.8	0.85	0.0092	0.86	7.2	0.036	7.5	0.44	0.040	0.48			
Sm	7.6	0.56[a]	8.2	0.42	0.0005	0.42	2.5	0.006	2.5	0.14	0.008	0.15			
Gd	6.8	0.33[a]	7.1	0.52	0.33[a]	0.85	1.8	0.005	1.8	0.14	0.006	0.14			
Dy	9.1	0.22[a]	9.3	3.6	0.22[a]	3.8	2.2	0.004	2.2	0.88	0.004	0.89			

[a] Detection limit

Tabel II. VR en verwaarloosbare toevoeging (VT) voor oppervlaktewater (opgelost), sediment en bodem

Element	**oppervlakte water (µg/L)**				**sediment (mg/kg d.s.)**				**bodem (mg/kg d.s.)**	
	zoet		**zout**		**zoet**		**zout**			
	VT	**VR**	**VT**	**VR**	**VT**	**VR**	**VT**	**VR**	**VT**	**VR**
Y	0.062	0.28	0.0072	0.22	13.9	30.7	1.61	20.2		
La	0.10	0.18	0.010	0.02	46.8	83.6	4.68	48.8		
Ce	0.22	0.35	0.0015	0.13	187.3	256.2	1.28	93.9	0.440	9.4
Pr	0.09	0.17	0.0092	0.09	58.1	66.1	5.94	16.8		
Nd	0.014	0.40	0.0086	0.009	7.2	43.2	4.36	44.8		
Sm	0.076	0.64	0.0042	0.005	25.2	30.9	1.39	8.9		
Gd	0.068	0.40	0.0052	0.34	17. 9	23.2	1.37	7.1		
Dy	0.091	0.31	0.036	0.26	22.3	26.2	8.84	12.9		

Summary

In this report maximum permissible concentrations (MPCs) are derived for Rare Earth Elements (REEs), which are also known as lanthanides. MPCs are derived using data on (eco)toxicology and environmental chemistry, and represent the potential risk of the substances to ecosystems. Applying a factor of 100 towards the MPCs yields the negligible concentrations (NCs). The REEs selected for derivation of environmental risk limits in this report are Yttrium (Y), Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), Samarium (Sm), Gadolinium (Gd), and Dysprosium (Dy). This selection is based on their relative abundance in the environment and the availability of toxicity data.

Since REEs are natural compounds, the added risk approach (Crommentuijn *et al.*, 1997a) is used to derive MPC values. The MPC for naturally occurring substances is defined as the sum of the maximum permissible addition (MPA), which can be calculated from the available toxicity data, and the background concentration (C*b*). For recalculation of soil concentrations of REEs into a 'standard soil' with set percentages of lutum and organic carbon, no equations have been developed until now. Extensive data-sets would be needed to develop these relationships, which are not available for the Dutch situation yet.

The total amount of toxicity studies for freshwater and saltwater organisms to base the MPA upon is limited. Because of the low solubility products of REE-carbonates, -phosphates and -fluorides, assaying of toxicity is very hard. Precipitates develop before and during testing, and initial concentrations can drop to <10 % within 24 hours. Only tests in which measured concentrations are reported are therefore considered suitable for risk assessment purposes.

To derive MPAs for fresh and saltwater (Table I), often an assessment factor of 1000 had to be used. Although the number of data is small, marine organisms appear more sensitive to REEs than freshwater organisms. For other REEs than shown in Tables I and II, no toxicity data are available to base an MPA upon. However, in view of the mechanism of action of the REEs, we expect that concentrations related to ecotoxicological risks for the other REEs will be in the same order of magnitude.

Since toxicity data for soil or sediment dwelling organisms lack, MPAs for soil and sediment are derived using equilibrium partitioning. For this purpose, field-derived partition coefficients were preferred over lab-derived partition coefficients (Table 4.2.). The MPA-values based on sediment-porewater partitioning are used in the derivation of MPCs.

To assess the possibility of secondary poisoning by REEs, data on bioaccumulation factors (BCFs) for REEs were collected. They appeared to be limited, and often contradictory. No studies on the toxicity due to secondary poisoning are included in the present report.

C*b* for soil and sediment is defined as the 90th-percentile value of the concentrations in relatively pristine areas. Concentrations in fresh surface water are below the detection limit. Detection-limits of the REEs are taken as background level for fresh surface water and salt surface water, unless a second study reported other measured concentrations for salt surface water. In reality, background concentrations might be lower than the detection limit, which would also result in a lower MPC. As analytical techniques have become more sensitive since the early nineties, it is recommended to do additional measurements on background

proposed for the compartment groundwater and as a consequence no MPC is derived for this compartment.

Table I lists the derived MPAs, C*b*s and resulting MPC for surface water (dissolved), sediment, and soil. For fresh surface water, the derived MPCs range from 1.8 µg/L for Nd to 22.1 µg/L for Ce. For salt surface water the derived MPCs are much lower, from 0.28 µg/L for Ce to 3.8 µg/L for Dy. MPC values for fresh water sediments are also higher than those for salt water sediments, whereas *Cb*s for salt water are only marginally higher for salt water sediments. For soil, only one K*p* was available (Ce), making derivation of MPC values for other REES impossible. Table II shows the corresponding NCs.
Dutch water concentrations, occurring in the Rhine estuary where is the highest emission, do not exceed the MPCs of the different REEs. The same holds for sediment concentrations of REEs. Occasionally, environmental concentrations of REEs exceed the NC-levels. Therefore, although the data are scarce, we conclude that REEs do not pose an acute threat to the Dutch ecosystem. However, water and sediment quality has not as yet reached the desired level (NC).

Table I. MPA, Cb and MPC for surface water (dissolved), sediment, and soil

Element	**surface water (µg/L)**						**sediment (g/kg d.w.)**						**soil (mg/kg d.w.)**		
	fresh			**salt**			**fresh**			**salt**					
	MPA	**C*b***	**MPC**	**MPA**	**C*b***	**MPC**	**MPA**	**C*b***	**MPC**	**MPA**	**C*b***	**MPC**	**MPA**	**C*b***	**MPC**
Y	6.2	0.22[a]	6.4	0.72	0.22[a]	0.94	1.4	0.017	1.4	0.16	0.019	0.18			
La	10.0	0.08[a]	10.1	1.0	0.010	1.01	4.7	0.039	4.7	0.47	0.044	0.51			
Ce	22.0	0.13[a]	22.1	0.15	0.13[a]	0.28	18.7	0.069	18.8	0.13	0.093	0.22	44	9.0	53
Pr	9	0.08[a]	9.1	0.92	0.08[a]	1.00	5.8	0.008	5.8	0.60	0.011	0.61			
Nd	1.4	0.39[a]	1.8	0.85	0.0092	0.86	7.2	0.036	7.5	0.44	0.040	0.48			
Sm	7.6	0.56[a]	8.2	0.42	0.0005	0.42	2.5	0.006	2.5	0.14	0.008	0.15			
Gd	6.8	0.33[a]	7.1	0.52	0.33[a]	0.85	1.8	0.005	1.8	0.14	0.006	0.14			
Dy	9.1	0.22[a]	9.3	3.6	0.22[a]	3.8	2.2	0.004	2.2	0.88	0.004	0.89			

[a] Detection limit

Table II. NA and NC for surface water (dissolved), sediment, and soil

Element	**surface water (µg/L)**				**sediment (mg/kg d.w.)**				**soil (mg/kg d.w.)**	
	fresh		**salt**		**fresh**		**salt**			
	NA	**NC**	**NA**	**NC**	**NA**	**NC**	**NA**	**NC**	**NA**	**NC**
Y	0.062	0.28	0.0072	0.22	13.9	30.7	1.61	20.2		
La	0.10	0.18	0.010	0.02	46.8	83.6	4.68	48.8		
Ce	0.22	0.35	0.0015	0.13	187.3	256.2	1.28	93.9	0.440	9.4
Pr	0.09	0.17	0.0092	0.09	58.1	66.1	5.94	16.8		
Nd	0.014	0.40	0.0086	0.009	7.2	43.2	4.36	44.8		
Sm	0.076	0.64	0.0042	0.005	25.2	30.9	1.39	8.9		
Gd	0.068	0.40	0.0052	0.34	17. 9	23.2	1.37	7.1		
Dy	0.091	0.31	0.036	0.26	22.3	26.2	8.84	12.9		

1. Introduction

1.1 The project ‘Setting Integrated Environmental Quality Standards’

This report is produced in the framework of the project 'Setting Integrated Environmental Quality Standards'. The aim of the project is to derive environmental risk limits for substances in the environment for the different compartments, air, water, sediment and soil. The environmental risk limits are subsequently set to environmental quality standards (EQSs) by the Ministry of Housing, Spatial Planning and the Environment (VROM). They are based on maximum permissible concentrations (MPCs) and negligible concentrations (NCs). MPCs are derived using data on (eco)toxicology and environmental chemistry, and represent the potential risk of the substances to ecosystems. Applying a factor of 100 towards the MPC yields the NCs. The process of deriving integrated EQSs is shown schematically in Figure 1.1.
In this report MPCs are derived for Rare Earth Elements (REEs), also known as lanthanides. In 1993 a report was written in which a preliminary risk assessment was performed for REEs (Maas and Botterweg, 1993). The results of this report were incorporated in a subsequent exploratory report (Slooff *et al.*, 1993). The function of this latter report was to obtain an overall picture on the potential risks of REEs. The data presented in both reports were used as starting point for the derivation of environmental risk limits in the present report.

The results obtained until now in the project ‘Setting Integrated Environmental Quality Standards' are laid down in several reports. The MPCs and NCs derived until 1997 are summarised by De Bruijn *et al.* (1999). Reuther *et al.* (1998) derived MPCs and NCs for aniline derivatives. Risk limits for boron, silver, titanium, tellurium, uranium and an organosilicon compound are derived in Van de Plassche *et al.* (1999), and recently MPCs have been proposed for PCBs (Van Wezel *et al.*, 1999a) and phthalates (Van Wezel *et al.*, 1999b).

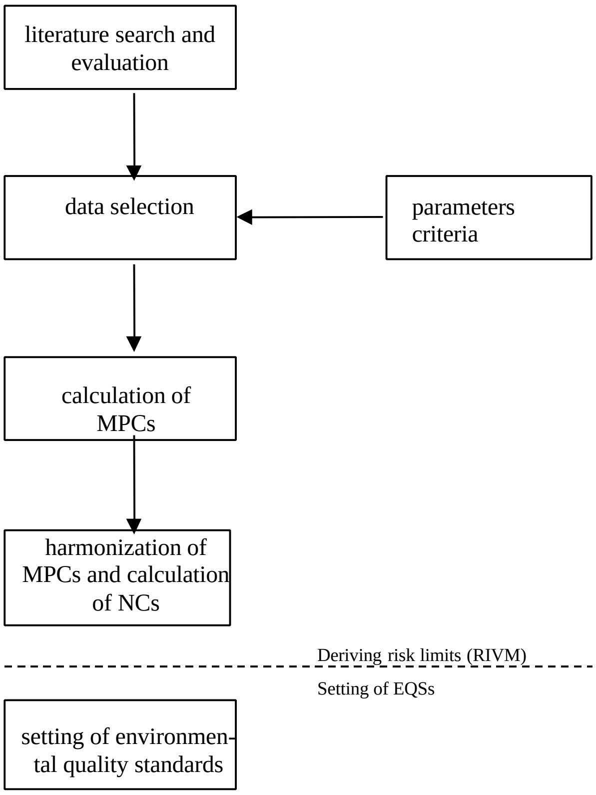

Figure 1.1. The process of deriving Integrated Environmental Quality Standards

1.2 Outline of the report

In the present report environmental risk limits are derived for Rare Earth Elements (REEs), also referred to as rare earths, rare earth metals or lanthanides. Chapter 2 gives general information concerning the selected REEs. Chapter 3 describes the method for selection of data and data handling and, subsequently, chapter 4 summarises the data on toxicity and bioaccumulation of REEs. The MPAs for freshwater, saltwater, sediment and soil are derived in the same chapter. Chapter 5 gives an overview of the environmental concentrations, leading to a proposal for the background concentrations. In chapter 6 MPC values are derived and harmonised between the compartments. In addition, NCs are derived. In chapter 7, the derived MPC and NC values are compared with the concentrations occurring in the environment.

2. Rare earth elements

Paragraph 2.1 gives general information concerning the Rare Earth Elements that have been selected for the present report. In paragraph 2.2 some information on the emission routes of these compounds in the Netherlands is given. Paragraph 2.3 outlines speciation processes of the Rare Earth Elements and paragraph 2.4 summarises the partitioning processes. Finally, paragraph 2.5 gives an overview of the mechanisms of toxic action of REEs.

2.1 Selected rare earth elements

The Rare Earth Elements (REEs) are listed in Table 2.1 and their place in the periodic system is shown by Figure 2.1. The REEs selected for derivation of environmental risk limits in this report are the same as the ones presented in the 'Exploratory report Rare Earth Metals and their compounds' (Slooff *et al*. 1993), *i.e.* Y, La, Ce, Pr, Nd, Sm, Gd, and Dy. This selection is based on their relative abundance in the environment.

Table 2.1 List of rare earth metals

Element	**Symbol**	**CAS-number**
Scandium	Sc	7440-20-2
Yttrium*	Y	7440-65-5
Lanthanons/lanthanides:		
Lanthanum*	La	7439-91-0
Cerium*	Ce	7440-45-1
Praseodymium*	Pr	7440-10-0
Neodymium*	Nd	7440-00-8
Promethium**	Pm	7440-12-2
Samarium*	Sm	7440-19-9
Europium	Eu	7440-53-1
Gadolinium*	Gd	7440-54-2
Terbium	Tb	7440-27-9
Dysprosium*	Dy	7429-91-6
Holmium	Ho	7440-60-0
Erbium	Er	7440-52-0
Thulium	Tm	7440-30-4
Ytterbium	Yb	7440-64-4
Lutetium	Lu	7439-94-3

* For these REEs MPCs will be derived

** Promethium is unstable and only occurs in spontaneous nuclear fission products of uranium ores

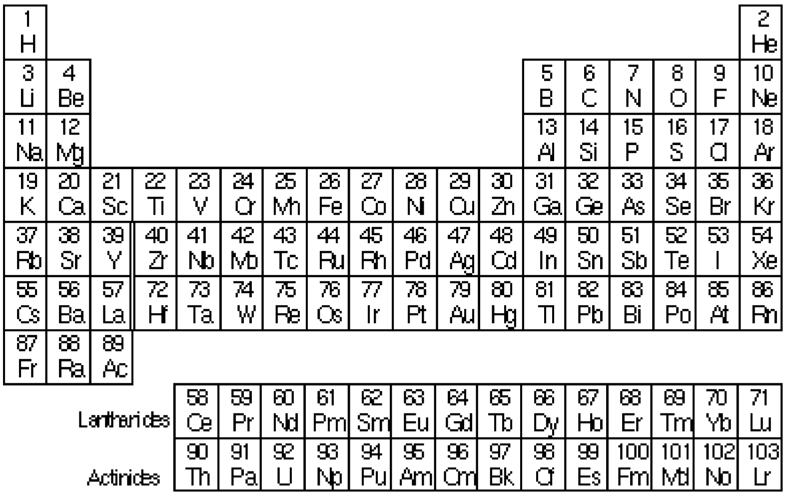

Fig. 2.1. Periodic table of elements, indicating the rare earth elements (REEs)

2.2 Emission routes in the Netherlands

From the literature, 160 mineral ores are known that contain Rare Earth Elements at levels of up to 60%, of which only a few are interesting for commercial purposes (cited in Maas and Botterweg, 1993; and cited in Slooff *et al.*, 1993). Approximately 80% of the REE mineral supplies are found in China (Annema, 1990; cited in Slooff *et al.*, 1993), whereas REE-containing ores are not found in the Netherlands (Janus *et al.*, 1995). REEs are imported in the Netherlands for the use in a number of industries (electronics-, catalyst production-, glass/ceramics- and lamp industry). The products can subsequently be exported. Import of REE-containing ores has decreased dramatically over the last few years, from 3013 ton/year in 1992 to 57 and 200 ton in 1997 and 1998, respectively (CBS, 1992, 1999). Export of REE containing products has remained more or less equal: 61 ton in 1992, 57 ton in 1997 and 87 ton in 1998 (CBS, 1992, 1999). Because of the diversity of REE containing products it is not possible to estimate the total amount of REEs imported (both as REE-containing ore and REE-containing products) in the Netherlands (CBS, 1992; Annema, 1990; cited in Slooff *et al.*, 1993).

The catalyst and artificial fertiliser (*e.g.* phosphate fertiliser) producing industries are responsible for the principal emission of REEs to the Dutch environment. The main emission route is to surface water (Slooff *et al.*, 1993).

2.2.1 Rhine estuary

As stated above, the catalyst producing and phosphate fertiliser industries are responsible for the principal emission of REEs into the Dutch environment. Two large artificial fertiliser plants are located in the Rhine estuary (*i.e.* Kemira Pernis BV in Rotterdam and Hydro Agri BV in Vlaardingen), who both produce (200–250)*10^6 kg phosphate fertiliser each year (Janus *et al.*, 1995). Kemira decided to change its production process, and to switch to ore that contains lower concentrations of REEs. Recently, both Hydro Agri and Kemir intend to stop the production of phosphate fertiliser.

During extraction of the phosphate rock, waste phospho-gypsum is formed and emitted into the river. This gypsum slurry contains among other things (such as calcium, phosphate, sulphate and fluoride) REEs, concentrations being dependent on the composition of the ore.

Table 2.2 gives an overview of the 1994 emission into the water of several REEs by these industries (Bakkenist and Van de Wiel, 1995). Bakkenist and van de Wiel (1995) calculated the free concentrations of REEs near the discharge-point and concluded that close to this point mainly REE-fluorides will precipitate, whereas with increasing pH, a little further from the discharge-point, phosphates will dominate the precipitation.

It was shown that, especially close to Kemira Pernis, concentrations of all the REEs measured (*i.e.* Ce, La, Nd, Pr and Sm) were at least doubled when compared to sampling sites a 5 km further upstream (Bakkenist and van de Wiel, 1995). The emission of Hydro Agri accounted for just 5 % of the total emission and was therefore excluded from their calculations. Highest concentrations (in the sediment near Kemira) were 170 ppm Ce, 80 ppm La, 80 ppm Nd, 30 ppm Pr and 20 ppm Sm.

Table 2.2. Emission of REEs in 1994 into the surface water by two main producers of artificial fertiliser (ton/year, Bakkenist and van de Wiel, 1995)

	Y	**La**	**Ce**	**Pr**	**Nd**	**Sm**
Kemira Pernis	54	93	136	21	75	15
Hydro Agri	16	4	0	0	11	0

During the summer of 1997, the RIKZ[1] (Tijink and Yland, 1998) measured the concentrations of REEs in various compartments in the Rhine estuary and in the North Sea. Their results show that sediment concentrations of lighter REEs (Sc, Y, La, Ce, Pr and Nd) are higher than the concentrations of other REEs, and that these concentrations are significantly increased in the direct vicinity of the REE-emitting industries (1st Petroleum harbour). Concentrations ranged from < 0.1 ppm (Lu, North Sea) to >100 ppm (Ce, 1st Petroleum harbour). The composition pattern of REEs in sediments in the vicinity of the fertiliser factories does not significantly differ from that of the emitted gypsum, thus linking the emissions with the fertiliser factories. In pore water, concentrations of the lighter REEs again exceeded those of the heavier elements, and concentrations of these compounds were again higher in the vicinity of the source. Concentrations in the pore water ranged from < 0.001 ppb (Lu, Brienenoord, North Sea) to > 0.1 ppb (Ce, 1st Petroleum harbour). In the surface water, dissolved REE concentrations were found to be somewhat lower than in pore water, although the concentrations are in the same order of magnitude.

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[1] Abbreviation in Dutch for ‘National Institute for Coastal and Marine Management’.

Interestingly, a second concentration peak of REEs was found upriver, probably caused by tidal movement, resulting in sedimentation upriver (Bakkenist and van de Wiel, 1995, Tijink and Yland, 1998).
The same authors (Tijink and Yland, 1998) also pointed out another important (albeit indirect) source for the emission of REEs into the water: a dredge material dumping site 10 miles off the coast near Scheveningen (Loswal Noord). At this site, dredge material from the vicinity of the fertiliser factories is dumped. The dumping, during which the dredge material mixes with oxygen-rich water, most likely releases REEs from the sediment, causing elevated REE-concentrations in the pore water and surface water near this deposit.

Emission of REEs by the artificial fertiliser industry contributes to an increased concentration of dissolved and particulate REEs in the Wadden Sea, an internationally protected wetland in the North of the Netherlands (Tijink and Yland, 1998).

The fact that the REE-emitting factories are located in an estuarine environment complicates the speciation as described in paragraph 2.3. The variability in salinity and pH, and the composition of suspended matter, organic carbon content and Fe- and Mn-hydroxides, caused by the tidal movement, results in constantly changing equilibria between sediment, pore water and surface water and thus in continuously changing REE-concentrations (Bakkenist and van de Wiel, 1995).

2.3 Speciation processes

The name Rare Earth Elements is somewhat misleading, because these elements are neither rare, nor only occurring as earth (=oxide) elements. For example, the 'rare earth element' Ce is found more in the earth's crust than Pb (Brown et al., 1990). Furthermore, the name Rare Earth Metals suggests that this group be somehow related to the well-known heavy metals Cd, Cu and Zn. REEs belong to the group of the class A metals, having affinity for O-containing ligands, and do not form insoluble sulphides in anoxic environments as metals from the ‘borderline’ group (Cd, Cu and Zn) do (Nieboer and Richardson, 1980). They rather precipitate or complex with other ions, such as phosphate, hydroxide, carbonate, fluoride, and silicate. Like metals, REEs can be sorbed to organic matter or clay (Van Wezel *et al.*, 1997). Carbonate- and organic complexes with REEs are the most dominant species (Maas and Botterweg, 1993). The speciation and bioavailability of REEs depends (among other things) on pH, salinity (cf. Katkov, 1980), and the presence of negative counter ions. As a consequence, the speciation in saltwater is different from the speciation in freshwater. In saltwater, between 70 and 96% of the REEs is present as carbonate complexes, depending on the dissolved organic carbon (DOC) level. In freshwater, humate complexes play a more dominant role (Maas and Botterweg, 1993). The low solubility of REEs leads to low concentrations in solution.

REEs can be divided into two groups, the first of which is composed of the more soluble elements (La-Gd), and the second group consists of the less soluble elements (Tb-Lu). Generally, the solubility of REEs is low, due to complex-formation. For example, solubility products of REE-phosphates can be as low as 10^{-25} mol^2/L^2 (Liu and Byrne, 1997). Maas and Botterweg (1993) concluded that the solids La-fluoride, La-carbonate and La-phosphate control the water solubility of lanthanum (La). Of these, La-carbonate proved to be the most important at high pH, due to its relative abundance. The total dissolved amount of lanthanum and cerium will be low (approximately 1 µg/l, cited in Maas and Botterweg, 1993), due to processes as sorption and precipitation. The fraction free ion is very small and is expected to be in the order of 0.3 fM to 9 pM (Maas and Botterweg, 1993). The low water solubility of all REE-phosphates, carbonates and hydroxides has consequences for assaying their toxicity, because of the formation of precipitates during the test (Maas and Botterweg, 1993).

Table 2.3 summarises some physico-chemical properties of REEs. Some elements, like Eu and Ce, have more than one redox-state in which they can exist. Changes in the redox-state may change the bioavailability of an element (Bierkens and Simkiss, 1988). Under normal (oxic) circumstances REEs are present in the trivalent oxidation state (Cotton, 1991, De Baar *et al.*, 1991, Seaborg, 1993). However, under extreme ecological situations, changes in redox status may be important in the release and mobilisation of metals in marine sediments (Bierkens and Simkiss, 1988)

Table 2.3. Physico-chemical properties of REEs

Element	**Atomic number**	**Atomic weight**	**Valence**
Sc	21	44.96	3
Y	39	88.91	3
La	57	138.91	3
Ce	58	140.12	3 or 4
Pr	59	140.91	3
Nd	60	144.24	3
Pm	61	(145.00)	3
Sm	62	150.36	2 or 3
Eu	63	151.97	2 or 3
Gd	64	157.25	3
Tb	65	158.93	3 or 4
Dy	66	162.50	3
Ho	67	164.93	3
Er	68	167.25	3
Tm	69	168.94	3
Yb	70	173.04	2 or 3
Lu	71	174.97	3

2.4 Partition coefficients

Partition coefficients describe the equilibrium distribution of a substance over two or more compartments, whereas distribution coefficients represent empirical observations of concentrations in these compartments, without knowledge on the equilibrium status. Most partition coefficients reported in literature should in fact be named distribution coefficients. However, in this report, we shall simply name both partition coefficients.

Coughtry and Thorne (1983) report for Ce a distribution coefficient in soil (*i.e.* the ratio between the concentration in the soil and the concentration in the soil solution, $Kp_{(soil/w)}$) of 2000 L/kg dry soil. For other REEs, no partition coefficients in soil have been reported.
Maas and Botterweg (1993) give an overview of average partition coefficients between suspended and dissolved REEs in rivers. The log $Kp_{(sm/w)}$-values vary around 3. In oceans, the log $Kp_{(sed/w)}$ is around 4, with the exception of Ce, for which the log K*p* is around 5. This relatively high K*p* is caused by the low solubility of the main form of oceanic Ce, CeO_2, in which Ce is present as Ce^{4+}, as compared to other REE-species.

Tijink and Yland (1998) measured sediment–pore-water partition coefficients for various REEs at different sites in the Rijnmond-area. For the calculation of these coefficients, total sediment concentrations (after extraction with HF) and dissolved concentrations in pore-water (after 0.45 µm filtration) were used. The log $Kp_{(sed/pw)}$-values varied from 4.7 (Eu, Tm and Lu) to 6 (Ce, Pr, Nd and Yb). Log K*p*-values for partitioning between suspended matter and water (log $Kp_{(sm/w)}$ varied from 4.9 (Lu) to 6.9 (Dy). Lower values were usually found on a site in the North Sea, whereas in the Rhine estuary higher values (about one order of magnitude) were recorded. These differences may be caused by the relatively sandy composition of the North Sea sediment, and thus a lower binding capacity for REEs. Scandium, however, had a higher log $Kp_{(sm/w)}$ on the North Sea site. The reason for this difference is unclear. Tijink and Yland (1998) use an average log $Kp_{(sm/w)}$ of 5.1 ± 0.5 for all REEs.

Log $Kp_{(sed/pw)}$-values for REEs are relatively high compared to those of heavy metals such as Cu, Zn, Cd and Pb. The latter ones usually have log K*p*-values that are between 2.5 and 4 l/kg. This difference illustrates the relative high affinity of the REEs to sediment.

Stronkhorst and Yland (1998) report differences between laboratory and field derived partition coefficients between sediment and pore-water (log $Kp_{(sed/pw)}$), and between sediment and water (log $Kp_{(sed/w)}$), for various REEs (Table 2.4). Laboratory-derived values are about one order of magnitude lower than field-derived values. This difference is probably due to disturbance and subsequent oxidation of the sediment in the laboratory experiments, causing relatively high concentrations in the pore-water. In addition, increased decay of organic material in the disturbed sediments, involving reduction-processes, may contribute to release of REEs from sediment (Bierkens and Simkiss, 1988, Maas and Botterweg, 1993). For these reasons, field derived partition coefficients are preferred over laboratory derived values for calculation of MPCs.

When evaluating the partitioning data one must keep in mind that pH, the presence of negative counterions and the concentration of dissolved organic carbon (DOC) in the (pore)-water strongly influence the concentration of REEs in solution. When pH, DOC concentrations and negative counterion concentrations are high, a large part of the total dissolved REEs will not be present as free (3^+) ions. Calculation of partition coefficients with total dissolved REE concentrations may not represent 'true' partitioning.

Table 2.4. Log Kp values for REEs under laboratory and field conditions (Stronkhorst and Yland, 1998)

	Log K$p_{(sed/pw)}$ (l/kg)		**Log K$p_{(sed/w)}$ (l/kg)**	
Element	**lab**	**field**	**lab**	**field**
Y	4.65	5.35	5.18	6.04
La	4.85	5.67	5.52	6.37
Ce	4.94	5.93	5.78	6.31
Pr	4.87	5.81	5.69	6.34
Nd	4.86	5.71	5.67	6.27
Sm	4.80	5.52	5.61	5.63
Eu	4.51	5.35	5.63	5.54
Gd	4.74	5.42	5.58	5.71
Tb	4.74	5.45	5.58	5.83
Dy	4.76	5.39	5.50	5.91
Ho	4.71	5.36	5.46	6.20
Er	4.72	5.36	5.37	6.01
Tm	4.67	5.29	5.33	5.74
Yb	4.75	5.36	5.35	5.87
Lu	4.65	5.24	5.30	5.87

Sed = total sediment concentrations
pw = dissolved pore water concentrations (0.45 µm)
w = dissolved water concentrations, above the sediment (0.45 µm)

2.5 Mechanisms of toxic action

Although much knowledge is available about physico-chemical properties and industrial applications, data on the biological effects of REEs are scarce. There are no indications that Rare Earth Elements are essential to humans and animals (Van Dijk-Looyaard and Montizaan 1986). For plants, no data concerning essentiality are available either. It is suggested that lanthanides may increase the yield of crop plants (for a review see Lepp, 1997). However, the effects of application of REEs as fertiliser range from stimulation to reduction of growth. This may both depend on the element in question and environmental factors such as Canutrition (Lepp, 1997). Conclusive evidence on a positive effect of REEs on plant growth is to the present day not available.

The mechanisms of the toxic action of REEs known so far include (Gale, 1975, Rogers *et al.*, 1980, Clarke and Hennessy, 1981, Martin, 1983 (in Aruguete *et al.*, 1998), Plaha and Rogers, 1983, Washio and Miyamoto, 1983, Bierkens and Simkiss, 1988, Corzo and Sanders, 1992, Cheng *et al.*, 1997, Lepp, 1997, Haftka and Weltje, 1999):

- competition between Ca/Mg and La, disrupting for instance bone-integrity and cellular signalling;
- replacement of Ca/Mg;
- reaction with proteins in which Ca/Mg are not usually involved;
- substitution of Fe by Sc;
- substitution of other elements;
- lipid-peroxidation due to redox cycling of REE that can exist in more than one oxidation state;
- phosphate deficiency, due to precipitation of phosphate-REEs.

These mechanisms have been observed in a wide variety of organisms, such as micro-organisms, nematodes, crustaceans, insects, mammals and plants. Since the mechanisms observed are very aspecific, one might assume that all species may exhibit similar sensitivity towards REEs.

Exposure to excess concentrations of REEs may lead to a multitude of effects, such as ataxy, suppressed respiration headache and fever (for an extensive review see Slooff *et al.*, 1993). Cerium is supposed to be a renal and hepatotoxic substance (Gao *et al.*, 1996, Ma *et al.*, 1996). REEs do not seem to be mutagenic or carcinogenic themselves, although exposure does seem to facilitate formation of tumours (Maas and Botterweg, 1993).

3. Methods

3.1 General scheme

The maximum permissible concentrations and negligible concentrations are derived as described in Kalf *et al*. (1999), and the methods generally applied within the project 'Setting Integrated Environmental Quality Standards' (De Bruijn *et al.*, 1999).
In short, data on chronic and acute toxicity for aquatic and terrestrial species of a compound are searched for, evaluated, and selected or rejected. For compounds with a log K*ow* higher than 5.0, or for compounds for which there is an expectation for secondary poisoning due to strong bioaccumulation or a low depuration rate, also toxicity data for mammals and birds are searched for. The maximum permissible concentration (MPC) is derived using either the refined assessment method as described by Aldenberg and Slob (1993), or assessment factors as laid down in the Technical Guidance Document (ECB, 1996) or the so-called modified-EPA assessment factors (Kalf *et al.*, 1999). The MPCs for sediment and soil are harmonised according to the equilibrium partition theory. In this way it is prevented that a concentration on an MPC-level in one compartment leads to exceeding the MPC in another compartment. Finally, the NCs are calculated.

3.2 Data collection

An on-line literature search was performed until the summer of 1999. The TOXLINE and BIOSYS databases were used.

3.3 Data selection

A toxicity study is considered reliable if the design of the experiment is in agreement with international accepted guidelines, e.g. OECD guidelines. To judge studies which have not been performed according to these guidelines, criteria are developed within the framework of the project 'Setting Integrated Environmental Quality Standards' (De Bruijn *et al.*, 1999, Kalf *et al.*, 1999).
In this report data on the toxicity of the REEs yttrium (Y) lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), gadolinium (Gd), and dysprosium (Dy) will be used to derive Maximum Permissible Concentrations (MPCs) and Negligible Concentrations (NCs).
Data used for this derivation must comply with a number of criteria (Slooff, 1992):

- only toxicity tests carried out under laboratory conditions are selected for derivation of environmental risk limits;
- only toxicity tests using pure substances can be used;

- toxicological effect data affecting the population dynamics (such as survival, growth and reproduction) are solely taken into account. These are usually expressed as L(E)C50 (short-term tests, duration less than or equal to four days) or NOEC (long-term tests, only for micro-organisms NOECs may be derived from experiments lasting less than four days);
- if for one species several toxicity data based on the same toxicological endpoint are available, the geometrical mean is used;
- if for one species toxicity data, based on different toxicological endpoints, are available, the most critical value is selected. If more than one value for this endpoint is available, the geometrical mean for this endpoint is used;
- if toxicity data are available for several life stages, and a certain life stage appears to be more sensitive to the toxicant, this result may be used for derivation of MPCs and NCs;
- next to nominal concentrations, actual concentrations have to be reported. The latter will be used for derivation of MPCs and NCs.

3.4 Extrapolation towards an MPCs and NCs

Currently used extrapolation methods used to derive MPCs are the so-called refined effect assessment or statistical extrapolation method (Aldenberg and Slob, 1993) and the preliminary effect assessment (ECB, 1996) or the modified EPA-method (Kalf *et al.*, 1999). The statistical extrapolation method can be used only if chronic toxicity data (NOECs) for species of at least four different taxonomic groups are available. The preliminary effect assessment and modified EPA-method can be used if NOECs of less than four different taxonomic groups or if only acute data are available. For description of these methods, see Crommentuijn *et al.* (1997a) and Kalf *et al.* (1999).

3.5 Harmonization between the compartments

The MPC-value for one environmental compartment must not lead to exceeding MPC-values for other environmental compartments. Therefore, harmonisation between the different compartments is needed. For this purpose, the Equilibrium Partitioning (EP) method is used (Di Toro *et al.*, 1991). In addition, equilibrium partitioning can be used to derive MPCs for soil and/or sediment from MPCs if toxicity data are not available for these compartments. Three important assumptions are made when the EP-method is applied:

1. sorption of the compound to the organic carbon in sediment particles and its concentration in (pore) water are assumed to be in equilibrium, to be described by a partition coefficient (Kp);
2. bioavailability, accumulation and toxicity are assumed to be closely related to pore water concentrations;
3. sensitivity of soil or sediment dwelling organisms is assumed to be equal to that of aquatic organisms.

Since knowledge on the influence of soil or sediment characteristics on bioavailability of metals in general and REEs in particular is lacking, the use of a simplified model such as the EP-method can be justified.

To calculate soil or sediment concentrations from water concentrations with the EP-method, the following formula has to be applied:

$$C(\text{soil/sediment}_{EP}) = C(\text{water}) * K_p$$

in which

$C_{(\text{soil/sedimentEP})}$ = concentration in soil or sediment using the EP-method (mg/kg)
$C_{(\text{water})}$ = concentration in water (mg/L)
Kp = partition coefficient (L/kg)

Because toxicity data for specific groundwater-dwelling organisms lack, the toxicity data for aquatic organisms are used for the derivation of MPCs for groundwater, even though sensitivities of surface water species and groundwater species are bound to differ (GZR, 1995).
Harmonization has not been carried out for air-concentrations.

3.6 The added-risk approach

In Van de Meent *et al*. (1990) the first MPCs and NC for naturally occurring compounds were derived. However, for some of the substances tested, these MPC and NC values were lower than their background concentrations. A methodology to solve this problem was proposed by Struijs et al. (1997). Crommentuijn *et al.* (1997a) slightly modified the method of Struijs *et al.* and defined the MPC for naturally occurring substances as the sum of the Maximum Permissible Addition (MPA), which can be calculated from the available toxicity data, and the background-concentration (C*b*):

$$MPC = MPA + Cb.$$

The MPA is calculated using a similar approach as the MPC for substances having no natural background concentrations.
This ‘added risk approach’ has originally been used for heavy metals (Crommentuijn *et al.*, 1997a), but was designed for naturally occurring substances in general. Since REEs are natural compounds as well (with the exception of Pm, which has no stable isotopes and thus no natural background), the added risk approach is used (where possible) to derive MPC values.
Thus, for application of the added risk approach data on background levels are required. It is not clear whether or not and if so, which part of the background concentrations of REEs is

bioavailable. As is done by Crommentuijn *et al*. (1997a), the availability of the background concentration of REEs is set at 0%, thus ignoring the ecotoxicological implications of the background concentrations. Therefore, in the above formula, possible toxic effects of the background are ignored. Effects of the background concentrations are not considered to be negative *per se*, rather from a policy point of view than from evidence that these concentrations do indeed not threaten organisms. The evolutionary pressure of this concentration, although it may lead to disappearance of species at a given location, can lead to increased biodiversity in the world as a whole.

3.6.1 Derivation of negligible concentrations (NCs)

NCs are, by definition, derived by division of the MPCs by a factor 100, to take combination toxicity into account (VROM, 1989) as species are, in the environment, usually exposed to mixtures of chemicals that may have additive or synergistic toxic effects. For substances with a natural background, the NC is calculated as: NC = C*b* + (MPA/100).

3.7 Specific remarks considering REE-data

For heavy metals, specific calculations can be made to standardise soil concentrations so that comparison of toxicity data becomes easier. Actual concentrations are then recalculated into so-called ‘standard soil’ concentrations. This recalculation is done with with empirical regression relations, in which soil concentrations are related to the organic carbon content and the clay content of the soil. For recalculation of soil concentrations of REEs into 'standard soil', such equations have not been developed until now. Extensive data-sets would be needed to develop these relationships, and these data-sets are not yet available for the Dutch situation yet. Therefore, for the REEs concentrations will not be recalculated to concentrations in a 'standard soil'.

For some elements, such as organo-tin compounds (Crommentuijn *et al.*, 1997b), a huge difference has been noted between sensitivity of marine and fresh water species. If the same holds true for REEs, different MPCs will be derived for both aquatic compartments.

4. Results

4.1 Toxicity data

4.1.1 Aquatic toxicity data

The aquatic toxicity data found in the literature are presented in Appendix 2 for freshwater and saltwater organisms. REEs are in general introduced as chloride-salts in the toxicity tests. The total amount of studies for freshwater and saltwater organisms is limited. Because of the low solubility products of REE-carbonates, -phosphates and -fluorides, assaying of toxicity is very hard. Precipitates develop before and during testing (Maas and Botterweg, 1993). Maas and Botterweg (1993) observed that, without preincubation, initial concentrations dropped to < 10 % within 24 hours. Therefore, it is essential that the *actual* and not the *nominal* concentrations are measured and reported. In Slooff *et al.* (1993), Maas & Botterweg (1993) and Van Wezel *et al.* (1997), a number of tests are mentioned that do not meet this requirement. In these tests only nominal and not actual concentrations are reported (Van Urk, 1977, Khangarot, 1991, Ten Berge and Boerboom-Schreerder, 1977). We tried to recalculate the nominal concentrations mentioned by the authors with the speciation programme GECHEQ, version 6.01 (Verweij, 1996). For this purpose, the stability constants database was extended with recent data on REE complexes and precipitates. However, the reported compositions of the media are incomplete, seriously hampering speciation calculations. Therefore, in the present report these studies are neither incorporated nor used. Only tests in which measured concentrations are reported are considered suitable for risk assessment purposes.

In addition, several tests have been performed with gypsum slurry or wastewater (Ten Berge and Boerboom-Scheerder, 1977, Maas and Botterweg, 1993, NOTOX 1995ef). In these studies, REEs were not added as pure substances and must therefore be ignored.

In 1992 TNO[2] (Hooftman *et al.*, 1992 in Maas and Botterweg, 1993; Bowmer *et al.*, 1992 in Maas and Botterweg, 1993) carried out toxicity experiments of REE-chlorides with saltwater fish and crustaceans on behalf of the RIZA. In these studies actual concentrations are measured and reported. Den Ouden (1995) carried out short-term and long-term experiments with freshwater fish and crustaceans in which also actual concentrations were measured. NOTOX (1995a-d) performed a number of studies for lanthanum with freshwater algae, crustaceans and fish. In addition, they assessed the toxicity of La for the bacterium *Pseudomonas putida*. However, these experiments were not carried out with more or less constant exposure concentrations, because the solutions were diluted just before use, thus not

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[2] Abbreviation in Dutch for ‘Netherlands Organization for Applied Scientific Research’.

allowing equilibrium to be established. The authors try to correct for the difference between initial and actual concentrations by averaging the concentrations over the exposure duration. In this fashion they modify the measured 21-day NOEC of 0.09 mg/L for *Daphnia magna* to an average exposure concentration of 0.15 mg/L. The *P. putida* test is considered to be invalid because La concentrations dropped below the detection limit.

4.1.2 Soil and sediment toxicity data

No experimental toxicity data are available for soil and sediment dwelling organisms.

4.2 Derivation of MPAs for water

Appendix 1 shows an overview of the toxicity data used for derivation of the Maximum Permissible Addition (MPA). Table 4.1 gives the derived MPAs for fresh and saltwater, together with the assessment factor used (ECB, 1996) to derive the MPAs. The ratio of acute toxicity data for fresh- and marine organisms is consistently higher than 1 (p<0.05, one-tailed t-test). This indicates that marine organisms are more sensitive to REEs than freshwater organisms, even though the number of data is small. No such comparison could be made for chronic toxicity data, since chronic toxicity data for salt water organisms were not available.

The observation that saltwater species seem to be more sensitive to REE-toxicity is in contrast with heavy metals, in which case saltwater species are less sensitive than freshwater species (Hall and Anderson, 1995). Free metal concentrations of REEs will probably be lower in salt water than in fresh water, due to the presence of a higher concentration of counter ions and complexing agents. Furthermore, salt water has a higher pH. Assuming that only free ions are available for uptake, one would expect that bioavailability in salt water would be lower than in fresh water. On the other hand, if organisms can take up REE-complexes, as well as ions, one might expect increased bioavailability in salt water. However, neither possibility is reflected by lower BCF-values in salt water (paragraph 4.4). An intrinsic higher sensitivity of saltwater species to REEs, although unlikely as argued in chapter 2, might play a role. This possibility cannot be excluded on basis of the present toxicity studies.

In addition, in both fresh and salt water, crustaceans appear to be more sensitive to REEs than fish are (p<0.05, one-tailed t-test of the ratio between both). Since the datasets are limited (one species of freshwater crustacean, one saltwater species of crustacean, and likewise for the fish), this observation may not be representative for taxonomic groups of fish and crustacean as a whole.

One might argue that, when crustaceans are consistently more sensitive to REEs than fish, the assessment factor for extrapolation of the MPA could be reduced. However, only two taxonomic groups, each represented by two species, have been examined. Therefore, the assessment factor was not lowered.

The toxicity ranking differs between fresh and saltwater as well. For freshwater organisms, Ce seems to be the least toxic element and Nd and La the most toxic. For saltwater organisms, Ce is the most toxic element, and Dy the least toxic.

For other REEs than these shown in Table 4.1. (and 4.2.), no toxicity data are available to base an MPA upon. However, in view of the mechanism of action of the REEs, we expect that concentrations related to ecotoxicological risks of the other REEs lay in the same order of magnitude.

Table 4.1. MPAs derived for REEs, including methodology

Element	**Fresh water MPA (µg/l)**	**Method**	**Salt water MPA (µg/l)**	**Method**
Y	6.2	$LC50_{aquamin}/1000$	0.72	$LC50_{aquamin}/1000$
La	10	$NOEC_{aquamin}/10$	1.0	$LC50_{aquamin}/1000$
Ce	22	$LC50_{aquamin}/1000$	0.15	$LC50_{aquamin}/1000$
Pr	9	$LC50_{aquamin}/1000$	0.92	$LC50_{aquamin}/1000$
Nd	1.4	$LC50_{aquamin}/1000$	0.85	$LC50_{aquamin}/1000$
Sm	7.6	$LC50_{aquamin}/1000$	0.42	$LC50_{aquamin}/1000$
Gd	6.8	$LC50_{aquamin}/1000$	0.52	$LC50_{aquamin}/1000$
Dy	9.1	$LC50_{aquamin}/1000$	3.6	$LC50_{aquamin}/1000$

$LC50_{aquamin}$ = lowest aquatic LC50, $NOEC_{aquamin}$ = lowest aquatic NOEC

4.3 Derivation of MPAs for soil and sediment

In this paragraph MPAs for soil and sediment are presented. Since toxicity data for soil or sediment dwelling organisms lack, MPAs will be derived using equilibrium partitioning (paragraph 3.5). For this purpose, field-derived partition coefficients are preferred over lab-derived partition coefficients.

As reported in paragraph 2.4, a general partition coefficient for Ce in soil of 2000 l/kg, *i.e.* log $Kp_{(soil/w)} =$ 3.3. Partition coefficients for other REEs in soil are not available. For sediment, MPAs are given for both partitioning between sediment and water and for partitioning between sediment and pore-water. The calculated MPAs for soil and sediment are given in table 4.2. It should be noted that K*p*s measured in an estuarine situation (Stronkhorst & Yland, 1998) were used to calculate MPAs for fresh and salt sediment. However, the same study indicated that differences in K*p* with salinity were within one order of magnitude.

The results show that for soil, MPAs will be 44 mg/kg for Ce, for other REEs no MPAs can be derived by equilibrium partitioning. For freshwater-sediments, MPAs based on $Kp_{(sed/w)}$, will vary from 2.6 g/kg for Nd to 44.9 g/kg for Ce. Based on sediment – pore water partitioning, $Kp_{(sed/pw)}$, these values change to 718 mg/kg for Nd and 18.7 g/kg for Ce. For saltwater-sediments MPAs, based on $Kp_{(sed/w)}$, will vary from 179 mg/kg for Sm to 2.9 g/kg for Dy. Based on $Kp_{(sed/pw)}$, these values change to 137 mg/kg for Sm and 884 mg/kg for Dy. Because one may expect pore water concentrations to correlate best with bioavailability, we propose to use the MPA-values based on sediment-pore-water partitioning (the two columns on the total right) for derivation of MPCs.

Table 4.2. MPAs for soil and sediment, based on equilibrium pore-water/sediment partitioning or based on water/sediment partitioning

			MPA-sed, based on sediment-water partition coefficient			**MPA-sed, based on sediment-porewater partition coefficient**		
Element	**Soil Log K*p*[1]** L/kg	**MPA soil** mg/kg d.w.	**LogK*p* (sed/w)[2]** L/kg	**MPA sediment (fresh)** mg/kg d.w.	**MPA sediment (salt)** mg/kg d.w.	**LogK*p* (sed/pw)[2]** L/kg	**MPA sediment (fresh)** mg/kg d.w.	**MPA sediment (salt)** mg/kg d.w.
Y	-	-	6.04	6798	789	**5.35**	1388	161
La	-	-	6.37	23442	2344	**5.67**	4677	468
Ce	**3.30**	44.0	6.31	44918	306	**5.93**	18725	128
Pr	-	-	6.34	19690	2013	**5.81**	5811	594
Nd	-	-	6.27	2607	1583	**5.71**	718	436
Sm	-	-	5.63	3242	179	**5.52**	2517	139
Gd	-	-	5.71	3487	267	**5.42**	1789	137
Dy	-	-	5.91	7397	2926	**5.39**	2234	884

The bold K_p's are used for the derivation of MPCs

1. Cougthrey and Thorne, 1983
2. Stronkhorst and Yland, 1998

4.4 Bioaccumulation

To assess the possibility of secondary poisoning by REEs, data on bioaccumulation factors (BCFs) for REEs were collected (Table 4.3). They appeared to be limited, and often contradictory (Slooff *et al.*, 1993). For Dy, Ce, and Gd BCFs range from 5-100 L/kg and 1,000-5,000 L/kg for marine fish and zooplankton, respectively (IAEA, 1985; cited in Slooff *et al.*, 1993). The BCFs reported for Sm by Lembrechts and Köster (1989, in Maas and Botterweg, 1993) are in the same order of magnitude, 30-3,000 L/kg for marine and freshwater fish, marine crustaceans and marine molluscs. Sun *et al.* (1996) showed that BCFs vary considerably between different organs within carp (*Cyprinus carpio*). In this species, BCF-values (wet weight) for muscular tissue ranged from 0.86 L/kg for Nd to 1.66 L/kg for Pr. For the internal organ they varied from 634 L/kg for Nd to 978 L/kg for Sm.

Considerably higher BCFs were found in the Dutch Rijnmond area, where log BCF-values (dry weight) ranged from 3 – 5 for La, Ce and Nd (Tijink and Yland, 1998). Differences between salt and fresh water systems were not observed.

As stated above for calculations of partition coefficients, a smaller or bigger part of the total dissolved REEs may not be present in the ionic form, but rather be bound to DOC. Measuring total dissolved REE concentrations may then have repercussions on the calculation of BCFs.

Table 4.3. Bioaccumulation factors (BCFs) for REEs

Element (concentration, mg/L)	**species/group**	**marine/ fresh water**	**BCF (L/kg)**	**source**
Dy, Ce, Gd	fish	m	5-100	1)
Dy, Ce, Gd	zooplankton	m	1,000-5,000	1)
Sm	fish	m	3,000	2)
Sm	fish	f	30	2)
Sm	crustacean	m	3,000	2)
Sm	molluscs	m	5,000	2)
Sm	alga	m	5,000	2)
Ce, La, Nd, Pr, Sm	carp, muscle	f	0.22 – 1.10	3)
Ce, La, Nd, Pr, Sm	carp, skeleton	f	3.66 – 8.11	3)
Ce, La, Nd, Pr, Sm	carp, gills	f	11.2 – 18.8	3)
Ce, La, Nd, Pr, Sm	carp, internal organ	f	634 – 978	3)
La, Ce, Nd	bivalves	f/m	15,000 – 50,000	4)
La, Ce, Nd	worms	f/m	8,000 – 120,000	4)
La, Ce, Nd	crustacean	f/m	10,000 – 40,000	4)
Y	amphipod	f/m	7,413	5)
La	amphipod	f/m	28,840	5)
Ce	amphipod	f/m	48,978	5)
Pr	amphipod	f/m	38,905	5)
Nd	amphipod	f/m	29,512	5)
Sm	amphipod	f/m	17,783	5)
Eu	amphipod	f/m	11,220	5)
Gd	amphipod	f/m	13,183	5)
Tb	amphipod	f/m	12,882	5)
Dy	amphipod	f/m	9,550	5)
Ho	amphipod	f/m	8,511	5)
Er	amphipod	f/m	7,413	5)
Tm	amphipod	f/m	6,310	5)
Yb	amphipod	f/m	6,607	5)
Lu	amphipod	f/m	4,786	5)
REE	crop plants	-	0.1 – 10	6)
REE	waterplants	-	10 – 1,000,000	7)
REE	wild plants	-	100 – 36,000	8)

1)IAEA, 1985, in Slooff et al., 1993, 2)Lemrechts and Köster, 1989, 3)Sun *et al.*, 1996, whole fish exposure to Ce (0.27 μg/L), La (0.30 μg/L), Nd (0.29 μg/L), Pr (0.06 μg/L) and Sm (0.25 μg/L), 4)Tijink and Yland, 1998, field data, 5)Stronkhorst and Yland, 1998, BCF based on porewater concentrations, field data, 6) Rikken, 1995, literature review, based on total soil concentrations, 7) Van Dijk-Looyaard and Montziaan, 1986 8) Weltje, 1998, literature review, recalculated data, based on nutrient- or soil-solution-concentrations

Rikken (1995) concluded in a literature review that the availability of REEs for plants in soil is limited. Accumulation of REEs is found in the roots at very low concentrations. The BCFs found in crops for human and animal consumption ranged from $1*10^{-1}$ - $1*10$ L/kg (Table 4.3). This low value, compared to that in other plants, may be the result of the application of phosphate-fertiliser on these plots, causing precipitation and thus a decrease of the bioavailability of REEs. The maximum BCF found was 5 L/kg for *Phytolacca americana*. According to Van Dijk-Looyaard and Montziaan (1986) BCFs for water plants range from

10-1,000,000 L/kg. This huge difference between BCFs of terrestrial and aquatic plants disappears when the terrestrial data are based on the concentration of REEs in the nutrient or soil solution, *i.e.* 1000 – 36000 L/kg (Weltje, 1998).

Bioaccumulation seems to depend on both element specific properties and environmental factors. Bioaccumulation in the marine amphipod *Corophium volutator* decreases with increasing atomic numbers, from 26915 L/kg for Ce to 10000 L/kg for Lu (Stronkhorst and Yland, 1998). The magnitude of the BCF also depends on the circumstances of the experiment: Stronkhorst and Yland (1998) reported a difference in BCF values between laboratory and field conditions, with lab-BCFs about one order of magnitude higher. This may be a consequence of the disturbance of the sediment before use in the laboratory, and therefore increasing bioavailability.

However, bioaccumulation may be underestimated, because the calculations are usually based on nominal concentration, and not on actual concentrations, which are much lower in most studies. In addition, actual measured concentrations may not be completely bioavailable. Therefore, one must keep in mind that reported BCFs might underestimate the real situation.

Bioaccumulation calculations from soil to plant, based on total plant BCFs, may not be correct if only part of the plant is eaten, as root concentrations of REEs usually exceed those of the stem and the seeds (Hong *et al.*, 1997). With the exception of root crops, bioaccumulation factor (BAF) values and thus probability of bioaccumulation will be overestimated. The likelihood of biomagnification in the food chain may be overestimated in a similar fashion. In addition, the reported BCF values above do not indicate that REEs are highly bioavailable for animals. We support the conclusion of Slooff *et al*. (1993), that biomagnification will not be likely. Therefore, no studies on the toxicity due to secondary poisoning will be included in the present report.

5. Environmental concentrations

Typically, concentrations of REEs in the earth's crust show a zigzag-pattern, with concentrations of lanthanides with even atomic numbers exceeding those of the odd-numbered ones (Fig 5.1.). In addition, concentrations of lanthanides tend to decrease with increasing atomic number. This is called the Oddo-Harkin's rule (Markert, 1987). Complete listings of concentrations reported in this paragraph can be found in Appendix 3.
During analysis of Sc, Ca can interfere. However, using the right analytical-chemical procedure, this problem can be circumvented (Os and Walraven, 1997).

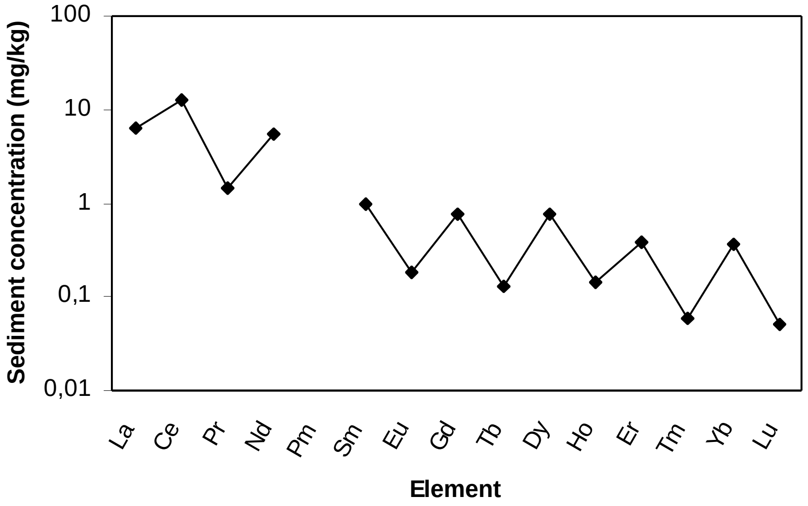

Figure 5.1. Distribution pattern of REEs in soil (from Markert, 1987)

5.1 Environmental concentrations: groundwater and surface water

Stuyfzand (1991) published a list of concentration-ranges of trace elements, including REEs, in Dutch water (fresh and salt surface water and ground water, Appendix 3.a.1). The concentrations ranged from below detection limits for most REEs to a maximum for La of 2 µg/L in groundwater with $pH \geq 6.2$. For more acidic groundwater ($pH < 6.2$) concentration ranged from 0.05 µg/L for Yb to 105 µg/L for La. Others, such as Van Steenwijk *et al.* (1992) and Verweij *et al.* (1994, 1995, incorporated into Appendix 3.a.1), reported much higher concentrations of REEs in groundwater used for the preparation of drinking water. These values were usually found in the 'raw' groundwater. Concentrations of REEs in the raw water again correlated well with the pH, concentrations being higher when the pH was lower (Verweij *et al.*, 1995). Appendix 3.a.1. shows that background concentrations in groundwater vary substantially, possibly partly explained by pH variations of the groundwater. For reason of this high variability, no general background concentration is proposed for the compartment groundwater and as a consequence no MPC is derived for this compartment.

However, in the drinking water, prepared from this raw water, concentrations of REEs dropped below the detection limits. Occasionally, concentrations in drinking water exceed the detection limits, as in Bilthoven, De Haere, and Epe (Verweij *et al.*, 1994), where concentrations of Y, La, Ce and Nd could be as high as 8-14 µg/l. Although these values clearly are exceptions, they are reported in Appendix 3.a.2. One has to keep in mind that cleanup procedures for making drinking water out of raw water may have improved since.

Slooff *et al.* (1993) listed concentrations of REEs in fresh and salt surface water. In fresh water, concentrations of REEs were usually below the detection limit, and in salt water they were below 1 ng/L. This confirms the data of Stuyfzand (1991), presented in Appendix 3.a.1. One has to keep in mind that analytical techniques, such as HR-ICP-MS, have been developed since (Zhu, 1999).

Tijink and Yland (1998) deal with environmental concentrations of REEs in the Rhine estuary (Appendix 3.a.3). One might expect that this area represents an environmental situation with elevated concentrations in the Netherlands, since it is influenced by several large emission sources (see paragraph 2.2.1). This is indeed shown by Appendix 3.a.3: concentrations of especially the lighter REEs clearly exceed those listed in Appendix 3.a.1 and those listed by Slooff *et al.* (1993).

5.2 Environmental concentrations: suspended matter and sediment

Slooff *et al.* (1993) report average REE concentrations in sediments and suspended matter in Dutch fresh water systems. REE concentrations range from below detection limit to 125 mg/kg in allegedly unpolluted areas (Appendix 3.b.1). Unfortunately, sediment and suspended matter concentrations are not separated, as in van Son (1994) and Tijink and Yland (1998), both reported in Appendix 3.b as well.

Van Son (1994, Appendix 3.b.2) showed that in suspended matter from fresh water systems, REE-concentrations were mostly around or below 1 mg/kg. Only on one site (Eemdijk) concentrations were higher (*i.e.* 6 mg/kg Sc, 5 mg/kg Ce, and 2.5 mg/kg for Y, La and Nd). In the Rhine estuary (Tijink and Yland, 1998, Appendix 3.b.3) the lowest REE-concentrations in suspended matter are comparable to the highest concentrations listed by van Son (1994). These concentrations are found in suspended matter from the relatively unpolluted North Sea site (Terheijde 30). Much higher concentrations are found at the other sampling sites, the difference being mostly a factor 10-20.

One can see more or less the same picture for sediment concentrations (Appendix 3.b.4), although sediment concentrations exceed the suspended matter concentrations. These lower suspended matter concentrations may reflect the decreased emission of REEs into the surface water during the 1990s. Remarkably, saltwater sediment concentrations were higher than fresh water sediment concentrations. Sediment concentrations in fresh water sediments ranged from around 0.2 mg/kg for Lu to 50-100 mg/kg for Ce.

Concentrations in the Rhine estuary (Appendix 3.b.5) are the highest at the Nieuwe Maas site, the 1st Petroleum harbour site and the Botlek site. These concentrations are at least twice those from the concentrations listed by Slooff *et al.* (1993), ranging from 0.25-0.5 mg/kg for Lu to 50-180 mg/kg for Ce. However, the concentration listed by van Son (1994, Appendix 3.b.4) are higher than those listed by Slooff *et al.* (1993), indicating that Slooff *et al.* (1993) may have used suspended matter concentrations.

5.3 Environmental concentrations: pore water

Tijink and Yland (1998) collected pore water from sediments in the Rhine estuary. Since pore water concentrations are supposed to correlate better with bioavailability for sediment dwelling organisms than surface water or sediment concentrations, the reported concentrations are listed in Appendix 3.c.1. Concentrations of REEs in the surface water, as shown by Appendix 3.a.3, are in the same order of magnitude as the concentrations reported for pore water below. Comparison of the Tijink and Yland data with background concentrations, however, is impossible, since no data are available on background concentrations of REEs in pore-water.

5.4 Environmental concentrations: soil

Soil concentrations of unpolluted soils are shown by Appendix 3.d. (Stuyfzand, 1991). In addition, Van Duijvenboden et al. (1992) published average concentrations of several REEs in a variety of soils. Cerium and lanthanum appear to be the most abundant REEs in the unpolluted soil. Soils, polluted with REEs are listed in Slooff *et al.* (1993). These soils can contain up to 700 mg/kg La, 900 mg/kg Ce, 400 mg/kg Nd and 100 mg /kg Pr.

5.5 Background concentrations (C*b*)

Table 5.1. summarises the above paragraphs on environmental concentrations in surface water (both fresh and salt), sediment and soil. The background concentration for soil is defined as the 90th-percentile value of the concentrations in relatively pristine areas (Van den Hoop, 1995). For more information on the variability of C*b* it is referred to appendix 3. Concentrations reported in the Rhine estuary (Tijink and Yland, 1998) are considered anthropogenic and are therefore omitted from the calculation of the background concentrations. This leaves a limited set of data to calculate the background concentrations. In addition, concentrations in fresh surface water were all below the detection limit (Van Son, 1994). These detection-limits (Van Son, 1994) of the REEs are taken as background level for fresh surface water and salt surface water, unless Stuyfzand (1991) reported other measured concentrations for salt surface water. In reality, background concentrations might be lower

which would also result in a lower MPC. As analytical techniques have become more sensitive since the early nineties, it is recommended to do additional measurements on background concentrations in surface waters. In addition, concentrations for groundwater and soil have been reported as ranges, which makes calculation of 90th-percentile values impossible. For these ranges, the lowest reported value or the detection limit reported by Van Son (1994), when the lowest reported value was below the detection limit of the respective report, is taken as background concentration. The reported values are sometimes lower than the detection limits reported by Van Son (1994), probably because of the use of other analytical techniques.

We cannot conclude that these background concentrations only have natural sources, since data on pre-anthropogenic concentrations are lacking.

Table 5.1. Background concentrations of REEs in surface water, sediment and soil

Element	**surface water**		**sediment[3]**		**groundwater[2, 4, 5]**		**soil[2, 6]**
	FRESH[1]	**SALT[2]**	**FRESH**	**SALT**	**PH ³ 6.2**	**PH £ 6.2**	
	(µg/L)		**(mg/kg d.w.)**		**(µg/L)**		**(mg/kg d.w.)**
Sc	<2.80*	0.0007	9.8	12.9	0.001	0.013	0.9
Y	<0.22*	<0.22*	16.8	18.6	0.416	0.077	
La[7]	<0.08*	0.012	36.8	44.1	<0.08*	2	5.0
Ce	<0.13*	<0.13*	68.9	92.6	0.956	<0.13*	9.0
Pr[7]	<0.08*	<0.08*	8.0	10.9	0.125	<0.08*	
Nd	<0.39*	0.0092	36.0	40.4	<0.39*	1	40
Sm	<0.56*	0.00045	5.7	7.48	<0.56*	0.1	0.7
Eu	<0.17*	0.00013	1.2	1.22	<0.17*	0.020	0.1
Gd	<0.33*	<0.33*	5.3	5.65	0.198	<0.33*	
Tb	<0.10*	0.00014	0.70	0.79	<0.10*	0.04	0.1
Dy	<0.22*	<0.22*	3.9	4.05	0.069	<0.22*	
Ho	<0.09*	<0.09*	0.68	0.70	<0.09*	<0.09*	
Er	<0.14*	<0.14*	3.9	1.83	0.072	<0.14*	
Tm[7]	<0.07*	<0.07*	0.26	0.25	0.175	<0.07*	
Yb	<0.13*	0.00082	1.6	1.61	<0.13*	0.05	0.6
Lu	<0.05*	0.00015	0.22	0.23	<0.05*	<0.05*	0.11

1. Detection limits with ICP-MS (van Son, 1994)
2. Stuyfzand, 1991
3. Van Son, 1994, 90th-percentile values
4. Verweij *et al.*, 1994
5. Verweij *et al.*, 1995
6. Van Duijvenboden et al., 1992
7. Concentrations of La, Pr and Tm, tested with Kolmogorov-Smirnov, were not distributed normally ($p< 0.05$)

* detection limit (Van Son, 1994)

6. Derivation of MPCs and NCs

As stated in paragraph 1.6, Maximum Permissible Concentrations (MPCs) can be calculated from MPAs by addition of the background concentrations (C*b*). Negligible Additions (NAs) can be derived as MPA/100, after which the background concentration will be added, resulting in Negligible Concentrations (NCs). Table 6.1. lists the derived MPA, background concentration and resulting MPC for surface water, sediment, and soil. The REEs for which Environmental Risk Limits could be derived are Y, La, Ce, Pr, Nd, Sm, Gd and Dy. For fresh surface water, the derived MPC range from 1.8 µg/L for Nd to 22.1 µg/L for Ce. For salt surface water, however, the derived MPCs are much lower, 0.28 µg/L for Ce to 3.8 µg/L for Dy. This reflects the fact that marine organisms are more sensitive to REEs than fresh water organisms. The same pattern can be seen for sediments, MPC values for fresh water sediments being much higher than those for salt water sediments, whereas background concentrations for salt water sediments are (marginally) higher than background concentrations for fresh water sediments. For soil, only one K*p* was available (Ce), making derivation of MPC values for other REES impossible. Table 6.2 shows the corresponding NCs. These MPCs and NCs can be considered as harmonised, because the EP-method has been used for derivation of soil and sediment MPCs. No further harmonisation is needed.

Table 6.1. MPA, Cb and MPC for surface water, sediment, and soil

Element	**surface water (µg/L)**						**sediment (g/kg d.w.)**						**soil (mg/kg d.w.)**		
	fresh			**salt**			**fresh**			**salt**					
	MPA	**C*b***	**MPC**	**MPA**	**C*b***	**MPC**	**MPA**	**C*b***	**MPC**	**MPA**	**C*b***	**MPC**	**MPA**	**C*b***	**MPC**
Y	6.2	0.22[a]	6.4	0.72	0.22[a]	0.94	1.4	0.017	1.4	0.16	0.019	0.18			
La	10.0	0.08[a]	10.1	1.0	0.010	1.01	4.7	0.039	4.7	0.47	0.044	0.51			
Ce	22.0	0.13[a]	22.1	0.15	0.13[a]	0.28	18.7	0.069	18.8	0.13	0.093	0.22	44	9.0	53
Pr	9	0.08[a]	9.1	0.92	0.08[a]	1.00	5.8	0.008	5.8	0.60	0.011	0.61			
Nd	1.4	0.39[a]	1.8	0.85	0.0092	0.86	7.2	0.036	7.5	0.44	0.040	0.48			
Sm	7.6	0.56[a]	8.2	0.42	0.0005	0.42	2.5	0.006	2.5	0.14	0.008	0.15			
Gd	6.8	0.33[a]	7.1	0.52	0.33[a]	0.85	1.8	0.005	1.8	0.14	0.006	0.14			
Dy	9.1	0.22[a]	9.3	3.6	0.22[a]	3.8	2.2	0.004	2.2	0.88	0.004	0.89			

[a] Detection limit

Table 6.2: NA and NC for surface water, sediment, and soil

Element	**surface water (µg/L)**				**sediment (mg/kg d.w.)**				**soil (mg/kg d.w.)**	
	fresh		**salt**		**fresh**		**salt**			
	NA	**NC**	**NA**	**NC**	**NA**	**NC**	**NA**	**NC**	**NA**	**NC**
Y	0.062	0.28	0.0072	0.22	13.9	30.7	1.61	20.2		
La	0.10	0.18	0.010	0.02	46.8	83.6	4.68	48.8		
Ce	0.22	0.35	0.0015	0.13	187.3	256.2	1.28	93.9	0.440	9.4
Pr	0.09	0.17	0.0092	0.09	58.1	66.1	5.94	16.8		
Nd	0.014	0.40	0.0085	0.009	7.2	43.2	4.36	44.8		
Sm	0.076	0.64	0.0042	0.005	25.2	30.9	1.39	8.9		
Gd	0.068	0.40	0.0052	0.34	17. 9	23.2	1.37	7.1		
Dy	0.091	0.31	0.036	0.26	22.3	26.2	8.84	12.9		

7. Comparison of MPCs with environmental concentrations

Water concentrations that occur in the area of the Netherlands having the highest emission, the Rhine estuary, do not exceed the MPCs of the different REEs (compare Table 6.1 with Appendix 3.a.3). The same holds true for sediment concentrations of REE (compare Table 6.1 with Appendix 3.b.5). Occasionally, environmental concentrations of REEs exceed the NC-levels (compare Table 6.2 with Appendix 3.a.3 and 3.b.5). This happens mostly in water concentrations at the Botlek, Loswal Noord and Terheijde 30-sites, where concentrations of La, Nd and Sm are 1.5 – 15 times the NC. For sediments, only in the 1st Petroleum Harbour concentrations exceeding the NC are found, up to two times. For soil, no comparison could be made, due to lack of data. Therefore, although the data are scarce, we may conclude that REEs do not pose an acute threat to the Dutch ecosystem. However, water and sediment quality has not as yet reached the desired level (NC). Therefore, measures to further reduce emission are recommended. The termination of emission by the phosphate fertiliser industry, this year, can be considered as an important step in that direction.

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Appendix 1 Mailing list

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Appendix 2 Toxicity data

2.1. *Acute* ***toxicity of rare earth metals to freshwater organisms.***

Organism	A	Test-type	Test-sub. purity	Test-water	pH	Hardness mg CaCO$_3$/l	Exposure-time	Crite-rion	Result mg/l		Reference
Yttrium											
Crustacea											
Daphnia magna, <24 h	Y	S	-	am	6.6-8.0	210	48 h	EC50	6.2[a]	α	Den Ouden (1995)
Pisces											
Brachydanio rerio	Y	R	-	am	6.8-8.4	210	96 h	LC50	14	α	Den Ouden (1995)
Lanthanum											
Algae											
Scenedesmus subspicatus	-	-	-	-	-	-	72 h	EC50	1.3		NOTOX proj. no. 143358
Crustacea											
Daphnia magna, <24 h	Y	S	-	am	6.5-8.2	210	48 h	EC50	24[a]	α	Den Ouden (1995)
Pisces											
Brachydanio rerio	Y	R	-	am	6.4-8.2	210	96 h	LC50	23	α	Den Ouden (1995)
Cerium											
Crustacea											
Daphnia magna, <24 h	Y	S	-	am	6.2-8.0	210	48 h	EC50	22[a]	α	Den Ouden (1995)
Pisces											
Brachydanio rerio	Y	R	-	am	6.3-8.1	210	96 h	LC50	22	α	Den Ouden (1995)
Praseodymium											
Crustacea											
Daphnia magna, <24 h	Y	S	-	am	6.2-8.2	210	48 h	EC50	9.0[a]	α	Den Ouden (1995)
Pisces											
Brachydanio rerio	Y	R	-	am	6.2-8.0	210	96 h	LC50	25	α	Den Ouden (1995)

Organism	A	Test-type	Test-sub. purity	Test-water	pH	Hardness mg $CaCO_3$/l	Exposure-time	Criterion	Result mg/l		Reference
Neodymium											
Crustacea											
Daphnia magna, <24 h	Y	S	-	am	6.4-8.3	210	48 h	EC50	1.4[a]	α	Den Ouden (1995)
Pisces											
Brachydanio rerio	Y	R	-	am	6.5-8.4	210	96 h	LC50	21	α	Den Ouden (1995)
Samarium											
Crustacea											
Daphnia magna, <24 h	Y	S	-	am	6.3-8.2	210	48 h	EC50	7.6[a]	α	Den Ouden (1995)
Pisces											
Brachydanio rerio	Y	R	-	am	6.3-8.0	210	96 h	LC50	22	α	Den Ouden (1995)
Gadolinium											
Crustacea											
Daphnia magna, <24 h	Y	S	-	am	6.5-8.2	210	48 h	EC50	6.8[a]	α	Den Ouden (1995)
Pisces											
Brachydanio rerio	Y	R	-	am	6.5-8.0	210	96 h	LC50	19	α	Den Ouden (1995)
Dysprosium											
Crustacea											
Daphnia magna, <24 h	Y	S	-	am	6.5-8.1	210	48 h	EC50	9.1[a]	α	Den Ouden (1995)
Pisces											
Brachydanio rerio	Y	R	-	am	6.2-8.0	210	96 h	LC50	25	α	Den Ouden (1995)

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[a] immobility

2.2. *Chronic* ***toxicity of rare earth metals to freshwater organisms.***

Organism	A	Test-type	Test-sub. purity	Test-water	pH	Hardness mg CaCO$_3$/l	Exposure-time	Crite-rion	Result mg/l		Reference
Yttrium											
Crustacea											
Daphnia magna, <24 h	Y	R	-	am	-	210	21 d	NOEC	0.3[a]	α	Den Ouden (1995)
Daphnia magna, <24 h	Y	R	-	am	7.8-8.7	210	21 d	NOEC	0.7[b]	α	Den Ouden (1995)
Daphnia magna, <24 h	Y	R	-	am	7.8-8.7	210	21 d	NOEC	0.4[c]	α	Den Ouden (1995)
Pisces											
Brachydanio rerio, ELS	Y	R	-	am	-	210	30 d	NOEC	2.8[d]	α	Den Ouden (1995)
Brachydanio rerio, ELS	Y	R	-	am	-	210	30 d	NOEC	2.8[e]	α	Den Ouden (1995)
Brachydanio rerio, ELS	Y	R	-	am	7.5-8.4	210	30 d	NOEC	2.8[b]	α	Den Ouden (1995)
Brachydanio rerio, ELS	Y	R	-	am	7.5-8.4	210	30 d	NOEC	1.2[c]	α	Den Ouden (1995)
Lanthanum											
Algae											
Scenedesmus subspicatus	-	-	-	-	-	-	72 h	NOEC	1.4		NOTOX 1995c
Crustacea											
Daphnia magna	-	R	-	-	-	-	21 d	NOEC	0.1		NOTOX 1995a
Pisces											
Cyprinus carpio	-	R	-	-	-	-	21 d	NOEC	0.26		NOTOX 1995d
Neodymium											
Crustacea											
Daphnia magna, <24 h	Y	R	-	am	7.6-8.7	210	21 d	NOEC	1.6[b]	α	Den Ouden (1995)
Daphnia magna, <24 h	Y	R	-	am	7.6-8.7	210	21 d	NOEC	1.6[c]	α	Den Ouden (1995)
Dysprosium											
Crustacea											
Daphnia magna, <24 h	Y	R	-	am	-	210	21 d	NOEC	<0.2[a]	α	Den Ouden (1995)
Daphnia magna, <24 h	Y	R	-	am	7.9-8.5	210	21 d	NOEC	>2.1[b]	α	Den Ouden (1995)
Daphnia magna, <24 h	Y	R	-	am	7.9-8.5	210	21 d	NOEC	>2.1[c]	α	Den Ouden (1995)
Pisces											
Brachydanio rerio, ELS	Y	R	-	am	-	210	30 d	NOEC	3.0[d]	α	Den Ouden (1995)
Brachydanio rerio, ELS	Y	R	-	am	-	210	30 d	NOEC	3.0[e]	α	Den Ouden (1995)
Brachydanio rerio, ELS	Y	R	-	am	6.7-8.4	210	30 d	NOEC	2.6[b]	α	Den Ouden (1995)
Brachydanio rerio, ELS	Y	R	-	am	6.7-8.4	210	30 d	NOEC	3.8[c]	α	Den Ouden (1995)

a reproduction
b mortality
c fitness
e dry weight

2.3. *Acute* ***toxicity of rare earth metals to saltwater organisms.***

Organism	A	Test-type	Test-sub. purity	Test-water	pH	Salinity ‰	Exposure-time	Crite-rion	Result mg/l		Reference
Cerium											
Crustacea											
Acartia tonsa, 6-8 days old	Y	S	100 %	nw	6.4-8.1	28	48 h	LC50	0.15	α	Bowmer et al (1992) in Maas and Botterweg (1993)
Pisces											
Poecilia reticulata, 1.9 cm, 0.15 g	Y	R	100 %	nw	6.9-8.1	28	96 h	LC50	11.2	α	Hooftman et al (1992) in Maas and Botterweg (1993)
Dysprosium											
Crustacea											
Acartia tonsa, 6-8 days old	Y	S	100 %	nw	6.4-8.1	28	48 h	LC50	3.6	α	Bowmer et al (1992) in Maas and Botterweg (1993)
Pisces											
Poecilia reticulata, 1.9 cm, 0.15 g	Y	R	100 %	nw	6.9-8.1	28	96 h	LC50	15.4	α	Hooftman et al (1992) in Maas and Botterweg (1993)
Gadolinium											
Crustacea											
Acartia tonsa, 6-8 days old	Y	S	100 %	nw	6.4-8.1	28	48 h	LC50	0.52	α	Bowmer et al (1992) in Maas and Botterweg (1993)
Pisces											
Poecilia reticulata, 1.9 cm, 0.15 g	Y	R	100 %	nw	6.9-8.1	28	96 h	LC50	10.8	α	Hooftman et al (1992) in Maas and Botterweg (1993)
Lanthaan											
Crustacea											
Acartia tonsa, 6-8 days old	Y	S	100 %	nw	6.4-8.1	28	48 h	LC50	1.04	α	Bowmer et al (1992) in Maas and Botterweg (1993)
Pisces											
Poecilia reticulata, 1.9 cm, 0.15 g	Y	R	100 %	nw	6.9-8.1	28	96 h	LC50	47	α	Hooftman et al (1992) in Maas and Botterweg (1993)
Neodymium											
Crustacea											
Acartia tonsa, 6-8 days old	Y	S	100 %	nw	6.4-8.1	28	48 h	LC50	0.85	α	Bowmer et al (1992) in Maas and Botterweg (1993)
Pisces											
Poecilia reticulata, 1.9 cm, 0.15 g	Y	R	100 %	nw	6.9-8.1	28	96 h	LC50	9.6	α	Hooftman et al (1992) in Maas and Botterweg (1993)

Acute toxicity of rare earth metals to saltwater organisms - continued

Organism	A	Test-type	Test-sub. purity	Test-water	pH	Salinity ‰	Exposure-time	Crite-rion	Result mg/l		Reference
Praseodymium											
Crustacea											
Acartia tonsa, 6-8 days old	Y	S	100 %	nw	6.4-8.1	28	48 h	LC50	0.92	α	Bowmer et al (1992) in Maas and Botterweg (1993)
Pisces											
Poecilia reticulata, 1.9 cm, 0.15 g	Y	R	100 %	nw	6.9-8.1	28	96 h	LC50	4.5	α	Hooftman et al (1992) in Maas and Botterweg (1993)
Samarium											
Crustacea											
Acartia tonsa, 6-8 days old	Y	S	100 %	nw	6.4-8.1	28	48 h	LC50	0.42	α	Bowmer et al (1992) in Maas and Botterweg (1993)
Pisces											
Poecilia reticulata, 1.9 cm, 0.15 g	Y	R	100 %	nw	6.9-8.1	28	96 h	LC50	10.6	α	Hooftman et al (1992) in Maas and Botterweg (1993)
Yttrium											
Crustacea											
Acartia tonsa, 6-8 days old	Y	S	100 %	nw	6.4-8.1	28	48 h	LC50	0.72	α	Bowmer et al (1992) in Maas and Botterweg (1993)
Pisces											
Poecilia reticulata, 1.9 cm, 0.15 g	Y	R	100 %	nw	6.9-8.1	28	96 h	LC50	16.7	α	Hooftman et al (1992) in Maas and Botterweg (1993)

Appendix 3.a. Reported concentrations of REEs in water

3.a.1. Average concentrations of REEs in salt water, rainwater along the Dutch coast, Rhine water and concentration ranges in groundwater (in two pH classes, raw water) (Stuyfzand, 1991, Van Steenwijk *et al.*, 1992, Verweij *et al.*, 1994, 1995).

	Average concentration			**Dutch groundwater**	
Element	**salt water (µg/L)**	**rain water (µg/L)**	**Rhine water (µg/L)**	**pH ³ 6.2 (µg/L)**	**pH £ 6.2 (µg/L)**
Sc	0.0007	0.038	< d.l.	0.001 – 0.082	0.013 – 0.84
Y				0.416 – 12.218	0.077 – 2.68
La	0.012	< d.l.	< d.l.	< 0.1 – 7.653	2 – 1.3
Ce				0.956 – 10.640	< d.l. – 2.82
Pr				0.125 – 2.150	< d.l. – 0.30
Nd	0.0092	< d.l.	< d.l.	< 0.3 – 8.780	1 – 99
Sm	0.00045	0.06	< d.l.	< 0.02 – 1.953	0.1 - 29
Eu	0.00013	0.02	< d.l.	< 0.005 – 0.480	0.020 – 2.43
Gd				0.198 – 3.731	< d.l. - 4.357
Tb	0.00014	< d.l.	< d.l.	< 0.02 – 0.384	0.04 – 2.5
Dy				0.069 – 2.497	< d.l. - 3.015
Ho				< d.l. - 0.557	< d.l. - 0.627
Er				0.072 – 1.299	< d.l. - 1.487
Tm				0.175	< d.l. - 0.166
Yb	0.00082	< d.l.	< d.l.	<0.02 – 0.990	0.05 – 5.6
Lu	0.00015	< d.l.	< d.l.	< 0.005 – 0.405	< d.l. – 0.9

<d.l. below detection limit.

3.a.2. Maximum concentrations in drinking water (Verweij *et al.*, 1994).

Element	**Bilthoven**	**De Haere**	**Epe**
	Concentration in drinking water (µg/L)		
Sc	< d.l.	< d.l.	< d.l.
Y	1.188	14.22	2.540
La	< d.l.	8.693	1.749
Ce	0.549	11.81	1.824
Pr	0.071	2.420	0.467
Nd	0.355	9.934	1.840
Sm	0.094	2.184	0.388
Eu	< d.l.	0.525	0.100
Gd	0.218	3.791	0.529
Tb	< d.l.	0.475	0.088
Dy	0.150	2.722	0.407
Ho	0.055	0.566	0.103
Er	< d.l.	1.467	0.285
Tm	< d.l.	0.220	< d.l.
Yb	0.196	1.289	0.195
Lu	< d.l.	0.169	< d.l.

3.a.3. Concentrations of REEs in surface water of the Rhine estuary (Tijink and Yland, 1998).

Element	**Brienenoord**	**Nieuwe Maas**	**1^{st} Petroleum harbour**	**Botlek**	**Loswal Noord**	**Terheijde 30**
			Concentration in surface water (µg/L)			
Sc	1.2386	1.3845	0.0728	1.7631	0.0527	0.0472
Y	0.0352	0.0353	0.1155	0.0391	0.1499	0.0286
La	0.0200	0.0163	0.0850	0.0184	0.2040	0.0219
Ce	0.0437	0.0317	0.0955	0.0209	0.1221	0.0290
Pr	0.0055	0.0038	0.0163	0.0045	0.0358	0.0040
Nd	0.0177	0.0176	0.0627	0.0204	0.1466	0.0167
Sm	0.0145	0.0146	0.0283	0.0148	0.0605	0.0263
Sm ex	0.0028	0.0053	0.0131	0.0061	0.0288	0.0036
Eu	0.0022	0.0029	0.0039	0.0030	0.0036	0.0005
Gd	0.0140	0.0105	0.0167	0.0104	0.0203	0.0033
Tb	0.0011	0.0013	0.0017	0.0008	0.0029	0.0007
Dy	0.0096	0.0068	0.0116	0.0094	0.0162	0.0035
Ho	0.0014	0.0007	0.0024	0.0012	0.0035	0.0009
Er	0.0036	0.0031	0.0067	0.0038	0.0090	0.0022
Tm	0.0007	0.0008	0.0009	0.0007	0.0010	0.0005
Yb	0.0034	0.0036	0.0044	0.0049	0.0042	0.0018
Lu	0.0006	0.0005	0.0010	0.0013	0.0007	0.0006

Appendix 3.b. Reported concentrations of REEs in suspended matter and sediment

3.b.1. REE concentrations in sediments and suspended matter in fresh water systems (from Slooff *et al.*, 1993)

Location	**La**	**Ce**	**Nd**	**Gd**	**Sc**
	Concentration in sediment or suspended matter (mg/kg)				
Rhine (Lobith), 1991/1992	16 – 40	25 – 90	20 – 45	5 - 6	
Rhine (Hagestein), 1991/1992	13 – 24	21 – 54	13 – 27	4	7
Meuse (Eysden), 1991	8 – 22	12 – 29	12 – 22	4 - 7	
IJssel (Kampen), 1991	13	21	14	4	
Scheldt/Dintel, 1991	29 – 33	44 – 51	40 – 46	15 - 16	
Lake IJssel, 1991	3	7	< d.l.	< d.l.	
Dollard/Wadden sea, 1983	17 – 49	40 – 124	44 – 120		
Dollard/Wadden sea, 1988	12 – 24	27 – 50	15 – 31		
North sea, 1981	30	64	29		11
North sea, 1992	30 – 40	40 – 80	10 – 50		
range over all sampling points	3-49	7-124	<d.l.-120	<d.l.-16	

3.b.2. REE concentrations in suspended matter from fresh water (van Son, 1994)

Location	**Sc**	**Y**	**La**	**Ce**	**Pr**	**Nd**	**Dy**
	Concentration in suspended matter (mg/kg)*						
Bovensluis			0.43	0.61			
Borgharen		0.80	1.55	3.20	0.37	1.49	
Eemdijk	5.9	2.24	2.45	5.10	0.64	2.58	0.51
Eijsden		0.56	0.70	1.26	0.27	1.02	0.50
Haringvlietsluis			0.45	0.56	0.19		
Ketelmeer		0.51	0.55	0.88	0.18		
Lobith		0.45	0.52	0.69	0.18		
Amsterdam		0.70	1.11	1.60	0.28	1.00	
Sas van Gent			0.16				
Steenbergen			0.23	0.36			
Zeewolde			0.27	0.37			
range		0.5-2.2	0.2-2.5	0.4-5.1	0.2-0.6	1.0-2.6	

*figures are at least twice the detectionlimit. At the Eemdijk location also Er (0.29 mg/kg), Yb (0.33 mg/kg) and Lu (0.11 mg/kg) concentrations were about twice the detection limits. At the other locations, REE concentrations were lower than/around the detectionlimit.

3.b.3. Suspended matter concentrations of REEs in the Rhine estuary (Tijink and Yland, 1998).

Element	**Brienenoord**	**Nieuwe Maas**	**1st Petroleum harbour**	**Botlek**	**Loswal Noord**	**Terheijde 30**
			Concentration in suspended matter (mg/kg)			
Sc	22.4			27.3		9.36
Y	25.3			31.9		2.10
La	48.9			62.4		3.74
Ce	75.0			106		7.46
Pr	10.6			13.8		0.87
Nd	34.1			49.6		3.21
Sm	6.24			8.42		0.58
Eu	0.93			1.34		0.10
Gd	5.17			6.92		0.44
Tb	0.85			1.05		0.07
Dy	4.94			5.91		0.42
Ho	0.92			1.09		0.08
Er	2.64			3.03		0.22
Tm	0.39			0.42		0.03
Yb	2.59			2.67		0.19
Lu	0.38			0.39		0.03

3.b.4. Sediment concentrations of REEs (van Son, 1994).

Site[*]	f/ si/s[**]	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
		Concentration in sediment (mg/kg)[***]															
A	f	10.0	16.8	37	69	8.0	31	5.9	1.2	5.3	0.73	4.0	0.71	3.9	0.25	1.6	0.22
B	f	6.0	13.9	33	67	7.9	30	5.4	1.1	4.7	0.58	3.2	0.53	3.0	0.90	1.2	0.16
C	f	2.3	6.2	14	28	3.2	12	2.3	0.4	2.1	0.28	1.5	0.26	1.4	0.09	0.6	0.09
D	f	10.1	16.5	35	68	7.8	30	5.6	1.2	5.2	0.70	3.9	0.68	3.8	0.25	1.5	0.22
E	f	6.4	12.5	28	52	6.1	23	4.5	0.9	4.1	0.54	2.9	0.51	2.8	0.18	1.1	0.16
F	f	7.8	13.7	34	50	5.8	2.5	4.3	1.0	3.8	0.51	2.7	0.48	1.3	0.23	1.2	0.21
G	f	4.1	10.1	22	44	5.2	20	3.8	0.7	3.4	0.45	2.5	0.43	2.3	0.16	1.0	0.15
H	f	7.9	12.9	145	99	22.0	81	5.7	0.9	5.3	0.61	3.4	0.52	3.0	0.18	1.2	0.17
I	f	6.4	20.5	32	63	7.6	30	5.7	1.2	5.4	0.70	3.8	0.68	3.9	0.26	1.7	0.25
J	f	7.6	15.1	28	56	6.5	25	4.9	1.0	4.7	0.65	3.6	0.65	3.5	0.24	1.5	0.21
K	f	3.2	9.4	21	39	5.0	19.5	4.0	0.7	3.9	0.54	2.9	0.50	2.9	0.19	1.2	0.17
L	f	4.1	8.9	17	35	4.0	15	2.9	0.6	2.7	0.37	2.0	0.36	2.0	0.13	0.8	0.11
D	si	11.8	19.4	37	72	7.1	31	5.9	1.3	5.5	0.75	4.1	0.72	4.0	0.27	1.6	0.23
E	si	10.0	20.5	43	81	9.4	36	6.7	1.3	6.2	0.83	4.4	0.78	4.2	0.29	1.7	0.25
I	si	6.3	19.8	28	54	6.4	26	5.1	1.1	4.8	0.62	3.4	0.61	3.5	0.23	1.5	0.23
M	s	9.5	18.5	38	79	9.5	37	6.7	1.1	5.2	0.73	3.8	0.65	1.7	0.23	1.3	0.20
N	s	9.5	15.1	36	76	8.9	34	6.4	0.9	4.8	0.68	3.5	0.59	1.5	0.20	1.2	0.19
O	s	14.9	19.2	45	98	11.3	44	8.2	1.4	6.1	0.89	4.5	0.79	2.1	0.26	1.7	0.23
P	s	11.6	18.3	44	92	10.9	40	7.4	1.2	5.6	0.78	4.0	0.69	1.8	0.25	1.6	0.23
Q	s	11.7	11.7	25	55	6.4	24	4.5	0.9	3.4	0.50	2.6	0.46	1.2	0.17	1.0	0.15
R	s	12.2	16.9	31	67	8.1	31	6.0	1.2	4.6	0.67	3.5	0.64	1.7	0.21	1.4	0.20
S	s	11.2	15.5	30	66	7.7	29	5.5	1.1	4.3	0.62	3.3	0.59	1.6	0.21	1.3	0.18
T	s	10.8	13.4	24	51	6.1	23	4.5	0.9	3.6	0.54	2.8	0.51	1.4	0.19	1.1	0.17
U	s	10.5	14.5	28	59	7.1	27	5.2	1.0	4.1	0.61	3.2	0.57	1.5	0.20	1.3	0.19
V	s	12.7	16.8	30	64	7.6	29	5.7	1.1	4.5	0.68	3.6	0.65	1.7	0.24	1.4	0.21
range		2-15	6-21	14-145	28-99	3-22	12-44	2-8	0.4-1.3	2.1-6.2	0.3-0.9	1.5-4.4	0.3-0.8	1.2-4.2	0.1-0.9	0.6-1.7	0.1-0.3

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[*] A: Bovensluis, B: Borgharen, C: Eemdijk, D: Haringvlietsluis, E: Ketelmeer, F: Lobith, G: Houtribhaven, H: Amsterdam, I:Sas van Gent, J: Steenbergen, K: Zeewolde, L: Rotterdamse hoek, M: Noordwijk, N: Terschelling, O: Terschelling, 100 km out of the coast, P: Rottumerplaat, Q: Walcheren, R: Hanseert, S: Terneuzen, T: Vlissingen, U: Dollard, V: Eems

[**] f = fresh water; si = sieved (63 µm); s = salt water

[***] Figures are at least twice the detectionlimit.

3.b.5. Sediment concentrations of REEs in the Rhine estuary (Tijink and Yland, 1998).

Element	**Brienenoord**	**Nieuwe Maas**	**1^{st} Petroleum harbour**	**Botlek**	**Loswal Noord**	**Terheijde 30**
			Concentration in sediment (mg/kg)			
Sc	16.5	19.1	29.4	24.5	11.8	6.85
Y	19.1	39.1	56.4	20.4	16.5	3.77
La	26.6	37.9	93.8	27.2	25.1	6.33
Ce	51.9	64.0	183.3	51.0	48.0	12.5
Pr	6.06	8.29	21.5	6.18	5.85	1.42
Nd	23.2	32.7	82.5	23.8	22.3	5.38
Sm	4.34	6.17	13.5	4.51	4.17	0.99
Eu	0.79	0.99	2.26	0.68	0.62	0.18
Gd	3.53	5.43	11.4	3.77	3.38	0.78
Tb	0.58	0.89	1.65	0.61	0.54	0.13
Dy	3.38	5.49	9.45	3.62	3.15	0.76
Ho	0.62	1.08	1.72	0.68	0.58	0.14
Er	1.81	3.11	4.62	1.93	1.64	0.39
Tm	0.26	0.43	0.59	0.27	0.23	0.06
Yb	1.74	2.72	3.52	1.81	1.55	0.37
Lu	0.25	0.38	0.48	0.26	0.22	0.05

Appendix 3.c. Reported concentrations of REEs in pore water

3.c.1. Pore water concentrations of REEs in the Rhine estuary (Tijink and Yland, 1998).

Element	**Brienenoord**	**Nieuwe Maas**	**1st Petroleum harbour**	**Botlek**	**Loswal Noord**	**Terheijde 30**
			Concentration in pore water (µg/L)			
Sc	0.2060	0.3438	0.1748	0.4211	0.1160	0.0951
Y	0.0469	0.1761	0.1407	0.1246	0.1444	0.0572
La	0.0419	0.0834	0.1251	0.0632	0.0479	0.0603
Ce	0.0482	0.0775	0.1988	0.0649	0.0631	0.0753
Pr	0.0062	0.0127	0.0278	0.0087	0.0084	0.0101
Nd	0.0234	0.0636	0.1175	0.0683	0.0387	0.0365
Sm	0.0065	0.0188	0.0209	0.0210	0.0098	0.0066
Eu	0.0083	0.0057	0.0036	0.0154	0.0010	0.0005
Gd	0.0056	0.0207	0.0214	0.0178	0.0092	0.0056
Tb	0.0008	0.0031	0.0031	0.0055	0.0017	0.0010
Dy	0.0050	0.0228	0.0202	0.0472	0.0129	0.0062
Ho	0.0010	0.0047	0.0041	0.0069	0.0030	0.0013
Er	0.0028	0.0137	0.0177	0.0135	0.0100	0.0039
Tm	0.0005	0.0022	0.0016	0.0049	0.0015	0.0006
Yb	0.0017	0.0118	0.0091	0.0116	0.0106	0.0036
Lu	0.0006	0.0022	0.0015	0.0056	0.0018	0.0005

Appendix 3.d. Reported concentrations of REEs in soil

3.d.1. Soil concentration of REEs (Stuyfzand, 1991).

Element	**Soil concentration unpolluted soil (mg/kg)**	**grassland**		**farmland**		**orchard**		**woodland**
		(s)	**(p)**	**(s)**	**(c)**	**(s)**	**(c)**	**(s)**
					(mg/kg)			
Sc	7	1.3	3.3	1.5	7.4	2.0	8.0	0.9
La	40	7.1	11.7	8.6	25.1	10.7	29.9	5.0
Ce		12.9	22.3	15.5	50.6	21.2	56.9	9.0
Nd	(40)							
Sm	(7)	1.0	2.1	1.3	4.5	1.8	5.2	0.7
Eu	(2.3)	0.3	0.5	0.2	1.3	0.3	1.0	0.1
Tb	(1)	0.2	0.3	0.2	0.6	0.2	0.7	0.1
Yb	3	0.9	0.9	0.9	2.0	1.2	2.3	0.6
Lu	(0.7)	0.15	0.15	0.17	0.34	0.22	0.39	0.11

(s) sand
(p) peat
(c) clay