NATIONAL INSTITUTE OF PUBLIC HEALTH AND THE ENVIRONMENT
BILTHOVEN, THE NETHERLANDS

Report no. 734301014

Geochemistry of some rare earth elements in groundwater, Vierlingsbeek, the Netherlands

R. P.T. Janssen, W. Verweij and J.F.M. Versteegh

August, 1997

This investigation has been performed by order and for the account of the Ministry of Public Housing, Spatial Planning and the Environment, Directorate-General Environment, Directorate Drinking Water, Water, Agriculture

National Institute of Public Health and the Environment (RIVM), P.O. Box 1,
3720 BA Bilthoven, The Netherlands
Telephone: +31 - 30 - 274 91 11, telefax: +31 - 30 - 274 29 71

MAILING LIST

1-2	Directorate General for Environmental Protection, Directorate for Drinking Water, Water and Agriculture
3	Ir. P.J. Verkerk, Director for Public Health of the Environment
4	Dr.Ir. B.C.J. Zoeteman, Deputy Director-General for the Control of the Environment
5	Ir. G.W. Ardon, DGM-DWL
6	Ir. W. Cramer, DGM-DWL
7	Dr.Ir. B.J.A.M. Haring, DGM-DWL
8-15	Regional Inspectorate of Public Health and the Environment
16-40	Drinking Water Companies
41	Ing. A.D. Bannink, Water Company Oost-Brabant
42	Dr. B.J.H. van Os, RGD, Haarlem
43	Ing. H.Meijer, Water Company Gelderland
44	Drs. W.C.M. Bakkum, Water Company Gelderland
45	Ir. A.H. Bussemaker, IBC-DWL, RIMH Noord-Holland
46	Prof.Dr.Ir. H.J.W. de Baar, NIOZ, Texel
47	Prof. Dr. C.A.J. Appelo, VU Amsterdam
48	Ir. R. Kreutz, VEWIN
49	Ir. L.C. Rietveld, TU Delft
50	Ir. J.Q.J.C. Verberk, TU Delft
51	Prof.Ir. N.D. van Egmond, Directorate RIVM, Director Environment
52	Ir. A.H.M. Bresser, Director Laboratory for Water and Drinking Water Research, RIVM
53	Ir. F. Langeweg, RIVM
54	Drs. F. Kragt, RIVM-LWD
55	Drs. T. Aldenberg, RIVM-LWD
56	Ir. J. Hrubec, RIVM-LWD
57	Ir. J.H.C. Mülschlegel, RIVM-LWD
58	Ir. N. Jonker, RIVM-LWD
59	Drs. P. van Puijenbroek, RIVM-LWD
60	Ing. C.J. Dagelet, RIVM-LWD
61	J.E.M. van Koten-Vermeulen, RIVM-CSR
62	Drs. J.A. Janus, RIVM-CSR
63	Ir. G.J. Heij, RIVM-NOP
64	Drs. R. Ritsema, RIVM-LAC
65	Dr. J.L.M. de Boer, RIVM-LAC
66	Ing. T. van der Velde-Koerts, RIVM-LAC
67	D. Wever, RIVM-LBG
68	Drs. W.J. Willems, RIVM-LBG
69-71	Authors
72	Depot of Dutch Publications and Dutch Bibliography

73	Head Bureau Education and Public Relations, RIVM, Drs. J.A.M. Lijdsman-Schijvenaars
74	Bureau Registration RIVM-reports
75-76	Library RIVM
77-90	Spare copies RIVM

TABLE OF CONTENTS

ABSTRACT

Speciation calculations were carried out on groundwater samples to shed more light on the chemical processes of rare earth elements (REE). These samples were taken from seven boreholes at several depths near the drinking water pumping station, Vierlingsbeek, The Netherlands. Complexation and precipitation reactions including inorganic and dissolved organic carbon (DOC) compounds, were taken into account. The REE speciation showed REE^{3+}, $REE(SO_4)^+$, $REE(CO_3)^+$ and REE(DOC) to be the major species. Dissolution of REE-enriched solid phases probably does not account for the observed REEs in groundwater. This may be due to desorption of REEs on metal hydroxides. Multiple linear regression showed pH to be by far the most significant groundwater characteristic contributing to the variation in REE concentrations. Regression equations including only pH were derived to predict REE concentrations in groundwater.

SAMENVATTING

In de nabijheid van het drinkwaterpompstation Vierlingsbeek zijn uit zeven boorputten grondwatermonsters op verschillende diepten genomen. Speciatieberekeningen zijn uitgevoerd om meer inzicht te krijgen in de chemische processen van zeldzame aarden (REE). Bij de modellering is rekening gehouden met complexatie en precipitatieprocessen van opgeloste organische koolstof (DOC) en anorganische verbindingen. Uit de speciatieberekeningen bleek dat REE^{3+}, $REE(SO_4)^+$, $REE(CO_3)^+$ en REE(DOC) de belangrijkste species zijn. De aanwezigheid van de REE's in het grondwater wordt waarschijnlijk niet veroorzaakt door het in oplossing gaan van REE-bevattende vaste fasen, maar mogelijk door desorptie van REE's aan metaalhydroxiden. Via multiple lineaire regressie is aangetoond dat de pH verreweg de meest significante grondwaterkarakteristiek is welke de variatie in REE concentraties bepaalt. Regressievergelijkingen zijn afgeleid enkel op grond van de pH, waarmee REE concentraties in grondwater kunnen worden voorspeld. Voor de praktijk van de drinkwatervoorziening betekent dit dat pH-metingen (liefst in waarnemingsputten) een gemakkelijke en redelijk betrouwbare indicator vormen voor de concentratie zeldzame aarden.

1. INTRODUCTION

Rare earth elements (REE) occur in many naturally occuring minerals. Weathering processes, which may be enhanced by acidification of acid deposition, cause some release of these metals to the groundwater. This may lead to elevated levels of REE in groundwater. Because of the toxicological properties of REE, monitoring of groundwater which is used for drinking water production may be useful if relatively high concentrations of REE are expected.

A survey among 36 drinking water pumping stations in The Netherlands showed that at 18 stations one or more of the REEs were found in raw groundwater in concentrations above the detection limit (Verweij *et al.*, 1995). At three of these stations, REE concentrations were found higher than indicative admissible concentrations (IAC), values derived on a toxicological basis. At one of these pumping stations, Vierlingsbeek, concentrations for Y, La, Ce, Pr, Nd, Sm and Eu were measured above the detection limit, and for Y, La and Ce above the IAC.

A model for predicting REE concentrations based on easily accessible water characteristics, would be a very valuable tool for water quality purposes. However, until now the geochemistry of REEs in groundwaters is poorly understood. Verweij *et al.* (1995 and 1996) found correlations between REE concentrations and pH and to a lesser extent also bicarbonate. Chemical speciation calculations based upon thermodynamic principles, may shed more light on the chemical processes of REEs in groundwater.

Wood (1990) comprehensively reviews the available thermodynamic data for REE-inorganic complexes. REE should exibit strong, predominately electrostatic complexing with especially fluoride, sulfate, phosphate, carbonate and hydroxide. A considerable amount of concordant thermodynamic data are available for the hydroxide-, sulfate-, nitrate-, and chloride complexes of REE. Accurate stability constants of some REEs have been determined for carbonate complexes by Cantrell and Byrne (1987) and for phosphate complexes by Bingler and Byrne (1989) and Byrne *et al.* (1991). The stability constants of the remaining REEs were evaluated by interpolation (Millero, 1992; Lee and Byrne, 1992 and 1993). Stability complexes for REE-DOC complexes have not been measured or interpolated. Firsching and Brune (1991) report experimental measurements of REE-mineral solubility constants, showing that REE phosphates and carbonates are highly insoluble.

REE speciation calculations have mainly been carried out in seawater. REE speciation in seawater is dominated by carbonate complexation (Cantrell and Byrne, 1987). To our knowledge, speciation calculations of REEs based on measured data in groundwater, have not been carried out yet. It is expected that phosphate and sulfate may be the dominant species, dependent on pH and concentrations. In waters with high phosphate concentrations and/or less dominated by REE-carbonates (e.g. pore waters, rivers) REE complexation by phosphates may work out to be quite significant (De Baar *et al.*, 1991).

The present study concerns chemical speciation calculations of Vierlingsbeek pumping station to gain more insight in the chemical processes which may control REE concentrations in groundwater. The complexation of REE by dissolved organic carbon (DOC) was included in these speciation calculations. Moreover, we tested the hypothesis if concentrations of dissolved REEs are determined by dissolution of some REE-containing minerals, for instance some calcium-phosphate-mineral. To that end, we determined saturation indices of several minerals and compared to theoretically expected patterns. Finally, groundwater characteristics which significantly influence REE-concentrations were determined by multiple linear regression. Regression models were developed to predict REE-concentrations in groundwater.

2. MATERIALS AND METHODS

Sampling

Water samples were collected from seven bore holes nearby pumping station Vierlingsbeek in 1995. The bore holes serve to monitor drinking water quality in the surroundings of the pumping station. Water samples were collected at several depths at each bore hole. The depth at which samples were taken ranged from 2 to 41 m below the surface. The samples were taken from so-called minifilters, with screens only 5 cm at each depth. This ensures that the samples were not mixtures of several types of water. The pH and bicarbonate concentrations were measured in the field. The groundwater samples were filtered over 0.45 µm filters. The groundwater samples were acidified with concentrated nitric acid to set the pH 1 and used for the analysis of rare earth elements.

Analysis

Groundwater samples were analysed for some rare earth elements (Ce, Eu, La, Nd, Pr, Sm, and Y) by inductively coupled plasma mass spectrometry (ICP-MS). Details of the methods can be found elsewhere (De Boer *et al.*, 1996). Detection limits were 0.05 µg/l, except for La (0.2 µg/l).

Major cations and anions

Major cation and anion (except for bicarbonate) concentrations from the seven boreholes at each depth was taken from the datasets of the Water company Oost-Brabant (WOB). Water samples were collected regularly and analysed for many parameters including: pH, electric conductivity (EC), Cl^-, SO_4^{2-}, NO_3^- ,PO_4^{3-} ,Na , K, Mg, Ca, Mn, Fe, Al, and compounds oxidizable by $KMnO_4$. The datasets used in this study originate from water samples collected in the period from 1987 until 1991. The pH measured by the water company was occasionaly a little lower than the pH of the water samples for REE analysis. This might be due to ongoing acidification by acid deposition. However, it is assumed that the water compostion has not changed greatly during the time period of collection of the water samples for major cations and anions, and REE.

Chemical Speciation Calculations

Chemical speciation in the groundwaters was calculated by using the program GECHEQ, version 6, release 02 (Verweij, 1996). Next to the major cation and anion concentrations from the WOB-database and the measured pH, bicarbonate and REE concentrations, the following provisions were made before GECHEQ6 calculations were executed:

- Dissolved Organic Carbon (DOC) concentrations were estimated by the relation between compounds oxidizable by $KMnO_4$ and DOC in raw groundwater from pumping stations (REWAB dataset - water quality data from the Dutch water companies) according to: $[DOC]\ (mg/l) = 0.5488*[KMnO_4]\ (mg/l) + 0.2016$ ($n=788$; $R^2 = 0.87$).
- The GECHEQ6 program used at I=0 constants from the following sources:
  - Inorganic species (not REE) : NIST (1995)

Table 1. Complex forming constants for REE-DOC (shown as ^{10}log) as used in GECHEQ6. (Charges omitted for clarity.)

Site	Equilibrium	Y	La	Ce	Pr	Nd	Sm	Eu
1	$REE+DOC \leftrightarrows REE\text{-}DOC$	4.749	4.487	4.576	4.339	4.703	4.415	4.880
2	$REE+HDOC \leftrightarrows REE\text{-}DOC+H$	2.015	0.495	1.369	1.230	1.311	1.904	2.396
3	$REE+HDOC \leftrightarrows REE\text{-}DOC+H$	0.210	-1.109	-0.361	-0.515	-0.389	0.063	0.550
4	$REE+H_2DOC \leftrightarrows REE\text{-}DOC+2H$	-7.104	-9.169	-7.955	-8.051	-8.094	-7.118	-6.615
5	$REE+H_2DOC \leftrightarrows REE\text{-}DOC+2H$	-9.598	-11.385	-10.345	-10.463	-10.442	-9.662	-9.164

  - Y/REE-NO_3; -SO_4 ; -$(SO_4)_2$; -Cl; -Cl_2 and -OH : NIST (1995); Y/REE-$(OH)_2$: Turner *et al.* (1981)
  - REE-CO_3 and -$(CO_3)_2$: Lee and Byrne (1993); REE-HCO_3 : Millero (1992)
  - Y-CO_3 and -$(CO_3)_2$: Liu and Byrne (1995)
  - REE-PO_4 and -$(PO_4)_2$: Lee and Byrne (1992); REE-HPO_4; -$(HPO_4)_2$ and -H_2PO_4 : Millero (1992)
  - Y-PO_4; -($PO_4)_2$; -HPO_4; -$(HPO_4)_2$ and -H_2PO_4 : were assumed to be equal to the same complexes for Sm (Byrne and Lee, 1993)
  - Y/REE complexation by DOC was extrapolated from Cu complexation by DOC as modeled by Cabaniss and Shuman (1988a and 1988b). According to them, five metal binding sites on DOC can be distinghuised. They were able to define five complex forming constants for Cu with DOC, assuming that 50% of the measured [DOC] is reacting. Via a similar method and using linear free-energy relationships, we defined complex forming constants for each REE and Y with DOC (Table 1).
  - Precipitates were allowed to form , since they may be present as finely dispersed particles. Mineral solubility constants (not REE) as well as REE$(OH)_3$ and REE$_2(CO_3)_3$ solubility constants were taken from NIST (1995). Pure crystalline REE-phosphate precipitates were not allowed to form. Preliminary calculations (using constants taken from Firsching and Brune, 1991) showed that they occasionaly may be formed; however, it is assumed that these do not exist in natural systems (Byrne and Kim, 1993).
- The ionic strengths (I) of the groundwaters were calculated based upon the measured EC, according to the formula: I (mol/l) = 0.013*EC (mS/cm) (Griffin and Jurnak, 1973), and used as input in GECHEQ6.
- Redox- and adsorption equilibria were not included in the calculations.

3. RESULTS AND DISCUSSION

Chemical speciation calculations

REE concentrations in the groundwater samples for all seven bore holes are shown against depth in Figure 1. From all measured REE concentrations, Ce, Y, Nd and La have the highest concentrations especially near the surface. Sm, Pr and Eu concentrations are low or below the detection limit at nearly all depths. The differences in REE concentrations vary per bore hole, and are the highest at KP038 and KP040.

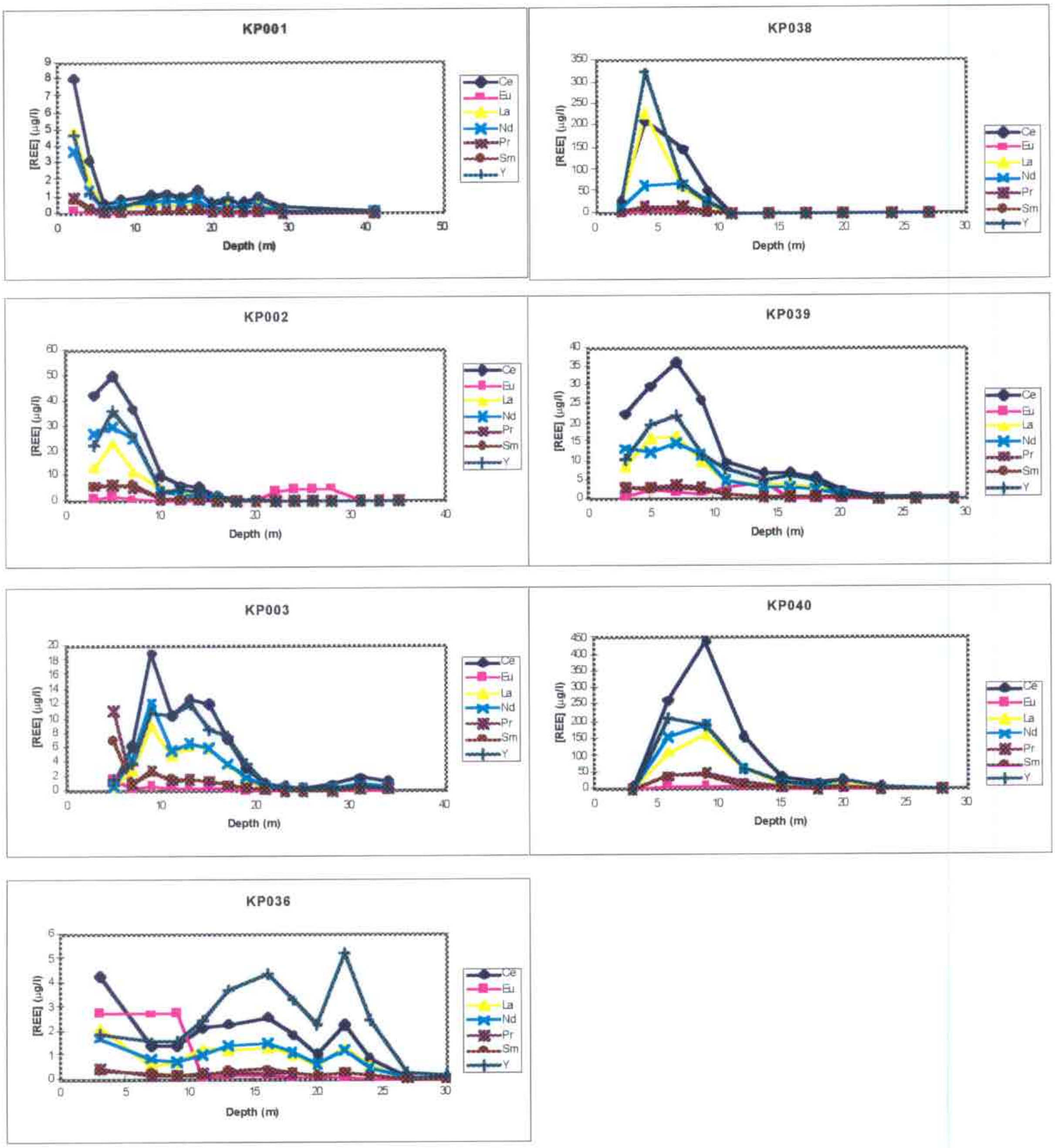

Figure 1. Total concentrations of the REEs (in µg/l) as a function of depth for the seven bore holes.

REE speciation of all seven bore holes at all depths is calculated by the computer program GECHEQ6. Measured pH, HCO_3^-- and REE-concentrations, and major cation and anion concentrations from the WOB-dataset were used as input parameters (Appendices I and II). REE speciation in groundwater of one typical bore hole (KP001) of the predominant species is presented in Figure 2. The contribution of each species to REE speciation is presented as a

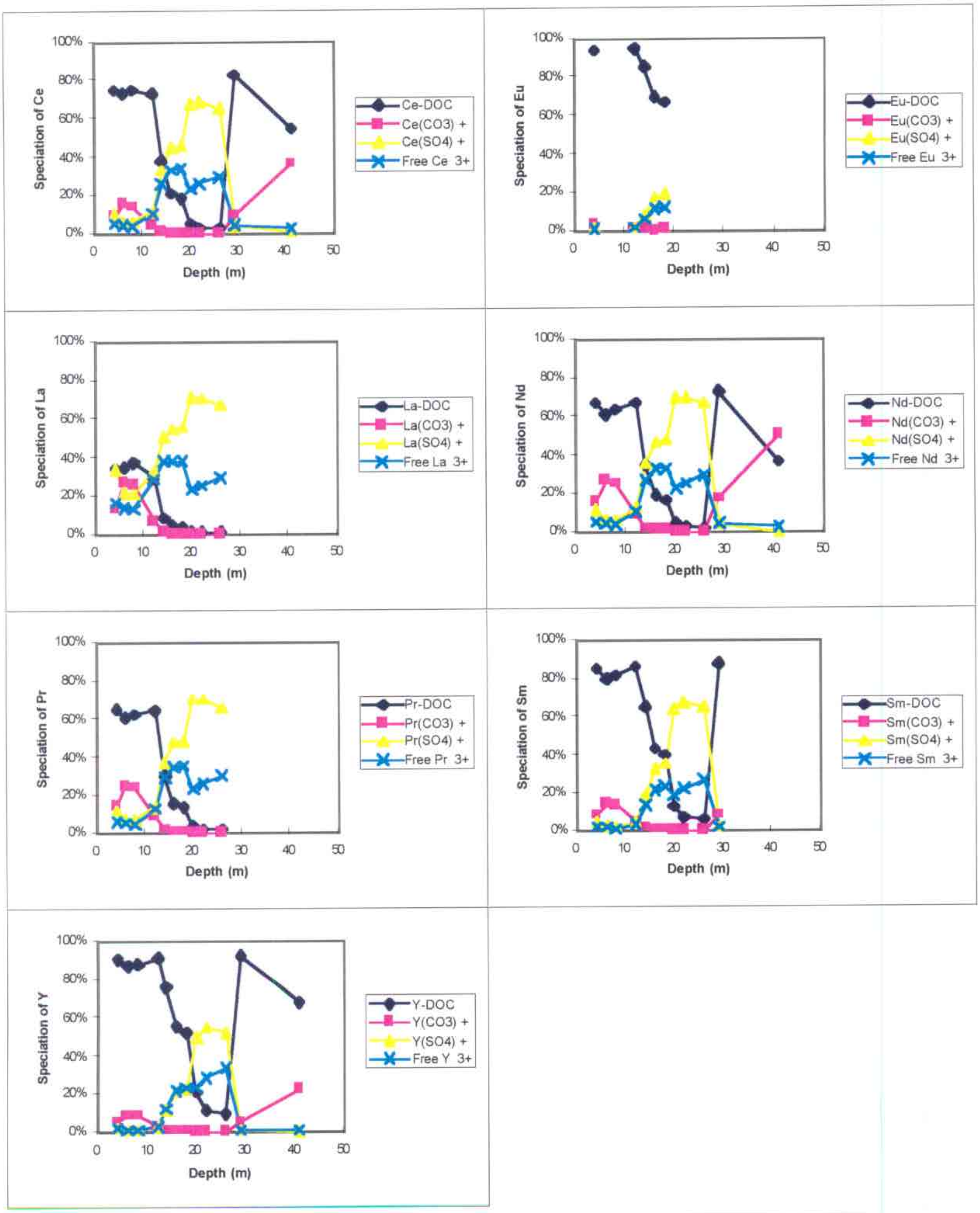

Figure 2. Speciation of the REEs (in %) as a function of depth for bore hole KP001.

percentage of the total REE concentration. The REE speciation shows REE^{3+}, $REE(SO_4)^+$, $REE(CO_3)^+$ and REE(DOC) being the major species. Especially REE complexes with sulphate and DOC are the predominant species. Despite that only a small fraction of sulphate and DOC is complexed with REE. Near the surface carbonate, bicarbonate and DOC are the predominant REE species. In deeper groundwater sulphate and free REE ions are the predominant REE species. The change of the REE speciation with depth seems to be related mainly to the concentrations of the complexing anions (compare Appendix 1 with Figure 2). The absence of REE-complexes of phosphate, chloride, nitrate and hydroxide (Figure 2), shows the negligible contribution of these species in all groundwaters. Surprising is the absence of REE-phosphate species, because in literature it was suggested that in groundwaters these species may be important. This is linked up with the relatively low phosphate concentrations and the complexation of most phosphate with aluminium and in some cases manganese.

Pure REE minerals (i.e. $REE(OH)_3$, $REE(PO_4)$, $REE_2(CO_3)_3$) may be present. These minerals could play a role in controlling the solubility of REEs. However, the speciation calculations showed that in none of the groundwaters a REE precipitate was calculated. Simple dissolution of the REE minerals does not provide an adequate explanation for the observed REEs in groundwater. In some cases $REE(PO_4)$ precipitates were calculated but according to Byrne and Kim (1993), these precipitates are not present in natural systems and thus neglected in the further speciation calculations. Moreover, REEs in groundwaters can reside in the crystal lattice of minerals like $CaCO_3$, apatite and metal-(hydr)oxides (Gosselin *et al.*, 1992). Dissolution of REE-enriched solid phases may account for the observed REEs in groundwater. An alternative hypothesis is that the concentration of dissolved REEs is controlled by pH-dependent adsorption/desorption to some solid phase, e.g. metal-(hydr)oxides. The speciation calculations actually did show the presence of metal-(hydr)oxides which may contain REEs. In the last section of this chapter these hypotheses will be discussed.

Relations between REE-concentrations and groundwater characteristics

To study the relation between REE concentrations and groundwater characteristics, multiple linear regression was carried out. This is subject of two considerations: (i) the most important groundwater characteristics influencing REE concentrations should be included in the regression equation, and (ii) correlation between groundwater characteristics should be avoided. Viz. (i) It may be assumed that among the measured groundwater characteristics influencing REE concentrations considerably are: pH, I (ionic strength, which is estimated from EC), DOC (estimated from compounds oxidizable by $KMnO_4$), Ca, Al, Fe, Mn, and major anions. The pH because it competes for binding sites and affects the surface charge; DOC and major anions because they complex REEs; Ca, Al, Mn and Fe because if present as particles they may bind or enclose REEs, and I because this is a measure of the total amount of ions. NO_3^- and PO_4^{3-} were not included because the speciation calculations showed that these anions were not important in complexing REEs. Besides, these anions were in many groundwaters determined below the detection limit. These missing data negatively influences the regression equations (i.e. reduces the number of observations, n). Viz. (ii) Correlations between groundwater characteristics was investigated by calculating a correlation matrix. This showed that pH and [HCO_3^-] were highly correlated (R= 0.90), and to a lesser extent also [Cl^-] and [SO_4^{2-}] (R=0.79). I (ionic strength) was correlated to [Cl^-] (R=0.69), [SO_4^{2-}] (R=0.79) and [Ca] (0.87). Highly correlated characteristics should not be both included in the regression model, since this does not add any further information. Therefore, [HCO_3^-] and I were not included. Since the speciation calculations showed that SO_4^{2-} is an important complexing anion for REEs, [Cl^-] was also excluded from the model.

As a measure of goodness-of-fit, we used R^2. Because the raw REE, anion and cation concentrations showed a log-normal distribution, the data sets used in this study were log transformed (except pH) before multiple linear regression was carried out, in order to meet the assumption of normality for the regression models (Heisterkamp *et al.*, 1992). By means of stepwise regression log REE concentrations were correlated to log-transformed groundwater characteristics. The equations obtained for each REE, and the significant groundwater characteristics ranked in order of importance are shown in Table 2.

The regression model is fairly sucessful in fitting the observed data: R^2 values are relatively high, and vary from 0.42 for Eu to 0.86 for Y. The table shows that pH significantly contributes to the variation in REE concentrations. SO_4 and DOC are other important groundwater characteristics. This corresponds with the importance of complexing REEs as shown earlier with the speciation calculations. The presence of Fe and Mn in some of the models may suggest that some REEs are bound or enclosed by Fe-Mn-(hydr)oxides. The absence of Ca in the models suggests that REEs are not enclosed by Ca-minerals. This is in line with the conclusions of the speciation calculations.

Table 2. Correlation between log [REE] in groundwater and log transformed groundwater characteristics according to: log [REE] = a* pH + b*log[DOC] + c*log[SO_4] + d*log[Fe] + e*log[Al] +f*log[Mn] + g*log[Ca] + h. The significant groundwater characteristics are ranked in decreasing order of importance.

	significant groundwater characteristics	model	n	R^2
Ce	pH>>DOC>SO_4	-1.03*pH+0.89*DOC-0.81*SO_4+6.96	50	0.81
Eu	Fe>pH	0.51*Fe-0.54*pH+2.61	29	0.42
La	pH>>SO_4~Mn~DOC	-0.98*pH-0.62*SO_4 -0.62*Mn+0.41*DOC+6.13	30	0.82
Nd	pH>DOC~SO4>Fe	-0.99*pH+0.72*DOC-0.88*SO_4 -0.15*Fe+6.53	49	0.85
Pr	pH>>SO_4>DOC	-0.97*pH-1.03*SO_4+0.55*DOC+6.43	31	0.82
Sm	pH>>SO_4>DOC	-0.92*pH-0.98*SO_4+0.51*DOC+6.10	32	0.82
Y	pH>>DOC>SO_4	-0.99*pH+0.67*DOC-0.49*SO_4+6.17	50	0.86

$p<0.05$ and concentrations in mg/l, except REE (in μg/l)

Table 3. Correlation between log [REE] in groundwater and pH.

	model	n	R^2
Ce	-0.88*pH+4.91	86	0.53
Eu	-0.30*pH+1.13	57	0.08
La	-0.68*pH+3.83	63	0.44
Nd	-0.86*pH+4.53	85	0.54
Pr	-0.74*pH+3.53	64	0.48
Sm	-0.71*pH+3.31	67	0.49
Y	-0.87*pH+4.84	86	0.64

$p<0.05$ and [REE] in µg/l

In case REE concentrations are predicted by considering all significant groundwater characteristics, two to four characteristics must be specified. By including only the most significant groundwater characteristic, pH, a simple relationship will be available (Table 3).

Table 3 shows that pH already explains a considerable part of the variation in REE concentrations. In Figure 3 (next page) the relations between pH and REE concentrations are shown. It appears that these relations are nearly the same for each REE, except Eu. This is comprehensible since the REEs form a coherent group of elements. For a practice-based approach, a regression equation including only pH, can be used to predict REE concentrations.

External validation of the pH-models

We have applied the regression models shown in Table 3 to data from drinking water pumping station 'De Haere', The Netherlands. At this bore hole 19 water samples were taken at different depths and analysed for REEs, pH and HCO_3^- by the RIVM in 1995. Predicted REE concentrations are in reasonable agreement with measured REE concentrations, especially for Eu and Y (Figure 4; page 17). In most cases the observed REE concentrations seem to be lower than the predicted REE concentrations. Predicted REE concentrations are within 1-1.5 order of magnitude of the observed REE concentrations. This may be due to the differences in soil types between the two pumping station areas and thus some differences in binding mechanisms of the REEs may occur. This implies that one should be careful to extrapolate the situation at the pumping station Vierlingsbeek to other locations. Combined with earlier observations about the relationship of REE-concentrations with pH (Verweij *et al.*, 1996), this does mean that measurement of pH (preferably in more or less undisturbed water) gives a satisfying estimate of REE-concentrations.

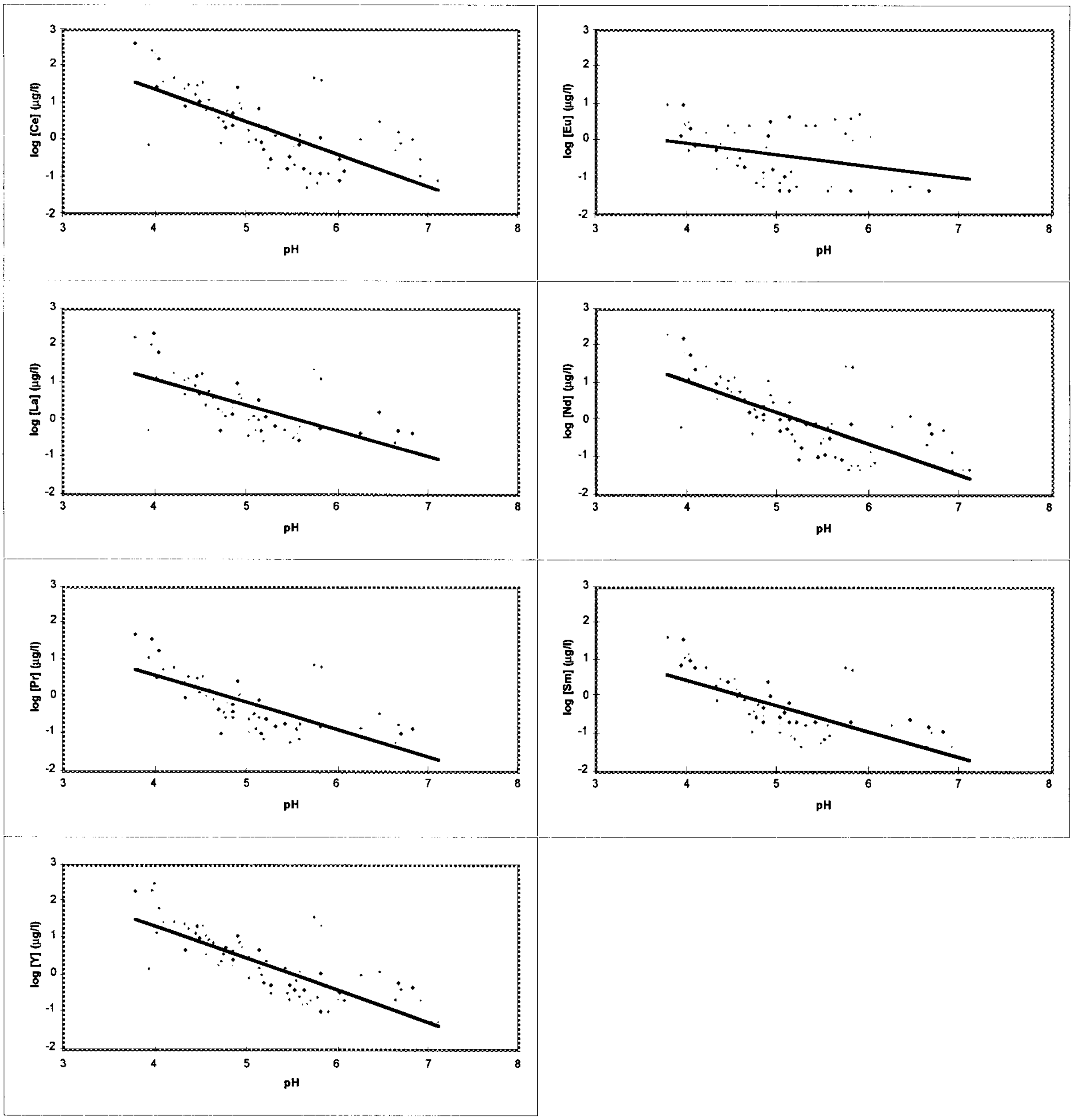

Figure 3. Total concentrations of the REEs (as log; in µg/l) as a function of pH for all seven bore holes, together with the regression lines (see Table 3).

Relations between REE-concentrations and saturation state of minerals

One could hypothesize that the pH of the groundwater controls the dissolution of some REE-containing mineral (e.g. a Ca-PO_4-mineral) and that, furthermore, that dissolution in turn controls the concentrations of dissolved REEs. If this is true, it implies that:

- as long as that mineral is still present in some amount:
  - the saturation index of the mineral equals 0 (by definition);
  - the concentrations of dissolved REEs increase when the pH decreases;
- as soon as all of the mineral has been dissolved:
  - the saturation index will drop below zero and decrease when the pH decreases;
  - the concentrations of dissolved REEs will remain constant.

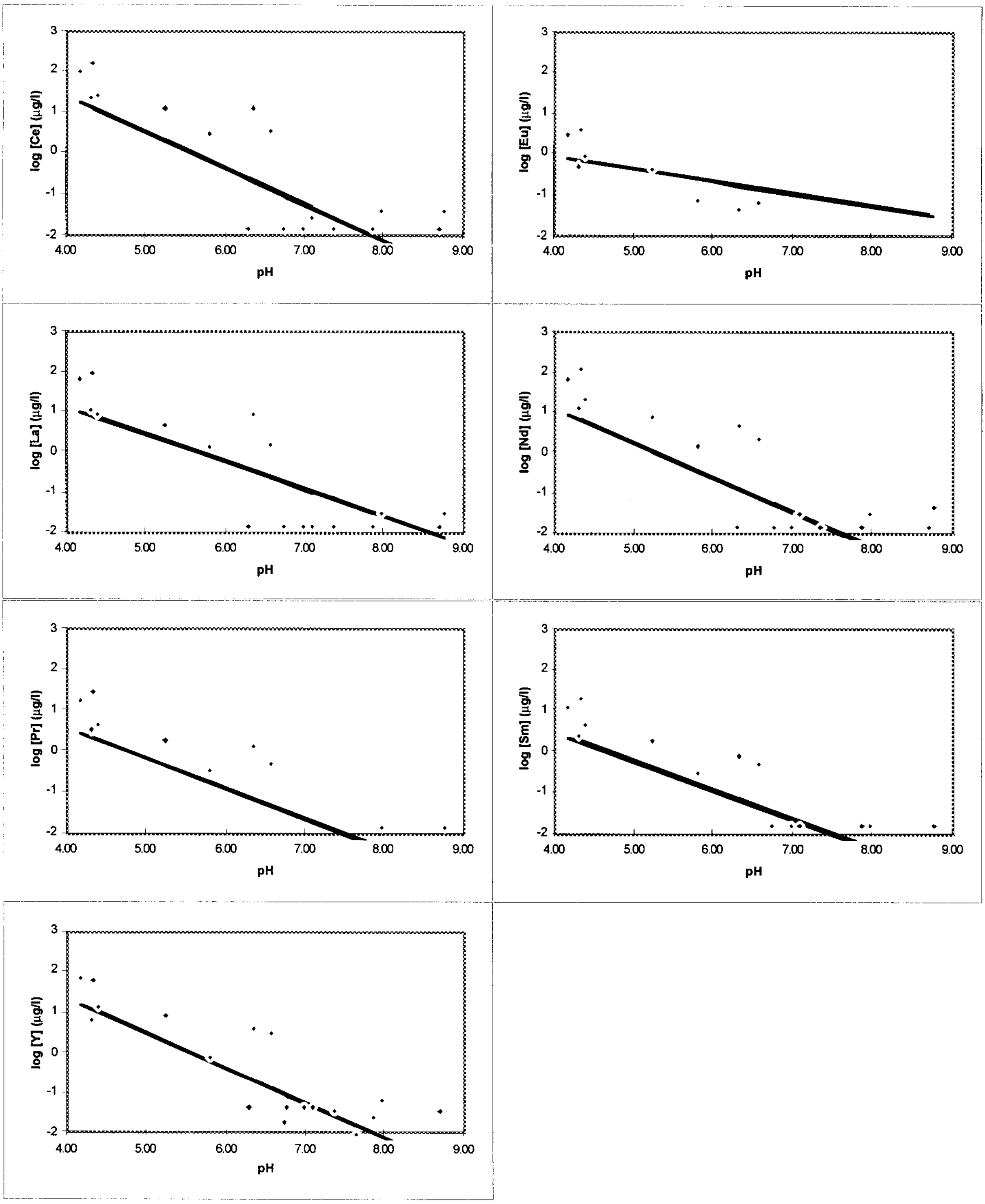

Figure 4. The *measured* total concentrations of the REEs (as log; in µg/l) as a function of pH at pumping station De Haere (data points) compared with the corresponding regression line obtained from data at pumping station Vierlingsbeek.

Before we compare the saturation indices as generated by GECHEQ with the above mentioned statements, we like to stress that not all relevant interactions will have been

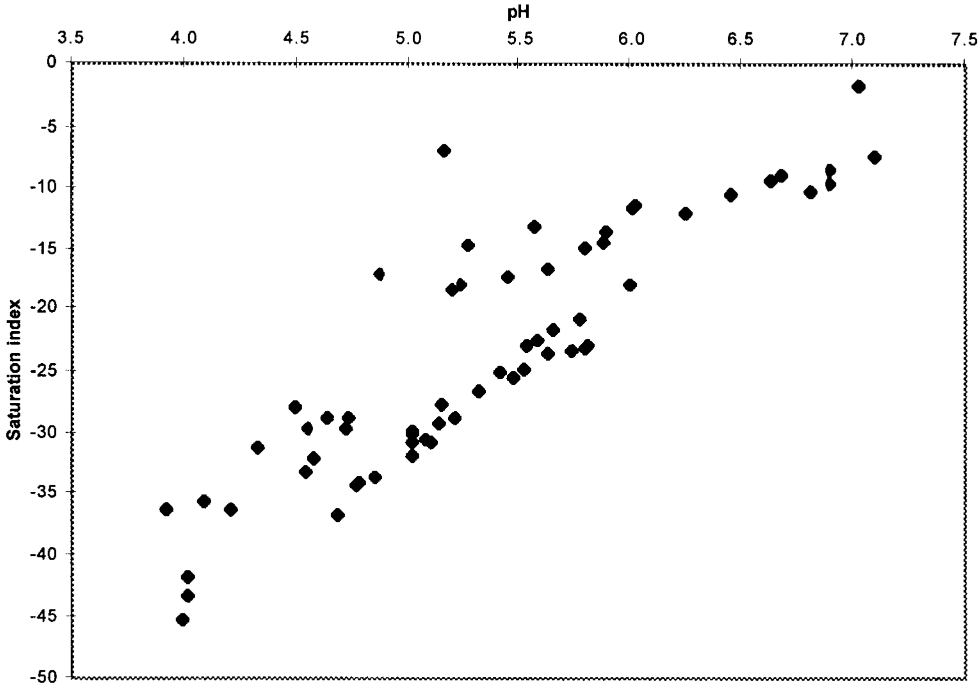

Figure 5. Saturation index of $Ca_5(PO_4)_3(OH)$ versus pH.

included in the speciation calculations. Interactions of calcium and phosphate with DOC are for instance not included, and could, if these interactions are significant, lead to too high values for concentration of free metals and ligands. This in turn could lead to saturation indices which are calculated to be higher than 0 (suggesting oversaturation) while no oversaturation actually exists.

In Figure 3 we have shown that the concentrations of dissolved REEs keep increasing when the pH decreases, so if the hypothesis which is described above is correct, there must be some amount of the mineral present, and the calculated saturation index must be 0 (ideally) or higher than 0 (in case interactions of calcium and phosphate with DOC are significant). Figure 5 shows that, for the example of $Ca_5(PO_4)_3(OH)$, this is definitely not the case. For the other included Ca-PO_4-minerals ($CaH(PO_4)$, $CaH_4(PO_4)_2$, $Ca_2(PO_4)(OH)$, $Ca_3(PO_4)_2$ and $Ca_4H(PO_4)_3$) it was not the case either.

The next step in analysing these data is to include other minerals than Ca-PO_4-minerals in the discussion. To that end, we selected those minerals whose calculated saturation index changes the least as a function of pH. Table 4 contains the "top 10" of minerals with the smallest (absolute value of the) slope of the saturation index as a function of pH.
In the case of $Fe(III)(OH)_3$ and $Al(OH)_3$ it is not likely that dissolution of the mineral controls REE-concentrations; adsorption to these minerals would be a more probable

Table 4. The 10 minerals with the smallest (absolute value of the) slope of the saturation index versus pH.

		saturation index		
mineral	slope	average	minimum	maximum
$Fe(III)(OH)_3$ (s)	0.00	0.00	0.00	0.00
$Ca(SO_4)$ (s)	-0.15	-1.76	-2.97	-1.10
$Al(OH)_3$ (s)	0.22	-0.46	-2.46	0.00
$Fe(III)(PO_4)$ (s)	0.46	-9.37	-11.39	-5.80
Al(PO4) (s)	0.60	-6.19	-7.80	-4.44
$Al_3(PO_4)_2(OH)_3$ (s)	1.36	-10.11	-13.22	-6.74
$Y(OH)_3$ (s)	1.55	-11.75	-15.37	-8.60
$Ce(OH)_3$ (s)	1.63	-13.90	-17.88	-10.49
$Zn(OH)_2$ (s)	1.70	-6.87	-9.86	-4.22
$Nd(OH)_3$ (s)	1.72	-12.27	-16.07	-8.72

explanation. Dissolution of $CaSO_4$ probably does not explain REE-concentrations either; the average saturation index of -1.65 in fact means a nearly hundredfold undersaturation.
For the other minerals the slope may be more or less constant, but the saturation index is much lower than 0; therefore, these minerals can not be assumed to control the concentrations of dissolved REEs.

Finally, to check the hypothesis that adsorption controls REE-concentrations, we made graphs of the percentage adsorbed REE versus pH, supposing that at the highest REE-concentration no REE is adsorbed anymore. The graphs looked like typical pH-dependent adsorption graphs, but this does not actually prove that adsorption controls REE-concentrations. It is an additional indication, however.

Unfortunately, based upon the speciation calculations no clear conclusions can be drawn if REE concentrations are controlled by dissolution or desorption of REEs. Adsorption, however is a likely explanation.

4. CONCLUSIONS

Chemical equilibrium modelling was used to get more insight in the chemical processes of rare earth elements (REE) in groundwater. The results showed that REE^{3+}, $REE(SO_4)^+$, $REE(CO_3)^+$ and REE(DOC) being the major species. They also showed that dissolution of REE-enriched solid phases probably does not account for the observed REEs in groundwater. Desorption of REEs may be a probable explanation. Multiple linear regression showed that pH is by far the most significant groundwater characteristic which contributes to the variation in REE concentrations. Also Fe and Mn contributed significantly , although to a much lesser extent, to the variation in REE concentrations. This may suggest that some REEs are bound to Fe-Mn-(hydr)oxides. Regression equations including only pH, were derived to predict REE concentrations in groundwater over a wide range of pH-values. External validation showed that these regression equations were reasonable successful to predict REE concentrations of groundwater of another drinkwater pumping station.

5. ACKNOWLEDGEMENTS

We thank Water Company Oost-Brabant and Water Company Gelderland for their permission for collecting the water samples used in this study. Moreover, we thank Water Company Oost-Brabant for providing data of the groundwater composition of the boreholes at Vierlingsbeek.

REFERENCES

Bingler, L.S. and Byrne, R.H. (1989). Phosphate complexation of gadolinium(III) in aqueous solution. Polyhedron 8:1315-1320.

Byrne, R.H. and Kim, K.-H. (1993). Rare earth precipitation and coprecipitation behavior: The limiting role of PO_4^{3-} on dissolved rare earth concentrations in seawater. Geochim. Cosmochim. Acta 57:519-526.

Byrne, R.H. and Lee, J.H. (1993). Comparative yttrium and rare earth element chemistries in seawater. Mar. Chem. 44:121-130.

Byrne, R.H., Lee, J.H. and Bingler, L.S. (1991). Rare earth complexation by PO_4^{3-} ions in aqueous solution. Geochim. Cosmochim Acta 55:2729-2735.

Cabaniss, S.E. and Shuman, M.S. (1988a). Copper binding by dissolved organic matter: I. Suwannee River fulvic acid equilibria. Geochim. Cosmochim. Acta 52:185-193.

Cabaniss, S.E. and Shuman, M.S. (1988b). Copper binding by dissolved organic matter: II. Variation in type and source of organic matter. Geochim. Cosmochim. Acta 52:195-200.

Cantrell, K.J. and Byrne, R.H. (1987). Rare earth element complexation by carbonate and oxalate ions. Geochim. Cosmochim. Acta 51:597-605.

De Baar, H.J.W., Schijf, J. and Byrne, R.H. (1991). Solution chemistry of the rare earth elements in seawater. Eur. J. Solid State Inorg. Chem. 28(Supplement):357-373.

De Boer, J.L.M., Verweij, W., Van der Velde-Koerts, T. and Mennes, W. (1996). Levels of rare earth elements in Dutch drinking water and its sources. Determination by inductively coupled plasma mass spectrometry and toxicological implications. A pilot study. Wat. Res. 30:190-198.

Firsching, F.H. and Brune, S.N. (1991). Solubility products of the trivalent rare-earth phosphates. J. Chem. Eng. Data 36:93-95.

Gosselin, D.C., Smith, M.R., Lepel, E.L. and Laul, J.C. (1992). Rare earth elements in chloride-rich groundwater, Palo Duro Basin, Texas, USA. Geochim. Cosmochim. Acta 56:1495-1505.

Griffin, R.A. and Jurinak, J.J. (1973). Estimation of activity coefficients from the electrical conductivity of natural aquatic systems and soil extracts. Soil Sci. 116:26-30.

Heisterkamp, S.H., Hoekstra, J.A. and Slob, W. (1992). Een inleiding voor opzet en statistische analyse van onderzoeksgegevens. RIVM report no. 959101003, Bilthoven, The Netherlands.

Lee, J.H. and Byrne, R.H. (1992). Examination of comparative rare earth elements complexation behavior using linear free-energy relationships. Geochim. Cosmochim. Acta 56:1127-1137.

Lee, J.H. and Byrne, R.H. (1993). Complexation of trivalent rare earth elements (Ce, Eu, Gd, Tb, Yb) by carbonate ions. Geochim. Cosmochim. Acta 57:295-302.

Liu, X. and Byrne, R.H. (1995). Comparative carbonate complexation of yttrium and gadolinium at 25°C and 0.7 mol dm^{-3} ionic strength. Mar. Chem. 51:213-221.

Millero, F.J. (1992). Stability constants for the formation of rare earth inorganic complexes as a function of ionic strength. Geochim. Cosmochim. Acta 56:3123-3132.

NIST (1995). Critical stability constants of metal complexes database, version 2.0. NIST Standard Reference Database 46. US Dept. of Commerce, Gaithersburg, MD.

Turner, D.R., Whitfield, M. and Dickson, A.G. (1981). The equilibrium speciation of dissolved components in freshwater and seawater at 25°C and 1 atm pressure. Geochim. Cosmochim. Acta 45:855-881.

Verweij, W., Van der Velde-Koerts, T., Ritsema, R. and Mons, M.N. (1995). Zeldzame aarden in ruw en rein water van freatische grondwaterwinningen. RIVM report no. 734301005, Bilthoven, The Netherlands.

Verweij, W., Mons, M.N., Ritsema, R. and Versteegh, A. (1996). Rare earth elements and beryllium in groundwater used for drinking water production: concentration and relationship to water quality. *In:* International Workshop, Natural origin inorganic micropollutants: arsenic and other constituents, Vienna, May 1996, pp. 63-70.

Verweij, W. (1996). GECHEQ, a GEoCHemical EQuilibrium model, version 6, release 02. RIVM, Bilthoven, The Netherlands.

Wood, S.A. (1990). The aqueous geochemistry of the rare-earth elements and yttrium. 1. Review of available low-temperature data for inorganic complexes and the inorganic REE speciation of natural waters. Chem. Geol. 82:159-186.

APPENDIX 1: GROUNDWATER COMPOSITION: GENERAL DATA

Groundwater composition with respect to pH, I, DOC, Mn, Al, Fe, and major anions and cations of the seven sampled bore holes nearby pumping station Vierlingsbeek.
The pH and HCO_3^- were measured in the field by RIVM. The other parameters were measured in the lab by Water Company Oost-Brabant.
DOC and I are calculated from the compounds oxidizable by $KMnO_4$ and EC respectively.

Depth (m)	pH	I (mmol/l)	HCO_3^- (mg/l)	Cl^- (mg/l)	SO_4^{2-} (mg/l)	PO_4^{3-} (mg/l)	NO_3^- (mg/l)	NO_2^- (mg/l)	NH_4^+ (mg/l)	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	Fe (mg/l)	Mn (mg/l)	Al (mg/l)	DOC (mg/l)
Bore hole KP001																	
2	4.33	NA	0.553	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
4	6.45	5.7	101.2	39	135	0.11	2.5	0.02	<0.05	23.5	5.0	61	9.7	0.35	<0.01	0.450	15.0
6	6.63	5.8	135.7	32	106	0.05	1.2	0.02	<0.05	19.5	5.0	70	8.6	0.06	0.16	0.220	12.3
8	6.68	5.5	125.9	32	113	0.05	1.5	0.02	<0.05	17	5.5	72	9.0	0.11	0.18	0.190	12.8
12	6.25	8.7	67.81	47	96	0.11	85.3	NA	3.9	33	38.0	70	14.3	0.03	0.44	0.050	18.3
14	5.79	8.1	28.33	44	110	0.09	91.9	0.13	0.72	29	10.0	81	20.0	0.08	0.57	0.070	9.5
16	5.54	5.9	22.48	34	96	0.06	67.8	0.28	<0.05	16.5	9.0	53	12.0	0.04	0.46	0.075	5.1
18	5.58	5.7	21.05	34	96	0.07	63.4	0.02	<0.05	16	7.5	52	13.8	0.11	0.31	0.100	4.0
20	5.53	7.2	12.73	35	230	0.08	<0.3	NA	0.06	17.5	10.0	59	20.0	4.5	0.28	0.190	2.1
22	5.15	6.0	9.079	35	190	0.11	<0.3	0.01	0.08	15	8.0	52	16.0	5.5	0.31	0.190	1.8
24	5.52	NA	16.53	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
26	5.16	5.9	7.752	34	150	0.22	<0.3	0.02	0.09	17	6.0	43	13.0	9.0	0.36	0.170	1.3
29	6.90	2.1	29.03	15	40	0.47	<0.3	0.08	0.20	6	1.7	16	1.7	22.0	0.30	0.350	3.8
41	7.03	2.7	119.4	9	8	1.17	<0.3	NA	0.32	5.5	1.4	37	2.3	8.8	0.50	0.008	2.9
KP002																	
3	5.81	5.3	41.15	13	40	0.01	144	NA	<0.05	9	28.0	34	6.2	<0.03	0.05	2.200	8.4
5	5.74	5.1	36.32	21	40	0.01	120	0.01	<0.05	20	17.0	42	4.9	<0.03	0.06	1.200	7.9
7	4.08	8.2	<0.005	32	64	0.06	200	0.01	2.4	11	54.0	55	7.8	0.10	0.52	1.500	7.6
10	5.14	7.2	5.522	39	92	0.03	130	0.02	0.81	16	16.0	57	18.5	0.04	0.49	0.080	2.1
12	4.78	6.1	2.480	37	109	0.02	78	0.03	<0.05	16.5	9.5	51	16.0	<0.03	0.39	0.190	1.3
14	4.85	6.0	2.838	37	95	0.02	78	0.03	<0.05	17	9.0	47	16.0	<0.03	0.35	0.130	1.3
16	5.02	5.6	4.491	37	95	0.04	68	0.04	<0.05	17	8.8	45	14.5	0.10	0.34	0.110	1.3
18	5.45	5.1	9.523	38	120	0.08	<0.3	NA	<0.05	17	6.0	37	15.0	3.9	0.33	0.040	0.5
20	5.24	4.6	6.258	38	98	0.07	<0.3	NA	<0.05	17.5	4.5	28	12.5	3.5	0.27	0.030	0.5
22	5.63	4.2	13.08	37	78	0.05	<0.3	NA	<0.05	16	4.0	27	11.2	5.5	0.36	0.018	0.5
24	5.80	4.4	17.71	37	84	0.08	<0.3	0.01	0.09	16	4.0	30	11.2	6.3	0.46	0.017	0.5
26	5.88	4.6	20.23	37	92	0.08	<0.3	0.01	<0.05	16	4.2	45	10.4	8.5	0.68	0.025	0.5
28	5.89	4.6	19.75	38	97	0.09	<0.3	0.01	0.05	16.5	4.5	40	11.5	8.5	0.39	0.020	0.5
31	6.90	4.7	65.47	37	77	0.13	<0.3	NA	0.15	13.5	3.0	48	7.8	6.5	1.50	0.030	0.5
33	7.10	3.4	66.40	22	47	0.69	<0.3	NA	0.20	8.5	2.0	38	4.8	2.7	2.20	0.080	0.8
35	6.90	2.0	63.88	10	21	0.84	<0.3	0.01	0.32	5.5	1.4	18	1.9	15.0	1.30	0.250	1.0
KP003																	
5	3.92	4.5	<0.005	15.5	60	0.08	82	NA	<0.05	9	25.1	28	6.8	<0.03	0.38	1.690	6.2
7	4.54	9.4	1.290	35	113	0.23	220	0.01	<0.05	19.5	22.0	97	11.0	0.08	1.50	1.375	4.0

9	4.32	6.4	0.203	28.5	67	0.15	145	NA	<0.05	12.5	18.4	69	2.3	<0.03	0.84	0.425	1.0
11	4.49	7.3	1.006	35.5	62	0.23	186	NA	<0.05	14	14.3	74	9.7	0.06	0.79	0.225	0.8
13	4.55	6.5	1.332	37	81	0.19	127	NA	<0.05	16	7.5	59	14.0	<0.03	0.94	0.250	1.0
15	4.58	6.5	1.648	37.5	77	0.10	115	NA	<0.05	17	6.8	53	16.0	<0.03	1.00	0.275	1.0
17	4.63	5.4	1.659	37	94	0.18	44.7	0.02	<0.05	17	6.1	40	16.0	0.04	0.36	0.175	<0.5
19	4.74	5.1	2.236	36	98	0.11	37.3	0.02	<0.05	17	5.5	38	13.0	<0.03	0.16	0.110	<0.5
21	5.02	4.2	3.411	36.5	95	0.15	<0.3	NA	<0.05	16	4.5	28	10.0	2.1	0.13	0.300	<0.5
23	5.19	3.7	5.378	33.5	75	0.14	0.97	NA	<0.05	14	4.2	23	7.7	4.4	0.14	0.075	<0.5
25	5.27	3.7	5.841	34	75	0.16	<0.3	NA	<0.05	14.5	4.2	21	8.1	6.2	0.15	0.020	<0.5
28	5.57	3.9	8.978	34	71	0.26	<0.3	NA	0.07	14.5	4.1	25	7.4	12.0	0.32	0.025	<0.5
31	6.65	1.4	32.98	8	23	<0.03	0.75	0.60	0.54	5.5	4.5	19	<1	5.0	0.11	0.750	9.5
34	6.81	1.4	46.77	7	10	0.08	<0.3	0.03	0.25	5.5	2.0	15	1.3	7.8	0.16	0.055	1.0
KP036																	
3	4.69	3.4	8.235	16.5	60	0.06	46.5	0.03	<0.05	7	1.8	15	3.0	0.20	0.18	10.250	11.5
7	5.41	11.4	26.33	69.5	191	0.05	168	0.03	<0.05	46	44.2	65	33.5	0.12	1.40	0.170	10.1
9	5.32	12.0	12.54	64	175	0.03	259	0.03	<0.05	31	17.6	76	49.8	<0.03	1.70	0.050	7.6
11	5.21	9.6	10.96	55	278	0.02	32.2	0.17	0.07	25	14.2	71	34.6	0.07	0.98	0.118	3.2
13	5.02	8.4	7.920	47.5	177	0.01	104	0.02	<0.05	22	12.1	65	23.7	0.03	0.60	0.062	2.4
16	5.08	8.0	8.719	48	159	0.02	100	0.02	<0.05	21.5	10.3	62	22.0	0.06	0.53	0.375	2.1
18	5.02	8.3	8.327	48	144	0.05	127	0.02	<0.05	21.5	9.8	65	22.4	0.07	0.50	0.390	1.6
20	5.10	6.3	8.563	44.5	129	0.02	51.8	0.04	<0.05	19.5	8.5	44	16.8	0.04	0.38	0.130	1.3
22	4.77	4.9	5.988	47	102	0.04	<0.3	0.02	18.5	18.5	5.1	31	12.4	4.1	0.24	0.210	<0.5
24	4.72	4.9	5.175	43	124	0.13	<0.3	0.02	0.05	19.5	5.6	33	14.0	3.7	0.23	0.150	<0.5
27	5.77	3.8	21.09	39	73	0.17	0.83	0.03	0.15	16	2.8	20	7.3	7.7	0.15	0.315	1.8
30	5.66	4.5	11.90	47.5	90	0.17	<0.3	0.21	0.23	13	3.8	28	8.0	12.2	0.23	0.460	0.8
KP038																	
2	4.02	6.1	<0.005	15	106	0.03	118	0.03	0.19	10	3.2	40	11.5	0.44	0.94	11.000	5.4
4	3.99	4.9	<0.005	16	116	0.04	67	0.01	0.09	8.5	2.2	12	4.0	2.3	0.20	18.200	5.1
7	4.01	2.2	<0.005	21	36	0.04	11.2	0.01	<0.05	7	1.4	6	6.0	0.14	0.21	3.000	1.8
9	4.21	4.2	<0.005	36	92	0.05	<0.3	NA	0.16	19.5	1.9	23	7.4	10.1	0.35	0.900	1.8
11	5.47	4.8	11.92	40	112	0.05	<0.3	0.01	0.22	21	2.0	30	8.0	19.5	0.45	0.055	1.3
14	5.52	4.9	13.01	43	110	0.05	<0.3	NA	0.25	21	1.9	30	7.8	21.5	0.48	0.075	1.6
17	5.63	4.8	14.68	42	106	0.05	<0.3	0.01	0.25	21	1.9	29	7.3	17.9	0.46	0.215	1.3
20	6.00	3.3	22.40	37	39	0.11	<0.3	0.02	0.28	13	1.4	23	3.1	12.5	0.23	0.205	1.0
24	6.02	3.6	19.10	42	52	0.20	<0.3	0.01	0.29	15	1.6	27	2.9	12.9	0.25	0.030	1.0
27	6.01	3.7	19.99	42	55	0.19	<0.3	0.16	0.40	14.5	1.5	28	2.9	17.0	0.29	0.015	1.3

KP039																	
3	4.87	8.6	6.343	31	180	NA	115	0.03	0.06	27	37.5	70	12.5	9.5	0.23	NA	20.5
5	4.46	8.3	1.000	32	100	NA	180	0.10	0.10	22	19.5	67	13.5	0.90	0.29	NA	7.3
7	4.52	11.4	3.514	56	160	NA	235	0.08	0.75	25	25.0	111	18.4	0.18	1.00	NA	5.7
9	4.89	12.4	7.998	61	165	NA	270	0.06	1.8	24	26.0	109	31.1	0.07	1.10	NA	6.2
11	4.92	11.1	8.231	45	135	NA	245	0.05	3.7	23	41.0	82	23.8	0.17	0.65	NA	5.1
14	5.13	9.2	9.365	38	150	NA	175	<0.01	0.65	19	22.5	82	20.6	0.03	0.60	NA	2.7
16	4.93	8.3	7.633	41	175	NA	99	0.01	<0.05	19	9.8	74	21.4	0.03	0.50	NA	1.8
18	4.85	8.1	6.947	42	180	NA	88	0.02	<0.05	19	9.1	70	21.0	0.04	0.49	NA	1.6
20	5.12	6.6	8.806	42	195	NA	<0.5	0.02	0.08	19	5.4	48	18.6	10.8	0.29	NA	0.8
23	5.25	5.4	9.467	40	130	NA	<0.5	0.02	0.15	18	3.8	32	12.8	11.7	0.25	NA	0.8
26	5.44	5.3	10.65	41	135	NA	<0.5	0.03	0.13	17	3.6	33	13.4	21.0	0.29	NA	0.8
29	5.68	3.2	12.16	34	69	NA	<0.5	0.05	0.20	9.5	2.9	21	5.1	14.6	0.20	4.200	1.0
KP040																	
3	4.84	NA	2.435	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
6	3.96	8.4	<0.005	31	125	NA	165	<0.01	<0.05	18	28.0	59	15.7	0.06	0.14	4.200	3.2
9	3.78	9.9	<0.005	29	120	NA	250	<0.01	<0.05	22	17.5	81	14.0	0.13	0.60	5.800	4.3
12	4.03	9.9	<0.005	37	115	NA	230	0.04	<0.05	18	19.0	91	20.2	0.43	0.95	NA	3.5
15	4.36	9.2	0.429	50	165	NA	135	0.02	<0.05	22	11.5	75	24.8	0.08	0.70	NA	3.2
18	4.43	9.2	0.929	49	165	NA	140	0.02	<0.05	23	10.0	77	26.8	0.06	0.65	NA	1.8
20	4.31	8.6	0.209	49	225	NA	63	0.03	0.07	22	10.0	71	25.2	0.13	0.60	NA	1.6
23	4.84	9.3	3.490	49	320	NA	<0.5	0.13	0.17	22	10.0	77	27.5	7.9	0.60	3.400	1.3
28	6.07	4.9	24.74	42	115	NA	<0.5	0.08	0.13	17	3.1	36	11.8	8.3	0.55	1.700	2.7

APPENDIX 2: GROUNDWATER COMPOSITION: REE-DATA

Groundwater composition with respect to REE as measured by the RIVM of the seven sampled bore holes nearby pumping station Vierlingsbeek.

Depth	Ce	Eu	La	Nd	Pr	Sm	Y
(m)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)
Bore hole KP001							
2	8.08	0.18	4.9	3.74	0.93	0.75	4.75
4	3.14	0.06	1.8	1.30	0.35	0.24	1.24
6	0.52	<0.05	0.3	0.23	0.06	0.05	0.22
8	0.83	<0.05	0.4	0.46	0.10	0.11	0.40
12	1.05	0.05	0.5	0.71	0.14	0.17	0.96
14	1.21	0.05	0.6	0.79	0.15	0.20	1.06
16	0.98	0.05	0.4	0.68	0.13	0.17	1.03
18	1.40	0.06	0.7	0.82	0.18	0.23	1.24
20	0.52	<0.05	0.3	0.29	0.06	0.09	0.70
22	0.67	<0.05	0.4	0.35	0.08	0.08	0.97
24	0.69	<0.05	0.3	0.30	0.07	0.08	0.37
26	0.92	<0.05	0.5	0.42	0.10	0.09	0.98
29	0.32	<0.05	<0.2	0.13	<0.05	0.05	0.20
41	0.06	<0.05	<0.2	0.04	<0.05	<0.05	0.05
KP002							
3	42.34	1.14	13.3	26.90	6.16	5.40	22.25
5	50.01	1.50	22.8	29.53	6.89	6.42	36.21
7	36.53	0.74	11.9	24.98	5.40	6.47	25.48
10	9.86	0.15	4.4	3.66	0.93	0.69	3.70
12	5.96	0.14	3.1	2.65	0.65	0.59	5.05
14	5.35	0.11	2.8	2.29	0.55	0.45	4.06
16	1.98	0.05	1.1	0.94	0.21	0.20	2.40
18	0.28	<0.05	<0.2	0.10	<0.05	<0.05	0.22
20	0.18	<0.05	<0.2	0.09	<0.05	<0.05	0.32
22	0.20	3.89	<0.2	0.09	<0.05	<0.05	0.15
24	0.13	4.21	<0.2	0.06	<0.05	<0.05	0.10
26	0.13	4.63	<0.2	0.06	<0.05	<0.05	0.12
28	0.13	5.18	<0.2	0.04	<0.05	<0.05	0.10
31	<0.05	<0.05	<0.2	<0.05	<0.05	<0.05	<0.05
33	0.08	<0.05	<0.2	0.04	<0.05	<0.05	0.05
35	0.11	<0.05	<0.2	0.04	<0.05	<0.05	0.06

KP003							
5	0.77	1.47	0.6	0.66	11.02	6.95	1.45
7	6.28	0.21	2.7	4.34	1.00	0.99	3.74
9	18.80	0.56	9.0	12.17	2.94	2.53	10.80
11	10.51	0.35	5.0	5.74	1.32	1.47	10.30
13	12.82	0.38	6.2	6.71	1.58	1.50	11.99
15	12.05	0.33	5.9	5.81	1.42	1.25	8.32
17	7.16	0.20	3.7	3.74	0.85	0.81	7.57
19	3.11	0.09	1.5	1.80	0.38	0.38	3.87
21	0.94	<0.05	0.4	0.50	0.11	0.11	0.85
23	0.57	<0.05	0.3	0.29	0.07	0.08	0.58
25	0.31	<0.05	<0.2	0.16	<0.05	0.05	0.32
28	0.80	<0.05	0.3	0.30	0.07	0.09	0.27
31	1.64	0.05	0.5	0.78	0.17	0.15	0.58
34	1.13	<0.05	0.5	0.53	0.13	0.12	0.46
KP036							
3	4.20	2.74	2.1	1.70	0.46	0.36	1.88
7	1.35	2.69	0.6	0.85	0.18	0.21	1.52
9	1.36	2.74	0.7	0.76	0.15	0.17	1.62
11	2.13	0.06	1.2	1.02	0.24	0.20	2.44
13	2.31	0.09	1.2	1.37	0.30	0.35	3.70
16	2.56	0.11	1.3	1.47	0.31	0.38	4.33
18	1.85	0.08	1.0	1.11	0.24	0.30	3.27
20	1.02	0.05	0.6	0.61	0.13	0.17	2.25
22	2.23	0.08	1.3	1.20	0.27	0.29	5.21
24	0.87	<0.05	0.5	0.45	0.10	0.12	2.44
27	0.07	<0.05	<0.2	0.04	<0.05	<0.05	0.24
30	0.06	<0.05	<0.2	<0.05	<0.05	<0.05	0.17
KP038							
2	27.45	0.58	12.7	13.24	3.20	2.44	13.95
4	212.95	2.80	229.7	62.46	17.04	10.51	322.15
7	144.87	3.16	61.1	68.40	16.56	13.91	62.97
9	50.35	1.64	19.3	28.17	6.50	6.68	29.36
11	0.38	<0.05	<0.2	0.25	0.06	0.06	0.52
14	0.22	<0.05	<0.2	0.12	<0.05	<0.05	0.39
17	0.17	<0.05	<0.2	0.10	<0.05	<0.05	0.36
20	0.07	<0.05	<0.2	0.06	<0.05	<0.05	0.29
24	0.08	<0.05	<0.2	0.06	<0.05	<0.05	0.22
27	0.31	1.35	<0.2	0.14	<0.05	<0.05	0.36

KP039							
3	22.52	0.71	8.3	13.37	3.02	3.31	10.40
5	29.86	2.74	15.7	12.16	3.16	2.59	19.99
7	35.83	1.66	16.7	14.60	3.52	3.19	22.00
9	26.22	1.40	10.1	11.71	2.76	2.54	11.50
11	9.68	3.37	4.9	4.90	1.13	1.08	7.63
14	6.87	4.56	3.5	3.23	0.77	0.68	4.79
16	6.87	0.17	3.8	3.17	0.75	0.66	6.12
18	5.35	0.14	2.8	2.45	0.59	0.51	4.61
20	2.37	0.05	1.0	1.08	0.27	0.21	1.53
23	0.31	<0.05	<0.2	0.19	<0.05	0.05	0.52
26	0.17	<0.05	<0.2	0.10	<0.05	<0.05	0.33
29	0.13	<0.05	<0.2	0.09	<0.05	<0.05	0.20
KP040							
3	2.97	0.06	1.8	1.43	0.37	0.30	1.99
6	263.76	9.13	112.3	156.07	37.92	36.22	211.00
9	442.06	9.28	163.9	194.48	49.29	39.99	191.74
12	158.81	2.31	61.7	60.39	16.92	9.95	61.87
15	32.37	0.81	13.4	15.13	3.61	3.23	19.43
18	16.77	0.35	8.4	7.33	1.86	1.41	12.76
20	23.68	0.58	11.7	10.21	2.52	2.12	23.50
23	2.40	0.06	1.4	1.04	0.25	0.20	2.73
28	0.15	<0.05	<0.2	0.07	<0.05	<0.05	0.20