Artificial Recharge of Groundwater, Peters et al. (eds) © 1998 Balkema, Rotterdam, ISBN 90 5809 017 5

An experiment on well recharge of oxic water into an anoxic aquifer

Hannie de Ruiter
WMO, Zwolle, Netherlands
Pieter J. Stuyfzand
Kiwa Research and Consultancy, Nieuwegein, Netherlands

ABSTRACT: The Drinking Water Company for the Dutch province of Overijssel (WMO) is investigating well recharge of semi-purified surface water at a future production plant Leeuwterveld. At a nearby existing conventional well field an injection experiment was carried out using one of the pumping wells for injection and another, at a distance of 85 m, as a recovery well. Two observation wells were placed between these two wells, each with 3 observation screens. For a period of 1.5 years oxic drinking water was injected into the anoxic aquifer. Chemical analysis of water samples shows that the injected water underwent reduction due to the oxidation of pyrite. The sequence of the release of heavy metals from pyrite, adsorption processes and cation exchange is demonstrated in graphs. The retardation of several parameters was calculated using natural tracers.

1 INTRODUCTION

The Drinking Water Company for the Dutch province of Overijssel (WMO)is investigating the possibility of implementing well recharge with semi-purified surface water at the future production plant Leeuwterveld (Fig. 1). In order to gain insight into potential problems, we carried out a recharge experiment. The purpose of this experiment was to gain insight in the character, the sequence and the time scale of changes to the water quality of the injection water on its way to the recovery wells. Other aims were to gain insight into the attainable injection rate and in potential problems of clogging. For the experiment we chose the nearby St Jans-klooster production plant which is hydrologically and chemically similar to the future recharge area. The experiment started in April 1996 and is still in progress. This paper presents the information collected up until June 1997 and focuses on hydro-chemical aspects.

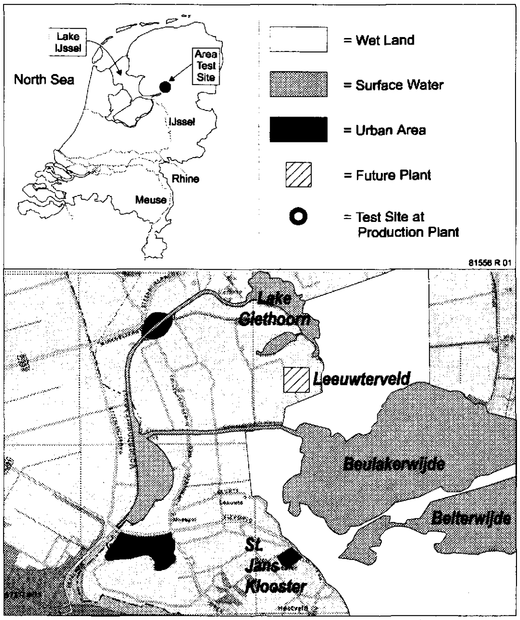

Figure 1. Situation of the present and future drinking water production plants and the test site

2 SET UP OF THE EXPERIMENT

2.1 *St Jansklooster as a test site*

The reasons for selecting St Jansklooster as a test site are: (1) The borehole descriptions of both sites show great hydrological similarity. (2) The quality of the water to be injected at the future production plant is almost identical to that of the drinking water produced by the St Jansklooster production plant. (3) The existing recovery wells and infrastructure of the production plant could be used, keeping the costs of the experiment low. (4) Two wells were especially suitable as they were situated in a favourable part of the flow domain, where the injection water could be recovered almost exclusively by one well.

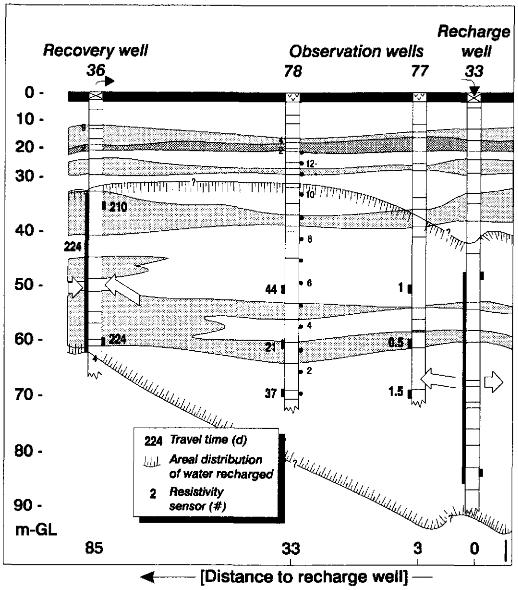

Figure 2. Set up of the test site with hydrogeological schematisation and the extent of the injected drinking water after 14 months (June 1997) with an indication of the mean travel times

2.2 *Set up of the experiment*

Injection started in April 1996 and stopped in December 1997. Drinking water from the St Jansklooster production plant was used. At the beginning of the experiment the injection rate was 30 m^3/h. After 3 months the rate was increased to 60-m^3/h to see what effect this would have. The extraction rate was kept fairly constant at 125 m^3/h throughout the experiment. The set up of the observation facilities is shown in Figure 2. Samples were taken just before the start and during the whole period of injection from the injected water, all 1.0 m screens and the total recovery water. The sampling frequency started off at once a week and was reduced during the experiment to once a fortnight.

The screens of the recovery well will be sampled for another half year after the injection stop. The samples were analysed for the main constituents using conventional techniques and for 7 trace elements using an ICP-MS cq AAS graphite furnace. Other regular measurements throughout the injection period comprised hydraulic heads at several depths and a weekly scan of the electrical resistivity sensors. The measured changes in their resistance are mainly due to the changes in the electrical conductivity of the groundwater which can be used as a multilevel tracer device. Halfway through the experiment we installed 5 parallel filters in a laboratory filled with samples from the aquifer. Two filters were used to simulate the clogging of the well and the other three to obtain insight into water-aquifer reactions during extremely short contact times.

3 HYDRO-GEOLOGICAL, GEO-CHEMICAL AND HYDRO-CHEMICAL ENVIRONMENT

The hydro-geological structure is shown in Figure 2. The recharged aquifer is composed of alternate coarse and fine-grained sand layers. The fine-grained layers are of limited horizontal extent. A peat layer confines the aquifer. Geo-chemically the composition of the aquifer is anoxic, without $CaCO_3$ and low in organic matter content. It contains some pyrite with traces of Co, Ni, Zn and As. At the adsorption complex we find significant amounts of NH_4^+, Fe^{2+} and Mn^{2+} though dominated by Ca^{2+}. CEC is rather low and we find no iron and manganese oxides. The native groundwater consists of surface water that has infiltrated through the anoxic bottom layers of the surrounding lakes and marshes (Fig. 1). As a result

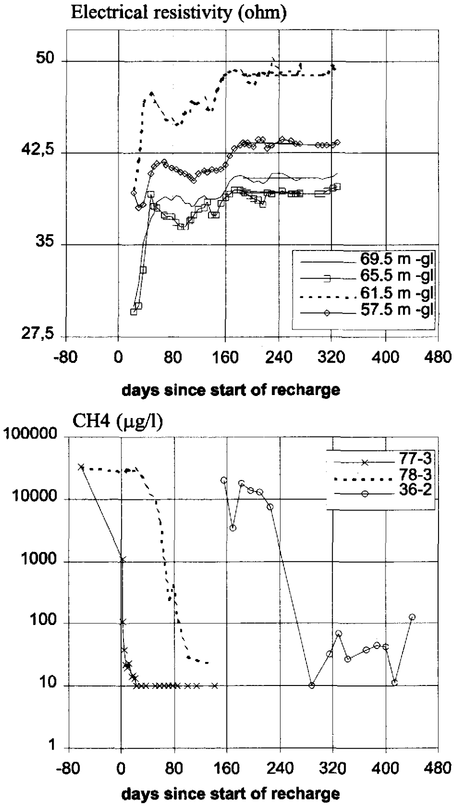

Figure 3. Electrical resistivity using permanent sensors in observation well 78 (at 33 m from the injection well) and methane concentration of the injected water and samples from the deepest filters of the observation wells 77, 78 and recovery well 36

this groundwater is deeply anoxic, high in HCO_3^-, Ca^{2+}, CH_4, NH_4^+ PO_4^{3-}, organic compounds and EC but it lacks SO_4^{2-} and NO_3^-.

4 RECOGNITION AND TRAVEL TIME OF THE INJECTED DRINKING WATER

The treatment of drinking water causes the injected drinking water to differ from the native groundwater (which is the source of drinking water). The treatment consists mainly of aeration in order to remove methane, iron and manganese. As a result we find O_2 and NO_3^- instead of NH_4, lower HCO_3^- concentrations, lower EC and no CH_4, Fe^{2+} and Mn^{2+}. Apart from these general differences we find some hydrochemical stratification in the aquifer. The groundwater in the upper part of the aquifer has lower concentrations of DOC and Cl^- than the injected water, whilst the groundwater in the bottom part has higher Cl^- concentrations. We used these parameters together with measurements of resistivity as tracers, to be able to recognise the drinking water and to calculate travel times (Fig. 2 and 3). From these calculated travel times we could discern the flow rates at different depths.

5 WATER QUALITY CHANGES ALONG THE FLOW PATH

The most important reaction that was seen to affect the quality of the injected water is pyrite oxidation. This reaction influences the redox parameters and trace elements. The changes in these parameters are discussed in this chapter. In table 1 the quality changes of injected drinking water are shown along the deepest flow path. Because the travel times of the injected water vary greatly, both horizontally and vertically, the chemical processes are compared according to the number of 'pore flushes' or bed volumes. This is the number of times that the injected water has passed through the aquifer at a particular point. After 2-6 'pore flushes' the injected drinking water has replaced the original groundwater for 100% but all soil reactions are still active.

5.1 *Redox parameters*

The following parameters play an active role in redox reactions: O_2, NO_3^-, NO_2^-, SO_4^{2-}, CH_4, Fe^{2+}, Mn^{2+} and NH_4^+ (Fig. 4 and 5). Oxidation of pyrite plays the leading role, shown by diminishing O_2 and NO_3^- and increasing SO_4^2. At the same time cation exchange restores equilibrium by release of Fe^{2+}, Mn^{2+} and NH_4^+ against capture of Ca^{2+}. Oxidation of organic matter does not seem to play an important role, as there has not been an increase of TIC (Total

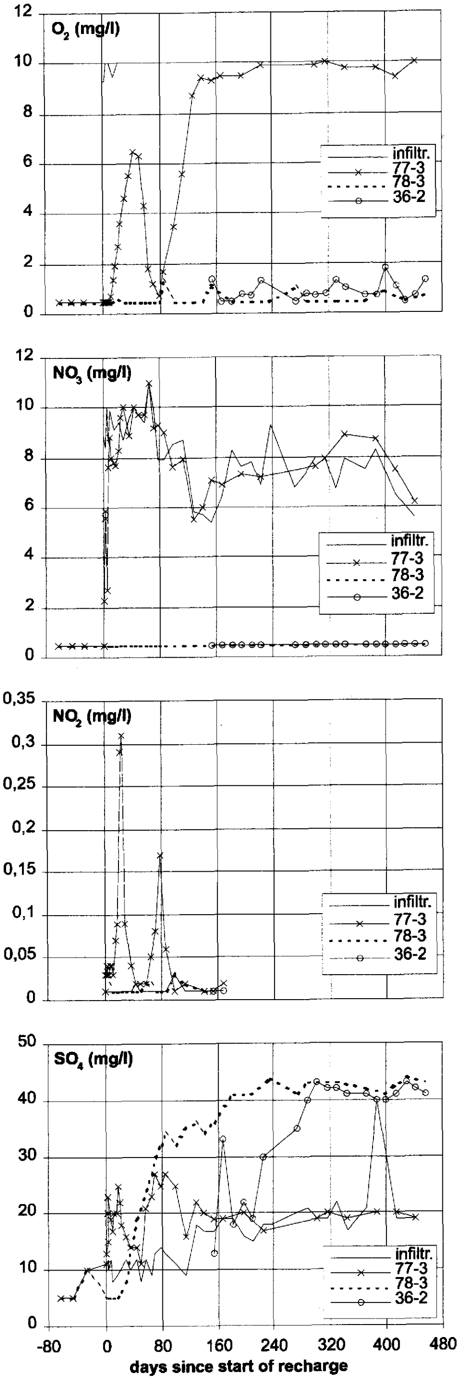

Figure 4. Concentration of 4 redox-parameters (oxygenated species) of the injected water and samples from the deepest observation screen of wells 77, 78 and 36 (at 3, 33 and 85 metres resp. 1, 37 and 224 days) from the injection well

Table 1. Mean quality of injected drinking water and mean quality at the deepest observation screens after 2-6 pore flushes (for well 36 after 2.1 pore flushes)

well nr		33	77	78	36
depth	m-GL	0	-70	-70	-60
distance	m	0	3	33	85
travel time	d	-	1.5	37	224
PF's	-	-	2-6	2-6	2.1
EC	µS/m	499	498	484	437
pH	-	7.51	7.39	7.19	7.27
O_2	mg/l	9.9	0.5	0.7	0.8
CH_4	mg/l	0.01	0.05	0.12	0.13
DOC	mg/l	7.2	7.0	6.1	5.3
Cl^-	mg/l	37.6	33	38.7	39
SO_4^{2-}	mg/l	10.8	19.8	35.7	42
HCO_3^-	mg/l	265	247	232	218
NO_3^-	mg/l	9.2	6.2	0.5	0.5
NO_2^-	mg/l	0.01	0.035	0.015	-
PO_4^{3-}	mg/l	0.09	-	0.32	0.23
Na^+	mg/l	20	19.8	20.2	19.7
K^+	mg/l	3.2	2.2	1.5	1.9
Ca^{2+}	mg/l	85.2	80.8	83.6	80
Mg^{2+}	mg/l	5.9	5.0	5.2	5.7
Fe^{2+}	mg/l	0.10	1.32	4.0	3.1
Mn^{2+}	mg/l	0.01	0.09	0.16	0.13
NH_4^+	mg/l	0.06	0.73	1.3	0.49
As	µg/l	1	7	5	3
Co	µg/l	1.4	1	< 2.3	2
Ni	µg/l	1.4	1.1	< 2.3	2
Zn	µg/l	23	9	9	2
$SI_{calcite}$	-	0.17	-0.02	-0.24	-0.18
TIC	mmol/l	4.69	4.50	4.57	4.12

Inorganic Carbon) while the increase of SO_4^{2-} definitely points to pyrite oxidation. Around the injection well, at short travel distances, the injected water shows for some time a lack of equilibrium. Measurable amounts of O_2 and NO_3^- are found together with Fe^{2+}, Mn^{2+}, NO_2^- and NH_4^+ in all screens of observation well 77 at 3 m from the injection well. This shows that thermodynamic equilibrium at that moment has not yet been reached. It takes about 15 days to reach equilibrium. It took 224 days, according to the concentrations of O_2, NO_3 and SO_4^{2-} to consume all of the pyrite during the first 3 m of aquifer passage (observation well 77). After about 5-11 days all Fe^{2+} and Mn^{2+} has been flushed out at observation well 77, but flushing at the other wells is not yet complete. The flushing of NH_4^+ is faster than that of Fe^{2+} and Mn^{2+} in all wells.

5.2 *$CaCO_3$-CO_2 parameters*

The following parameters play an active role in $CaCO_3$-CO_2 reactions: pH, Ca^{2+}, HCO_3^--, SI (calcite Saturation Index) and TIC (Total Inorganic Carbon). Due to a lack of $CaCO_3$ and readily degradable organic matter in the recharged aquifer, all observation screens show no increase of Ca^{2+}, HCO_3^- and TIC. On the contrary, pH, Ca^{2+}, HCO_3^-, TIC and SI decrease for a long time on their way to the extraction well. At observation well 77 the decrease in Ca^{2+} stops first (after 10 days) whilst the decrease in pH, HCO_3^-, TIC and SI stops when SO_4^{2-} production stops. The decrease in Ca^{2+} is caused by cation exchange with NH_4^+, Fe^{2+} and Mn^{2+},

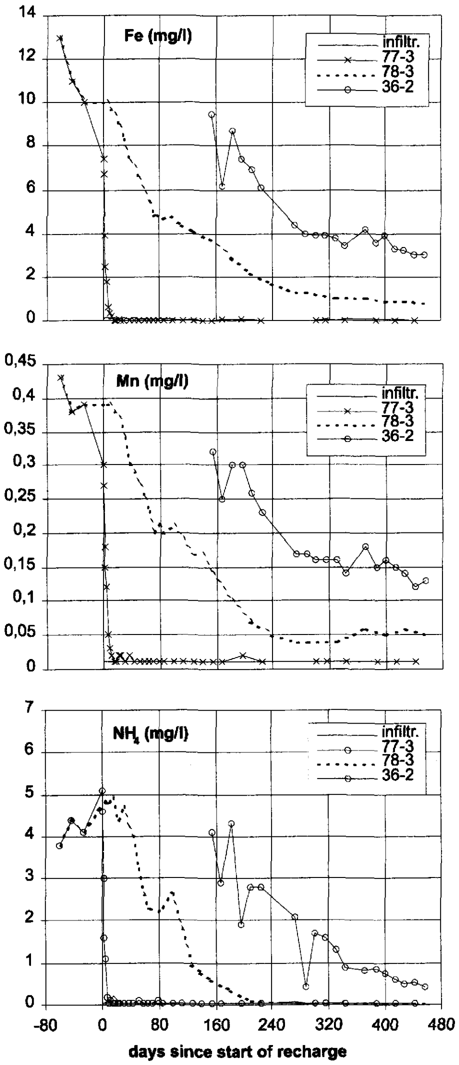

Figure 5. Concentration of 3 redox-parameters (reduced species) of the injected water and samples from the deepest observation screen of wells 77, 78 and 36 (at 3, 33 and 85 metres resp. 1, 37 and 224 days) from the injection well

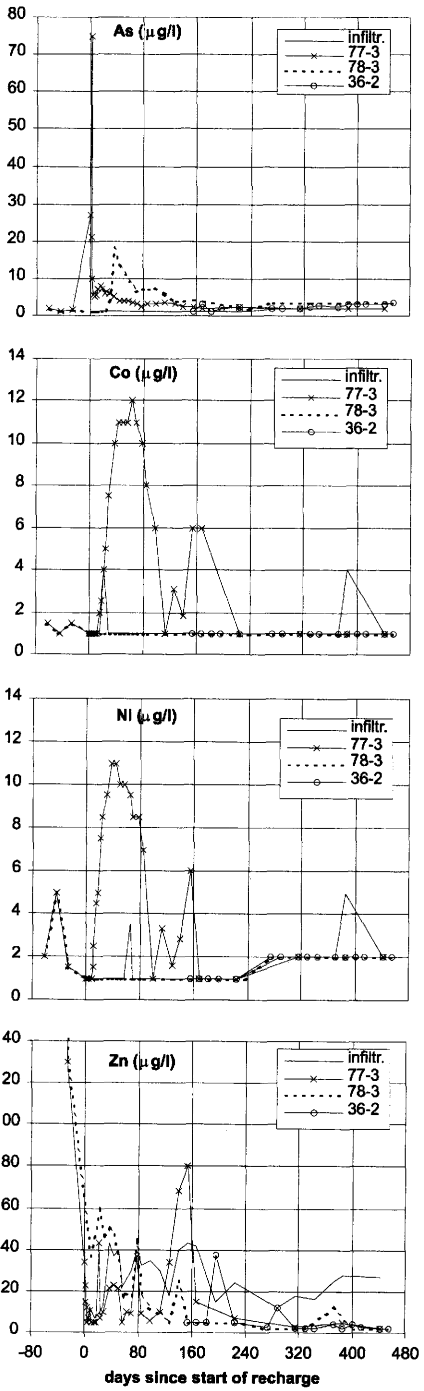

Figure 6. Concentration of 4 trace elements released from pyrite during aquifer passage. Shown are the injected drinking water and the samples from the deepest observation screens of the wells 77, 78 and 36 (at 3, 33 and 85 metres resp. 1, 37 and 224 days) from the injection well.

whilst the decrease in pH, HCO_3^-, TIC and SI is caused by internal pH buffering. Acid produced during pyrite oxidation is neutralised by the conversion of HCO_3^- into CO_2. TIC should not change by this reaction but it clearly does. This is probably caused by the escape of CO_2 during or after sampling.

5.3 *Trace elements connected with pyrite*

Trace elements that were detected in pyrite in significant amounts are: As, Co, Ni and Zn. The concentration of these elements increases to some tens of µg/l during aquifer passage (Fig. 6). They are clearly connected to pyrite as (1) their increase stops as soon as SO_4^{2-} production (a product of pyrite oxidation) stops; (2) their concentration peaks follow SO_4^{2-}; and (3) their concentration peaks approach the calculated pyrite-bound content as analysed from aquifer soil samples. Only arsenic has reached the recovery well up to date with its front flattened. Co, Ni and Zn got stuck between the observation wells 77 and 78, where especially freshly formed iron (hydr)oxides (a product from pyrite oxidation) adsorb them. Also Arsenic as AsO_4^{3-} is adsorbed by these oxides, but 10 % (as H_3AsO_3) escapes adsorption thanks to its lack of charge. That part reaches the recovery well at the same time as SO_4^{2-}. The retardation factor of Co, Ni and Zn is about 20 - 100 times that of SO_4^{2-} and arsenic because of adsorption. The reason is that 2^+ charged cations have stronger adsorption bonds. Therefore Co, Ni and Zn are not expected in this experiment to peak in the extraction well.

5.4 *Other parameters*

Of course Cl^- shows fully conservative behaviour and Na^+ is almost conservative. K^+ and Mg^{2+} however, are subject to cation exchange processes. They are being adsorbed after 5-10 days at observation well 77 and after 110-224 days at observation well 78. DOC (Dissolved Organic Carbon) decreases asymptotically along its flow path. Only about 1,1 mg C/l of the mean of the injected water, 6,4 mg C/l, seems to be decomposable. This means that the decomposition of DOC takes time.

CONCLUSIONS

The results of this recharge experiment have so far yielded many answers to the questions about the changes to the quality of the injection water on its way to the recovery wells. We gained insight into the character and sequence of the changes. As to the time scale, further calculations are planned using the mass balance approach and the model EASY-LEACHER (St, this volume). As for the clogging around the injection well, mixing of oxic and anoxic water might have resulted in precipitation of (hydr)oxides around the well. Its volume can be neglected however, as *doubling the injection rate did not influence* the injection cone very much. This leads to the conclusion that clogging is not a serious problem around the injection well. Around the recovery well however, we do foresee clogging as a result of mixing. Anoxic and oxic water will be extracted at the same time once oxic water breaks through. We will be able to quantify and to set a time scale when the results from the parallel filters, the flowmodel and EASY LEACHER are available. We are confident that the results of the experiment can be extrapolated to the future production plant Leeuwterveld because of the similarity of the two sites. So far the recharge of semi-purified surface water in the future production plant Leeuwterveld looks promising!

REFERENCES

Stuyfzand, P.J. & J.C. de Ruiter 1997. Kwaliteitsverandering van drinkwater bij diep-infiltratie te St. Jansklooster. Nieuwegein: Kiwa (in dutch)

Horn, P. van den & J.C. de Ruiter 1996. Infiltratieproef Sint Jansklooster: Onderzoeksplan. Zwolle: WMO (in dutch)

Stuyfzand, P.J. 1998. Simple models for reactive transport of pollutants and main constituents during artificial recharge and bankfiltration: infomi 3.1 and easy-leacher. (this volume).