Water quality changes following deep well injection of BWRO concentrate

Results from the BWRO pilots Noardburgum and Zevenbergen

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Front cover
Sampling of observation well B44C0729, pilot Zevenbergen, Brabant Water. Photo courtesy of Carl van Rosmalen (Brabant Water)

Preface

The BWRO pilots Noardburgum and Zevenbergen were initiated, operated and financed by water supply companies Vitens (Noardburgum) and Brabant Water (Zevenbergen). This support is gently acknowledged by the authors. This study was carried out within the framework of the Joint Research Programme (BTO) of the Dutch Waterworks, which is carried out by KWR Watercycle Research Institute. In addition, both pilots as well as this study were supported financially from various other sources:

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- Ate Oosterhof (Vitens)
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- Maarten Nederlof (KWR)
- Pieter Stuyfzand (KWR)
- Klaasjan Raat (KWR)

Summary

Brackish water reverse osmosis (BWRO) is an interesting source treatment option for drinking water, and under serious consideration in the Netherlands. The drivers consist of environmental problems like salinization of fresh water wells, drawdown of water tables in phreatic aquifers and increasing costs to produce drinking water from polluted, fresh groundwater. The major obstacle for large scale application of BWRO is the disposal of the membrane concentrate. Deep well injection into a (more) saline, confined aquifer is considered to be the best solution to this waste water problem, though permitting of deep well injection is still problematic. Bottleneck is the potentially negative effects of BWRO concentrate injection on the water quality of the disposal aquifer.

The effects of BWRO concentrate injection on the hydrochemistry of the disposal aquifer were studied at two pilot locations in The Netherlands: Noardburgum (water supply company Vitens) and Zevenbergen (Brabant Water). At both locations, brackish water was abstracted, desalinated using reverse osmosis (50% recovery) and the membrane concentrate was injected into a deeper, confined aquifer. Both BWRO concentrates fitted neatly into the natural chemical environment of the disposal aquifer. This was demonstrated for the major constituents and trace elements. At the Noardburgum site, injected BWRO concentrate passed through the aquifer almost unaltered, despite supersaturation towards several carbonate and phosphate minerals. At Zevenbergen, there were many hydrogeochemical interactions between the injectate and the aquifer, which resulted in a complex pattern of water quality changes, including precipitation of calcite and siderite, dissolution of minerals rich in magnesium and strontium, and sorption of phosphate, silica, arsenic and nickel from the injected solution. In comparison with the native groundwater, injection had no negative effects on the water quality of the disposal aquifer at Zevenbergen. At Noardburgum, iron was the only water quality parameter to increase (substantially) upon injection, resulting from the high iron levels in the BWRO concentrate. From an environmental viewpoint this increase in iron concentrations was irrelevant.

Membrane scaling and injection well clogging due to mineral precipitation were not a problem at the Noardburgum site. These operational problems did occur at Zevenbergen, however, even though mineral oversaturation levels were in the same order as at Noardburgum. The differences in mineral precipitation were due to differences in water quality of the BWRO concentrate (pH, Fe^{2+}) and the geochemistry of the disposal aquifers (texture, calcite content). The relatively high Fe, PO_4 and Mg concentrations at Noardburgum are likely hindering the kinetics of mineral precipitation. At Noardburgum, the RO could therefore be operated at 75% recovery, without introducing any technical problems. At Zevenbergen, even a recovery level of 50% was not (technically) sustainable, with aquifer and injection well clogging becoming problematic in the long run. Lowering the pH by dosing HCl or CO_2 to the RO concentrate could be a solution here.

The results of this study indicate that deep well injection can be an environmentally safe and technically feasible solution for the disposal of BWRO membrane concentrate. We believe current legislation and policy towards deep well injection is too rigid, focusing too much on the "standstill principle". We advocate the idea that the effects of BWRO injection on groundwater quality of the disposal aquifer should be evaluated in a wider context, and weighted against societal and environmental benefits of applying BWRO like counteracting salinization of fresh water wells.

Contents

1   Introduction

Countries in temperate climates are today seriously considering reverse osmosis of brackish groundwater (BWRO) as an option to prepare drinking water (Stuyfzand and Raat, 2010). The drivers consist of environmental problems like the salinization of aquifers, drawdown of water tables in phreatic aquifers and increasing costs to produce drinking water from heavily polluted, fresh groundwater. Even in the Netherlands, a country with abundant surface and groundwater resources, BWRO is currently under serious consideration (Kooiman et al., 2004; Nederlof and Hoogendoorn, 2005). The interest in BWRO was triggered by problems in the coastal zone, where a number of well fields suffer from salinization due to the upconing of brackish water. This upconing can be prevented by interception of the brackish water at greater depth (fresh keeper concept; Grakist et al., 2002; Kooiman et al., 2004; Oosterhof and Raat, 2010).

The major obstacle for large scale application of BWRO is the disposal of the membrane concentrate. At inland sites, membrane concentrate cannot be disposed to the sea and other disposal options, like discharge to surface waters, are often rejected by environmental laws. Deep well injection into a more saline, confined aquifer is considered to be the best solution to the waste water problem (Stuyfzand and Raat, 2010), though permitting of large scale BWRO plants still is problematic. Clear policy and legislation towards deep well injection of BWRO concentrate has yet to be defined in the Netherlands. Currently, Dutch authorities allow the disposal of membrane concentrate in the aquifer when the disposal has no negative effects on the aquifer and groundwater quality in the disposal aquifer. In practice, the stand-still principle is applied, meaning that injection of BWRO concentrate should not lead to an increase ("deterioration") of selected water quality parameters, including organic pollutants, metals, nutrients and halogens. Being a paleo-water, the brackish groundwater used as RO feed water is free of organic pollutants, but it can, by nature, be high in some metals (e.g., arsenic, strontium and barium), nutrients (ammonium, phosphate) and halogens (chloride, bromide and fluoride). Levels of (some of) these natural constituents may already be above maximum allowable concentrations in the RO feed water, and are increased even more in the concentrate.

The advantages of BWRO have triggered both water utilities Vitens and Brabant Water to start BWRO pilots, using deep well injection for concentrate disposal (Oosterhof et al., 2009). An important aim of the pilots is to make clear whether BWRO is indeed an interesting 'source-treatment' option for the preparation of drinking water, being technically feasible at competitive costs and attractive from an environmental viewpoint. The effects of concentrate injection on the hydrochemistry of the disposal aquifer thus need to be studied and evaluated against current legislation. It is foreseen that the results of the pilots will aid to the development of clear policy towards concentrate disposal in deeper aquifers in the Netherlands. In addition, the pilots should make clear which level of supersaturation the membrane concentrate may attain without clogging the injection well and its surroundings. Moreover, the pilots will provide information on efficiency and energy consumption by the ROs and on the water quality of the permeate water. Boron, for example, is found in high concentrations in brackish groundwater and is known to pass RO membranes to end up in the permeate. To a large extent, the success of the BWRO plant is dependent on the selection of source and disposal aquifers and the recovery level of the RO installation. These determine the water quality of feed water, permeate (boron), and the mineral saturation levels of the concentrate and associated risks for mineral precipitation in the RO and/or near the injection well.

This report presents the results from the BWRO pilots operated by Vitens (location Noardburgum) and Brabant Water (Zevenbergen). Focus is on the water quality changes in the disposal aquifer, following the deep well injection of BWRO concentrate. Water qualities of the BWRO concentrates are evaluated against the water quality of the native groundwater of the disposal aquifers, hydrogeochemical interactions between the injectate and the aquifer matrix are described and explained, and mineral precipitation and the risk of injection well and aquifer clogging are assessed. The report ends with an evaluation of the effects of deep well injection on the water quality of the disposal aquifers, including the environmental risks and benefits.

2   Materials and methods

2.1   Setup of BWRO pilots

The BWRO pilot plants are located near the municipalities of Noardburgum (Vitens), in the Dutch northern coastal zone, and Zevenbergen (Brabant Water), in the southwestern zone (Figure 1). The brackish groundwater in the sedimentary aquifers originates from Pleistocene and Holocene intrusions of the North Sea, and the repetitive trans- and regressions have resulted in a complex pattern of chloride concentrations, with several inversions present (Fig. 2 and 3).
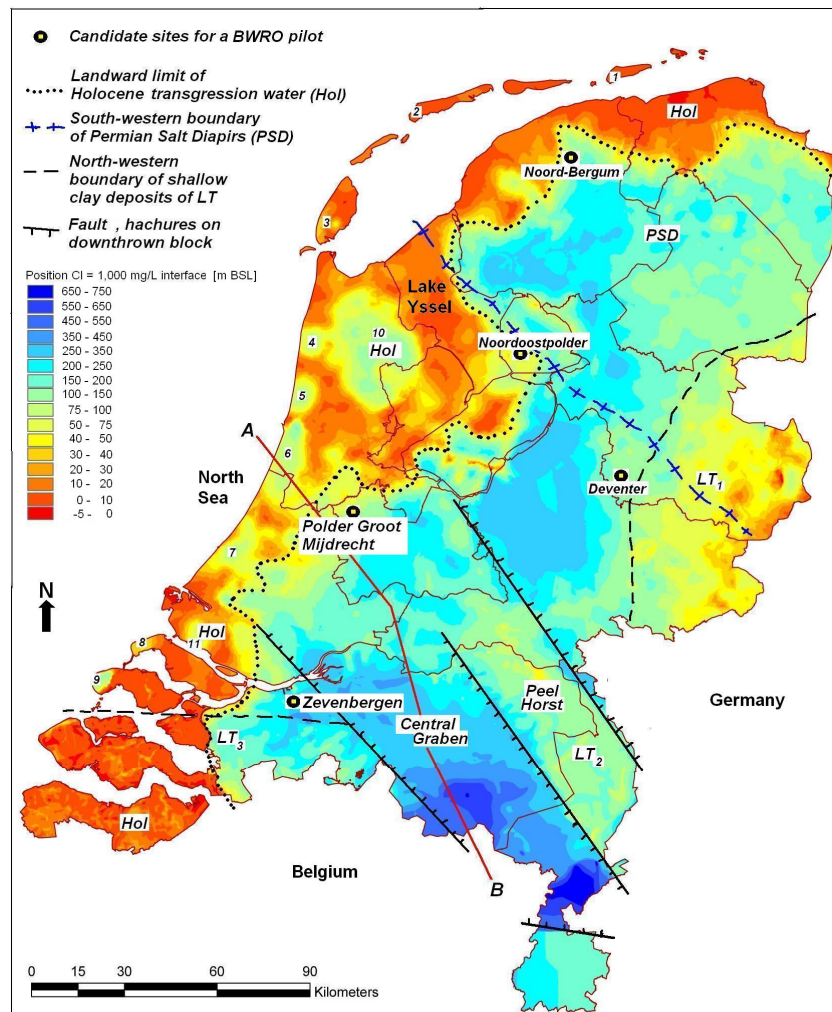
Figure 1. Position of the Noardburgum and Zevenbergen BWRO pilot plants. Also shown: depth to the 1,000 mg Cl/L isoline (in m below sea level; inversions excluded), approximate landward limit of the brackish to salt Holocene transgression waters (Hol), relatively shallow occurrences of marine deposits of late Tertiary to early Pleistocene age (LT), and relatively shallow Permian rock salt diapirs (PSD).

Setup of the pilot plants is presented in Figures 2 and 3. The pilot at Noardburgum is situated within a former well field, which was abandoned in 1993 because of salinization. The fresh keeper concept is applied at the site, by simultaneous abstraction of upper fresh and lower brackish groundwater (Fig. 1). The abstracted fresh water is transported directly to the purification plant at Noardburgum, while the brackish water is fed to an RO before transportation and post-treatment. Field test results from the Noardburgum fresh keeper are presented by Oosterhof and Raat (2010). At Zevenbergen, the pilot plant consists of a single brackish water abstraction well, no fresh water is abstracted. The abstraction well consists of two well screens, abstracting water from aquifers 2 and 4 at a rate of 49.2 and 0.8 m^3 hr^{-1},

respectively. The abstraction from aquifer 4 was included to guarantee that chloride levels of the RO feed water would remain above 300 mg/L throughout the duration of the Zevenbergen pilot.
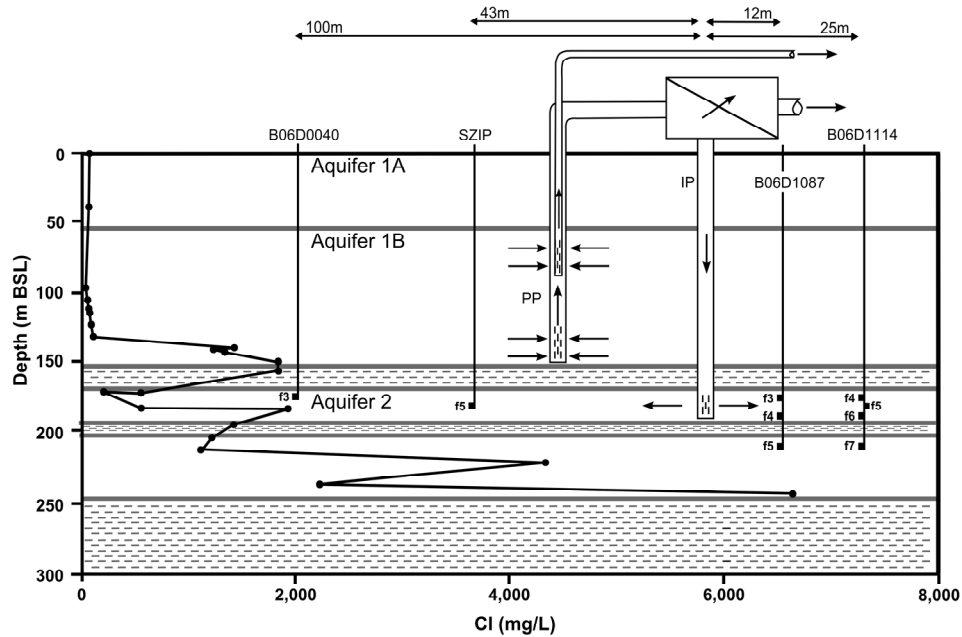
Figure 2. Setup of the fresh keeper and BWRO pilot Noardburgum (Vitens), including pumping (PP), injection (IP) and observation wells. Fresh and brackish groundwater were abstracted simultaneously from two depths in aquifer 1B, both at a rate of 50 m³ hr⁻¹. The RO installation operated at 50% recovery, splitting the brackish feed water in 25 m³ hr⁻¹ permeate and an equal amount of concentrate, which was injected into aquifer 2. Also shown is the chloride profile at the start of the pilot.

Brackish water is abstracted at a rate of 50 m³ hr⁻¹ at both sites. Both ROs initially operated at 50% recovery, resulting in a production of 25 m³ hr⁻¹ of permeate and concentrate, respectively. The relatively low recovery level was maintained to prevent severe mineral supersaturation of the concentrate, which could cause scaling of the membranes and/or clogging of the injection well and aquifer due to mineral precipitation. Antiscalants (e.g., polyphosphates) or acids, which are often used to prevent membrane scaling, were not used in RO process. This was an important prerequisite in the injection permits issued for the pilots. The RO recovery level was increased later on in both pilots, to test at which recovery levels membrane scaling and/or injection well clogging would become problematic. Again, we refrained from using antiscalants or acids. The concentrate was injected into a deeper, confined aquifer at both sites (Fig. 2 and 3), which is separated from the BWRO source water aquifer by an aquitard. Chloride levels in the disposal aquifers were in the same brackish range as the source (pumped) aquifers.
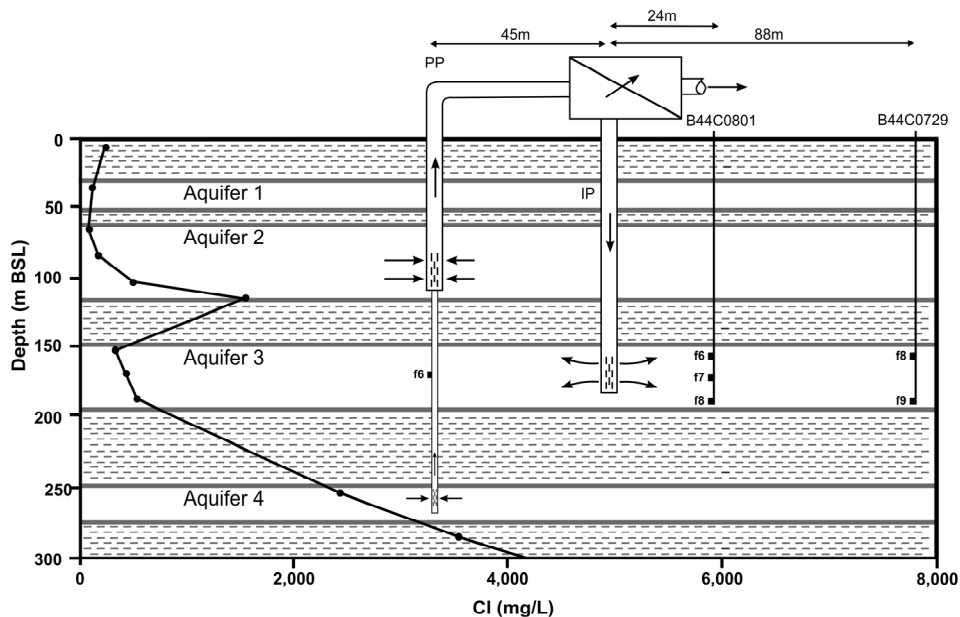
Figure 3. Setup of the BWRO pilot Zevenbergen (Brabant Water), including pumping (PP), injection (IP) and observation wells. The RO feed water was a mixture of water abstracted from aquifer 2 (49.2 m³ hr⁻¹) and aquifer 4 (0.8 m³ hr⁻¹). The RO installation operated at 50% recovery, rendering 25 m³ hr⁻¹ of permeate water and an equal amount of concentrate. BWRO concentrate was disposed by deep well injection into aquifer 3. Also shown is the chloride profile at the start of the pilot.

2.2 Hydrogeochemistry of source and disposal aquifer

2.2.1 Geochemistry of the disposal aquifer

Aquifer material was sampled during drilling of the monitor wells through core catchers ahead of the drilling casing. The sediment cores from core catchers, including their pore water, were immediately sealed on site using liquidized paraffin, and kept at 4°C in the dark until analysis. The anoxic samples were treated in a glove box under N_2 atmosphere and not dried at all, except for a fraction to determine its dry weight. All samples were sieved over 2 mm mesh to remove the gravel size fraction. Gravel consisting of quartz or siliceous rock was excluded from further analysis. Clay aggregates, peat, roots and shell fragments were grinded and restituted to the sieved sample. Sieved samples (the fraction < 2 mm plus grinded material) were manually homogenized and split into identical subsamples for separate analysis. The following bulk characteristics were determined:

- residues at 105°C (dry weight residue, needed to relate all analytical results to the dry weight fraction), 450°C (loss on ignition, a measure for total bulk organic material), and 1000°C (burning residue: measure for total carbonates), by thermogravimetric analysis (TGA; see for instance Dean, 1974; Rabenhorst, 1988). About 5 grams of field dry sample are used, and each heating step lasts for 16 hours followed by 4 hours of cooling in a desicccator.
- grain size analysis of the fraction <2mm (after treatment with HCl and H_2O_2 to remove cementing materials), by a FRITSCH Laser Particle Sizer A22. Clay and silt fractions were converted to the traditional grain size analysis with pipette and sieves, by the approach of Konert & Van den Berghe (1997).
- total organic C, total N and total S by pyrolysis and infra red gas detection. After acid washing to remove inorganic carbon and subsequent pyrolysis, C, N and S were measured on a LECO analyser. Total C was also measured without acid washing, for calculating total carbonates.
- total element content (53 species) using ICP-MS on an aqua regia extract.

The results of the geochemical background survey are shown in Table 1 for both the Noardburgum and Zevenbergen disposal aquifers. The Noardburgum disposal aquifer is composed of unconsolidated, coarse grained, well sorted fluvial sands of early Pleistocene age. It shows very low levels of reactive minerals due to lack of carbonate minerals, low concentrations of bulk organic material (BOM) and trace

elements, and a low CEC. Pyrite is present but practically not reactive when injecting a fluid without oxygen and nitrate. The Zevenbergen disposal aquifer is composed of unconsolidated, medium grained, marine sands of late Tertiary and early Pleistocene age with intercalated clay or loam layers. It contains many more reactive minerals than the Noardburgum disposal aquifer as can be derived from the high concentrations of carbonates, BOM, phosphate and, trace elements, the higher CEC and presence of much more pyrite. It was noted that the aquifer also contains some glauconite.

Table 1. Summary of the geochemistry of the disposal aquifers of Noardburgum and Zevenbergen. Element concentrations after aqua regia destruction.

	Description		Unit	N-Bergum	7-Bergen		Description		Unit	N-Bergum	7-Bergen
	Depth	from	m-LS	174	165		Depth	from	m-LS	174	165
	Depth	to	m-LS	179	176		Depth	to	m-LS	179	176
Specific	Clay	Fraction	%	2.4	5.1	**Trace Elements**	As	HNO3	ppm	0.6	29.2
	EC-H2O		uS/cm	140	450		B	HNO3	ppm	0.5	47
	BOM		%	0.31	0.76		Cd	HNO3	ppm	0.01	0.11
	CaCO3		%	0.00	18.04		Co	HNO3	ppm	1.2	9.0
	CEC		meq/kg	17.0	45.9		Cr	HNO3	ppm	5.8	64.6
	FeS2		ppm	670	6402		La	HNO3	ppm	2.5	11.2
Main	Al	HNO3	ppm	1250	7725		Ni	HNO3	ppm	4.0	15.6
	Ca	HNO3	ppm	300	77600		Pb	HNO3	ppm	1.5	8.5
	Fe	HNO3	ppm	4200	42825		Sb	HNO3	ppm	0.08	0.60
	K	HNO3	ppm	350	4350		Sr	HNO3	ppm	3	520
	Mg	HNO3	ppm	200	9750		Th	HNO3	ppm	0.85	2.90
	Mn	HNO3	ppm	65	195		U	HNO3	ppm	0.3	1.2
	Na	HNO3	ppm	75	848		V	HNO3	ppm	1.5	76.8
	P	HNO3	ppm	10	1040		Zn	HNO3	ppm	8	37

2.2.2 Native hydrochemistry

The native groundwater composition on site (prior to the start of the BWRO pilot) was analysed from all available monitor wells at the BWRO site, in both the brackish water source and disposal aquifer (Figs.2-3). Results of this survey are summarized in Tables 2 (Noardburgum) and 3 (Zevenbergen). Additional data (including trace elements) for the disposal aquifers can found in Tables 4 (Noardburgum) and 5 (Zevenbergen), and is discussed in Chapter 3.

Noardburgum

The source aquifer (#1B, Fig. 2) at Noardburgum shows fresh groundwater of the F3CaHCO3 type down to 130 m BLS and brackish groundwater of the b3CaCl- type between 130 and 155 m BLS. The fresh groundwater shows a slightly positive Base Exchange index (BEX) not deviating much from zero, which testifies of sufficient flushing of the upper part of this aquifer with fresh groundwater to equilibrate the cation exchange complex with fresh CaHCO3 water. The brackish groundwater in the deeper parts of this aquifer exhibits a significantly negative BEX indicating that the aquifer salinized with concomitant cation exchange of marine Na (+K+Mg) for continental (fresh) Ca. The exchange process consists of adsorption of Na (+K+Mg) and desorption of an equivalent amount of Ca. The disposal aquifer (#2) shows a very thin layer of salinized F3CaHCO3- water (with significantly negative BEX) on top of salinized brackish groundwater of the B3CaCl- and b2CaCl- type. The occurrence of the salinized brackish groundwaters in aquifer 1B and in aquifer 2 can be related to the excessive pumping of the aquifers for drinking water supply up to 1993. In 1993, the well field was shut, but the brackish groundwater was hardly replaced by fresh groundwater.

Most of the salinized groundwater at Noardburgum shows high concentrations of Ca, Fe, Mn, CH4, Ba and Sr, and relatively low levels for SO4, PO4 and NH4, and most trace elements (including B, Li and most heavy metals). This is typical for intruding sea water (Stuyfzand & Stuurman, 2008), which is confirmed by a normal Cl/Br ratio. The high methane concentrations likely point at passage of aquifer zones where methane was supplied from Holocene clay and peat layers. The position of well field Noardburgum then suggests that this high methane, salinizing brackish groundwater is derived from Holocene transgression water coming from the north or west. Most interestingly, below this high

methane salinizing groundwater we observed a transition to very low methane, strongly salinizing groundwater, at about 189 m BLS (Table 2). This water may have originated in the same way as the brackish groundwater on top, but in areas without Holocene clay and peat deposits, for instance in a Holocene sandy gully.

Table 2. Hydrochemistry of the Noardburgum BWRO source and disposal aquifer. Water was abstracted from aquifer 1B, at two depths: 67 - 86 (fresh water) and 134 - 148 m depth (brackish water, RO feed water). BWRO concentrate was injected in aquifer 2, at a depth of 173 - 192 m. Water types as defined by Stuyfzand (1993). BEX index indicates salinization (BEX < 0) or freshening (BEX > 0) of the local water. See text for further details.

Noord Bergum	CH4	Cl	HCO3	Ca	Sr	Fe	BEX	Watertype	B	Ba
			mg/L				meq/L		ug/L	
-63		51	362	108			0.6	F3CaHCO3o		
-73		70	373	117			0.0	F3CaHCO3o		
-85		35	389	100			1.4	F3CaHCO3+		
-87		31	401	108			0.5	F3CaHCO3		
-103		38	404	120			0.5	F3CaHCO3o		
-104		29	417	108			0.6	g3CaHCO3+		
-110		37	418	122			0.5	F3CaHCO3		
-115		49	437	123			0.2	F3CaHCO3		
-120		57	399	116			-0.1	F3CaHCO3		
-125		63	412	131			-0.1	F3CaHCO3o		
-127		66	394	130			-0.3	F3CaHCO3o		
-127		75	397	128			-0.5	F3CaHCO3o		
-134		510	358	274			-10.8	B3CaCl-		
-140		1200	322	555			-26.6	b3CaCl-		
-145		1800	272	764			-40.4	b3CaCl-		
-146		1800	270	762			-40.8	b3CaCl-		
-147		1800	267	717			-41.4	b3CaCl-		
AQUITARD 2										
-170	9.30	110	325	114	0.41	7.38	-1.3	F3CaHCO3-	24	44
-172	11.00	370	329	222	0.78	16.10	-7.4	B3CaCl-	21	128
-179	14.00	530	363	292	0.97	27.10	-11.3	B3CaCl-	14	186
-179	12.00	870	348	426	1.48	32.00	-17.1	B3CaCl-	28	789
-180	12.00	670	331	324	1.11	29.70	-14.8	B3CaCl-	18	226
-190	0.21	4200	223	1250	5.35	33.60	-82.2	b2CaCl-	43	1580
-191	0.09	4500	227	1370	5.98	34.00	-85.8	b2CaCl-	51	1660
-208	0.10	3200	240	1060	4.96	23.60	-64.1	b2CaCl-	60	624
-208	0.21	4100	233	1200	5.36	24.10	-81.0	b2CaCl-	63	829

Zevenbergen

The main source aquifer (#2, Fig. 3) at Zevenbergen shows a similar pattern as the source aquifer at Noardburgum. Fresh groundwater of the F3CaHCO3. type is found down to 87 m BLS, overlying brackish groundwater of the B3CaCl- and b3CaCl- type (87 to 120 m BLS). The deep source aquifer (#4) contains brackish groundwater probably with a freshened facies (BEX significantly positive). The doubt about BEX is based on the poor ionic balance of the only 2 samples available taken shortly after drilling. The disposal aquifer (#3) shows a very thin layer of f3NaCl water (with positive BEX) on top of freshened, brackish groundwater of the B3NaCl+ type. The occurrence of this freshened brackish groundwater can be related to expansion of the deep fresh groundwater body (with partial recharge in Belgium) in the Quaternary period. This groundwater is quite different from the native groundwater in the disposal aquifer at Noardburgum, by its positive BEX, much higher concentrations of Na, HCO$_3$, B, F, Li and Sr, and lower concentrations of CH$_4$, Ca, Fe, Mn, SiO$_2$, PO$_4$, TOC and Ba. Most of these differences relate to the complex hydrochemical changes during fresh and salt water intrusion, which result in clear correlations between for instance BEX with Ca, HCO$_3$, Fe, Mn, F, PO$_4$, B and Li (Stuyfzand, 1993, 2008). A very striking feature of groundwater in the deeper parts of aquifer #2 and in aquifer #3 is the anomalously high Sr content. This is probably caused by dissolution of high Sr carbonates, like dolomitic calcite or even dolomite. In the deeper parts of aquifer #2 cation exchange of Ca and Sr may add to the Sr anomaly.

Table 3. Hydrochemistry of the Zevenbergen BWRO source and disposal aquifer. RO feed water was a mixture of water abstracted from aquifer 2 (90 - 115 m depth; 49.2 $m^3 hr^{-1}$) and aquifer 4 (250 - 255 m depth; 0.8 m $m^3 hr^{-1}$). BWRO concentrate was injected in aquifer 3, at a depth of 168 - 182 m. Water types as defined by Stuyfzand (1993). BEX index indicates salinization (BEX < 0) or freshening (BEX > 0) of the local water. See text for further details.

Zeven Bergen	CH4	Cl	HCO3	Ca	Sr	Fe	BEX	Watertype	B	Ba
			mg/L				meq/L		ug/L	
-6	28.00	225	499							
-8		130	317							
-8	22.00	610	305							
-8	18.00	185	430							
AQUITARD 1										
-34	7.60	85	311							
-35		46	339							
-35	17.00	57	335							
-35	7.40	80	314							
AQUITARD 2										
-63	21.00	36	376							
-80		140	367	100	0.40	1.90	0.6	F3CaHCO3o	550	4
-80	6.40	110	402	102	0.41	2.00	0.8	F3CaHCO3	370	0
-83	3.50	130	382	106	0.50	1.90	0.7	F3CaHCO3o	280	6
-91		190	376	111	0.67	1.10	0.4	f3CaHCO3o	590	2
-98	1.50	275	358	132	0.87	1.80	-1.7	f3CaClo	590	0
-101	5.90	510	368	230	1.80	3.00	-6.5	B3CaCl-	520	10
-109		580	357	182	1.90	1.10	-4.4	B3NaCl-	760	4
-109	0.20	800	337	270	3.50	2.10	-9.1	B3CaCl-	690	8
-111	0.19	1100	348	380	5.60	3.20	-15.8	b3CaCl-	940	9
-114	2.30	1400	445	470	8.40	4.10	-19.3	b3CaCl-	560	31
AQUITARD 3										
-150	0.27	290	417	82	2.50	0.60	1.8	f3NaCl	1100	10
-166	0.07	375	431	78	4.70	0.72	2.2	B3NaCl	870	16
-168	0.06	385	444	64	4.60	0.69	2.8	B3NaCl+	1000	0
-169	0.38	375	418	99	3.50	0.96	0.8	B3NaClo	680	8
-173		400	449	62	4.50	0.64	3.2	B3NaCl+	940	4
-175	0.05	465	445	44	3.10	0.00	4.0	B3NaCl+	970	4
-176	0.06	435	452	52	4.10	0.56	3.5	B3NaCl+	1000	0
-181	0.05	420	448	52	4.00	0.00	3.5	B3NaCl+	880	4
-182	0.04	465	450	42	3.00	0.50	3.9	B3NaCl+	1000	0
-185	0.07	520	452	40	2.30	0.42	2.8	B3NaCl+	1100	34
AQUITARD 4										
-252		2400	676	29	1.20	0.03	3.2	b4NaCl	5600	11
-253	0.02	2600	700	1	1.20	0.20	-3.2	b4NaCl	7699	110
-284	0.06	3600								
-303	0.03	4400								

2.3 Monitoring program

A detailed monitoring program was developed to check on the performance of the RO installation and the abstraction and injection wells, and to follow water flow and water quality changes in the BWRO source and disposal aquifers. Performance of the RO installations was evaluated by online monitoring of the pressure drop over the membranes, the electrical conductivity of the feed water and BWRO concentrate, and the energy usage of the RO. In addition, water quality of the feed water, permeate and concentrate was analyzed regularly, for macro elements and a large set of trace elements. Performance of the abstraction and injection wells was monitored by online measurement of the abstraction and injection pressures. Pressure heads of the groundwater were determined online in several of the observation wells (Figs. 2 and 3), both in the source and disposal aquifers, providing information on water flow in these aquifers. Several observation screens in the disposal aquifers were equipped with electrical conductivity sensors, in order to carefully detect the breakthrough of the injected concentrate. At the Noardburgum site, special attention was paid to the development of the fresh-brackish interface in the source aquifer, following the simultaneous abstraction of upper fresh and lower brackish groundwater. The position of the interface was monitored online using a resistivity sensor installed along the pumping well.

Water quality changes in the disposal aquifers were monitored via several observation wells, at multiple depths. Location of these wells and the respective well screens are presented in Figures 2 and 3. Throughout this report, these well screens are referred to using a code containing information on pilot location, well screen depth and the distance from the observation well to the injection well. For instance, "Z24-176" refers to a well screen at Zevenbergen, at 176 m depth and a horizontal distance of 24 meters

from the injection well. Water quality samples were taken from the well screens at regular intervals, and analyzed for macro (always) and trace elements (several occasions). Sampling frequency was higher for observation wells close to the injection well. At breakthrough of the injectate, sampling was temporarily intensified.

2.4 Hydrogeochemical calculations

Various hydrochemical calculations were done by using Hydrogeochemcal, an EXCEL program developed by Stuyfzand (2010). Calculations included data control (via ionic balances and comparison of measured with calculated SEC), determination of the Base Exchange indeX (BEX; see Stuyfzand, 2010) and watertype classification (see Stuyfzand, 1986; 1993). With Geochemcal, an EXCEL program developed by Stuyfzand, all geochemical analytical data were transformed into reactive mineral contents or characteristics which require various corrections (Stuyfzand & Meima, 2000). Mineral saturation indices were calculated using PHREEQC-2 (Parkhurst and Appelo. 1999). The resulting saturation index SI is defined as

$$SI_M = log \ (IAP \ / \ K_S)$$

where IAP = Ion Activity Product of the mineral-water reaction in the sample (on a mol/kg water basis); and K_S = the corresponding solubility product in pure water, adjusted to the temperature and pressure of the sample.

3   Results and discussion

3.1   Concentrate water quality

Disposal of membrane concentrate in the subsoil is currently allowed in case the disposal has no negative impact on the aquifer and groundwater quality. In other words, the BWRO concentrate should fit into the natural chemical environment of the disposal aquifer. In permitting the two pilots, Dutch authorities followed the Water Framework Directive (WFD) and the chemical parameters listed therein. Being a paleowater, organic pollutants are absent in the feed water and (thus) in the membrane concentrate, reducing the relevant WFD-parameters to chloride, nitrogen (ammonium), phosphate, arsenic, nickel, lead and cadmium. In addition to these, a number of trace elements are included in the analysis below, as many of these can be present in brackish water at relatively high levels and can be relevant from the perspective of water treatment, clogging and tracing.

Water quality of the concentrate (50% recovery) and of the native water in the disposal aquifer are listed in tables 4 (Noardburgum) and 5 (Zevenbergen). Note in Table 4 that the ICP data for the Noardburgum concentrate were derived from samples taken at N12-179 (B06D1087-f3), after breakthrough of the concentrate in this well screen (as ICP analyses on trace elements were not performed for the Noardburgum concentrate). Water quality at N12-179 was a fair substitute for the water quality of the concentrate, as hydrochemical interactions between injected concentrate and the Noardburgum aquifer were almost absent (see section 3.2.1).

The chemical composition of brackish groundwater deviates from that of fresh water, not just for parameters like sodium and chloride, but for specific metals, nutrients and halogens as well. A number of elements can be found at elevated levels in brackish groundwater, including Fe, the halogens Br and F, the nutrients NH_4 and PO_4, and the trace elements As, B, Ba, Cr, Li, Ni and Sr. Typical for the BWRO concentrate at Noardburgum (Table 4) are the very high levels of Ca, Fe, HCO_3, and CH_4, and the elevated levels of Br, Ba, Sr and Li. Concentrations of (other) trace elements are very low, many below the detection limit. Two parameters (bromide and barium) were above the target levels for deep groundwater, which have been defined by the Dutch government. These target values, however, have been determined with fresh groundwater as a reference, and are of limited use for brackish groundwater systems. For example, concentrations of bromide, barium, cobalt, nickel, lead and selenium exceed the target values for deep groundwater at one or multiple depths in the Noardburgum disposal aquifer, by nature (Table 4). In a study on WFD threshold definition for the Rijn-West coastal area in the Netherlands, Passier et al. (2006) drew similar conclusions: different threshold values should be defined for fresh and brackish/salt groundwater bodies, respectively. Indeed, the National Institute for Public Health and the Environment (RIVM) has advised the Dutch authorities to develop different WFD threshold values for brackish/salt groundwater bodies in different regions of the Netherlands (Verweij, et al., 2008). A basis for such a framework is provided by Stuyfzand (1991, 1992), who presented guidelines for natural background levels of several trace elements in brackish and saline groundwaters, by linking these to the chloride, strontium and calcium concentrations. For now, a fair and straightforward way to evaluate the water quality of the concentrate is to compare it directly to the water quality of the native groundwater in the disposal aquifer, and to follow the WFD criteria that injection should not lead to a decline of the water quality of the disposal aquifer.

It was already noticed that the Noarburgum disposal aquifer is highly stratified with, for example, chloride levels increasing from 370 mg/L at the top of the aquifer (N25-172) to 4500 mg/L further down (N25-191, Table 4). The aquifer can be subdivided into two main chemical water types (Table 2): a B3CaCl- type, with a noticeable high CH_4 content, and a b2CaCl- type, with (very) high concentrations of Ca, Sr and Ba and low CH_4 levels. For most macro and micro water quality parameters, the concentrate falls within the water quality range of the disposal aquifer. For example, even though levels of Br, Ba, Sr and Li were elevated in the concentrate, they fit in the ranges of the native groundwater, mainly because of the high levels recorded in the lower part of the aquifer (N25-191, Table 4). The only exceptions were the macro parameters HCO_3, PO_4, TOC, Fe and Si. For all these parameters, levels were higher in the

concentrate than at any depth in the disposal aquifer. From an environmental viewpoint, the levels of the macro's HCO_3, TOC and Si are not relevant. Neither worrying was a PO_4 level of 0.70 mg/L, which is typically higher in brackish waters. Iron levels were extremely high in the BWRO concentrate, beyond the natural background levels, yet the environmental relevance of high iron in deep groundwater is limited. We thus conclude that, despite iron, the Noardburgum concentrate fits into the natural chemical environment of the disposal aquifer, for both macro and trace elements, and injection of the concentrate is not likely to cause a deterioration of the water quality in the disposal aquifer.

Similar to Noardburgum, the BWRO concentrate at Zevenbergen (Table 5) is characterized by high levels of HCO_3, Ca, Sr and Li. Contrasting are the levels of Fe, CH_4 and Ba, which were exceptionally high at Noardburgum, but relatively low in the Zevenbergen concentrate. Boron concentrations are high at Zevenbergen, in both the concentrate (1240 ug/L) and permeate (268 ug/L, data not shown). Unlike most other dissolved species, the small sized boron (mostly present in the feed water as undissociated boric acid, H_3BO_3) can pass RO membranes and end up in the permeate. Note that boron levels in the permeate approached the World Health Organization (WHO) drinking water standards of 500 ug/L.

The Zevenbergen disposal aquifer has a rather constant water quality, with the B3NaCl water type present at all depths, except for the uppermost part (Table 3). Likewise, the range for water quality parameters is much narrower here than in the highly stratified Noardburgum aquifer. In the concentrate, the macro parameters Cl, SO_4, Ca, Fe, SiO_2 and TOC exceeded the levels of the native groundwater, yet levels in the concentrate were not worrying from an environmental point of view. As mentioned, boron, lithium and strontium levels were high in the concentrate, but all fell within the ranges found in the disposal aquifer. Nickel levels in the concentrate were somewhat higher (2.6 ug/L) than in the disposal aquifer (< 1.0 ug/L), yet note that these levels are still within the natural levels for brackish groundwater (*cf.* Noardburgum). Concentrations for all other trace elements were very low. In summary, we conclude that the Zevenbergen concentrate fits into the natural chemical environment of the disposal aquifer.

In the above discussion, we did not consider mineral supersaturation and possible mineral precipitation from the concentrate. Tables 4 and 5 show that at both locations the concentrate was supersaturated (SI > 0.3) towards the carbonates calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$) and siderite ($FeCO_3$), hydroxyapatite ($Ca_5(PO_4)_3(OH)$) and quartz (SiO_2), and that, in addition, the Noardburgum concentrate was supersaturated towards rhodochrosite ($MnCO_3$) and vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$). Note that, despite the relatively high levels of strontium (both sites) and barium (Noardburgum), the concentrates were undersaturated towards the relevant minerals strontianite ($SrCO_3$) and barite ($BaSO_4$). Also, at both locations, the concentrate was (strongly) undersaturated towards $NiCO_3$. The supersaturation towards a number of minerals indicates that there was a chance of mineral precipitation in the injection well and/or disposal aquifer. From an environmental viewpoint, precipitation of the respective minerals is not relevant because of their natural abundancy in aquifers, unless it includes co-precipitation of undesired trace elements (which is not the case here). Precipitation does form an operational risk, as it may cause clogging of the injection well and/or the disposal aquifer. This is discussed in section 3.3.

Table 4. Water quality of the BWRO concentrate (time averaged) and the native groundwater of the disposal aquifer at Noardburgum (observation well N25, 3 depths). ICP data for the Noardburgum concentrate were derived from samples taken at N12-179 (B06D1087-f3), after breakthrough of the concentrate in this well screen. See text for further details.

Sample Label Depth	[m]	Concentrate# Conc n.a.	B06D1114-f4 N25-172 172	B06D1114-f5 N25-180 180	B06D1114-f6 N25-191 191	Target value deep groundwater
pH lab		6.97	6.85	6.78	6.7	
EC lab	[mS/m]	473	153	240	1026	
CH4	[mg/L]	15.7	11.0	12.0	0.1	
Cl	[mg/L]	1409	370	670	4500	
Br	[mg/L]	**5.5**	**1.3**	**2.5**	**15.1**	0.3
F	[mg/L]	0.1	0.1	0.1	0.0	0.5
HCO3	[mg/L]	671	329	331	227	
SO4	[mg SO4 / l]	<2.0	<2.0	<2.0	160	
PO4-total	[mg P/L]	0.70	0.2	0.18	0.13	
TOC	[mg/L]	9.60	4.2	4.7	2.7	
Na	[mg/L]	174	47	71.4	849	
K	[mg/L]	6.53	2.86	3.28	14.6	
NH4	[mg N/L]	1.45	0.74	0.9	4.4	
Ca	[mg/L]	754	222	324	1370	
Mg	[mg/L]	60.7	20.5	27.3	157	
Fe	[mg/L]	78.5	16.1	29.7	34	
Mn	[mg/L]	1.68	0.631	0.738	1.54	
Si	[mg Si/L]	30.0	14	14	13	
Al	[ug/L]	<4.0	<4.0	<4.0	<4.0	
As	[ug/L]	<1.0	3.1	1.9	<1.0	7.2
B	[ug/L]	24.6	16.9	14.1	32.9	
Ba	[ug/L]	**533**	128	**226**	**1660**	200
Be	[ug/L]	<0.01	<0.01	<0.01	<0.01	0.05
Cd	[ug/L]	<0.4	<0.4	<0.4	<0.4	0.06
Co	[ug/L]	<0.5	<0.5	<0.5	<0.5	0.7
Cr	[ug/L]	<0.3	<0.3	<0.3	<0.3	2.5
Cu	[ug/L]	<1.0	<1.0	<1.0	<1.0	1.3
Eu	[ug/L]	<0.3	<0.3	<0.3	<0.3	
La	[ug/L]	<0.5	<0.5	<0.5	<0.5	
Li	[ug/L]	22.3	8.5	11.9	30.2	
Mo	[ug/L]	<0.6	<0.6	<0.6	<0.6	3.6
Ni	[ug/L]	<1.0	**2.4**	1.5	<1.0	2.1
Pb	[ug/L]	<2.0	<2.0	<2.0	<2.0	1.7
Sb	[ug/L]	<3.0	<3.0	<3.0	<3.0	0.15
Se	[ug/L]	<7.0	<7.0	<7.0	<7.0	0.07
Sr	[ug/L]	2516	777	1110	5980	
Tl	[ug/L]	<5.0	<5.0	<5.0	<5.0	2
V	[ug/L]	<2.0	<2.0	<2.0	<2.0	1.2
Zn	[ug/L]	<0.1	<0.1	4.2	<0.1	24
Mineral saturation index (SI)						
Barite		n.a.	n.a.	n.a.	**1.24**	
Calcite		**0.72**	-0.05	-0.01	0.13	
Dolomite		**0.52**	-0.97	-0.92	-0.50	
Fluorite		-2.24	-2.66	-2.82	-3.37	
Gypsum		n.a.	n.a.	n.a.	-0.88	
Hydroxyapatite		**2.26**	-0.98	-1.08	-0.42	
Quartz		**1.21**	**0.87**	**0.87**	**0.86**	
Rhodochrosite		**0.44**	-0.18	-0.23	-0.39	
Siderite		**1.83**	**0.95**	**1.10**	**0.71**	
SiO2(a)		-0.14	-0.48	-0.48	-0.49	
Strontianite		-1.23	-1.99	-1.95	-1.71	
Talc		-1.84	-4.94	-5.08	-3.85	
Vivianite		**3.30**	**1.01**	**1.28**	0.04	
Witherite		-2.78	-3.63	-3.51	-3.17	

black bold = SI >0.3
red bold = value > target value deeper groundwater
= ICP data for the concentrate was derived from samples taken from M12-179 (B06D1087-f3) after breakthrough of the concentrate in this filter.

Table 5. Water quality of the BWRO concentrate (time averaged) and the native groundwater of the disposal aquifer at Zevenbergen (observation well Z24, 3 depths).

Sample		Concentrate	B44C0801-f06	B44C0801-f07	B44C0801-f08	Target value
Label		Conc	Z24-168	Z24-176	Z24-182	deep groundwater
Depth	[m]	n.a.	168	176	182	
pH lab		7.52	7.59	7.67	7.75	
EC lab	[mS/m]	256	164	176.5	191	
CH4	[mg/L]	1.4	0.06	0.06	0.04	
Cl	[mg/L]	583	385	435	465	
Br	[mg/L]	**1.8**	**1.2**	**1.3**	**1.5**	0.3
F	[mg/L]	0.3	**0.9**	**1.0**	**1.0**	0.5
HCO3	[mg/L]	752	444	452	450	
SO4	[mg SO4 / l]	7.77	3	1.77	2	
PO4-ortho	[mg P/L]	0.20	0.02	0.03	0.04	
TOC	[mg/L]	7.78	3.12	3.93	2.85	
Na	[mg/L]	328	270	290	300	
K	[mg/L]	12.4	14	20	26	
NH4	[mg N/L]	1.7	0.7	1.0	1.4	
Ca	[mg/L]	259	64	52	42	
Mg	[mg/L]	24.2	28	43	52	
Fe	[mg/L]	3.36	0.69	0.56	0.5	
Mn	[mg/L]	0.09	0	0.01	0.01	
Si	[mg Si/L]	19.9	10.0	9.8	9.1	
Al	[ug/L]	<4.0	<4.0	<4.0	18.9	
As	[ug/L]	2.0	<1.0	<1.0	<1.0	7.2
B	[ug/L]	1239	1000	1000	1000	
Ba	[ug/L]	4.5	18#	34#	30#	200
Be	[ug/L]	<0.01	<0.01	<0.01	<0.01	0.05
Cd	[ug/L]	<0.4	<0.4	<0.4	<0.4	0.06
Co	[ug/L]	<0.5	<0.5	<0.5	<0.5	0.7
Cr	[ug/L]	<0.3	<0.3	<0.3	<0.3	2.5
Cu	[ug/L]	<1.0	<1.0	<1.0	<1.0	1.3
Eu	[ug/L]	<0.3	<0.3	<0.3	<0.3	
La	[ug/L]	<0.5	<0.5	<0.5	<0.5	
Li	[ug/L]	42.7	36.4	41.9	47.8	
Mo	[ug/L]	<0.6	<0.6	<0.6	<0.6	3.6
Ni	[ug/L]	**2.6**	<1.0	<1.0	<1.0	2.1
Pb	[ug/L]	<2.0	<2.0	<2.0	<2.0	1.7
Sb	[ug/L]	<3.0	<3.0	<3.0	<3.0	0.15
Se	[ug/L]	<7.0	<7.0	<7.0	<7.0	0.07
Sr	[ug/L]	1700	4600	4100	3000	
Tl	[ug/L]	<5.0	<5.0	<5.0	<5.0	2
V	[ug/L]	<2.0	<2.0	<2.0	<2.0	1.2
Zn	[ug/L]	<0.1	<0.1	<0.1	<0.1	24
Mineral saturation index (SI)						
Barite		-2.17	-2.13#	-1.35#	-2.11#	
Calcite		**0.98**	**0.32**	**0.30**	0.28	
Dolomite		**1.09**	**0.47**	**0.71**	**0.84**	
Fluorite		-1.67	-1.11	-1.14	-1.24	
Gypsum		-2.45	-3.28	-3.62	-3.67	
Hydroxyapatite		**2.22**	-2.38	-2.43	-2.08	
Quartz		**1.02**	**0.71**	**0.70**	**0.66**	
Rhodochrosite		-0.25	-0.18#	-1.14	-1.08	
Siderite		**1.12**	**0.43**	**0.41**	**0.43**	
SiO2(a)		-0.33	-0.64	-0.65	-0.68	
Strontianite		-0.59	-0.31	-0.28	-0.35	
Talc		-0.28	-0.52	**0.43**	**1.01**	
Vivianite		0.13	-2.95	-3.03	-2.70	
Witherite		-4.11	-3.59#	-3.31#	-3.23#	

\# = determined 39 days after start injection
bold = SI >0.3
red bold = value > target value deeper groundwater

3.2 Water quality changes during injection

In the previous section, we showed that at both pilot locations the BWRO concentrate fits neatly into the natural chemical environment of the disposal aquifer, for macro as well as trace elements. This section focuses on water quality changes following injection, as caused by interactions between the injectate and the aquifer matrix and by precipitation from the injectate due to mineral supersaturation.

3.2.1 Noardburgum

Figure 4 shows the water quality changes of the BWRO concentrate and at the first observation well at Noardburgum, at 12 meters distance from the injection well (well screens N12-180, N12-191). Electrical conductivity (EC) and chloride were excellent tracers for breakthrough of the injectate, as indicated by the clear increase in conductivity for the top well screen (N12-180) and the decrease for the lower, more saline well screen (N12-191). Note that breakthrough occurred faster at N12-180 than at N12-191, indicating the higher hydraulic conductivity of the aquifer at 180 m depth. Breakthrough of parameters like Ca, Mg and Fe was not retarded compared to the conservative tracers. Moreover, there were no signs of any mineral precipitation taking place, as shortly after breakthrough levels for parameters like EC, HCO3, Ca, Mg and Fe simply equaled the levels in the BWRO concentrate. Similar results were found for the second observation well.
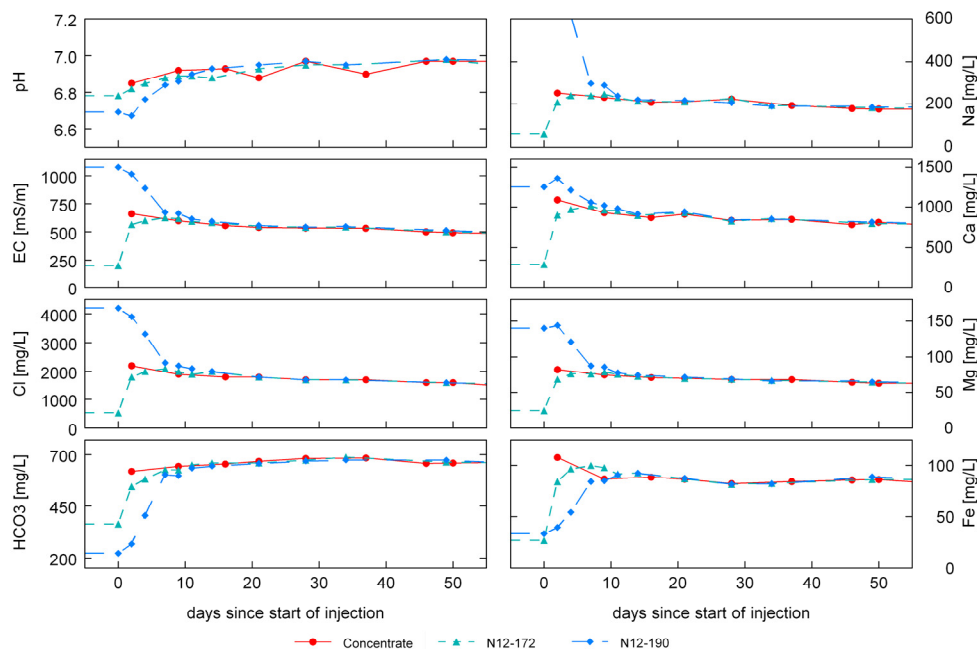

Figure 4. Breakthrough patterns for a selection of parameters at the first observation well of the Noardburgum pilot, at 12 meters distance from the injection well. Also shown is the quality of the injected BWRO concentrate.N12-172, t_{50} = 1.5 days; N12-190, t_{50} = 5 days (approximately).

Table 6 compares the (average) quality of the Noardburgum concentrate and the water quality in the three well screens of the second observation well (N25; B06D1114), after breakthrough of the injectate. Data are provided after flushing of the well screens with several (3 - 12) pore volumes of injectate ("pore flushes", PF). Similar to breakthrough patterns presented in Figure 4, the table indicates that the injectate undergoes little alterations while passing through the aquifer. For example, levels of the macro parameters EC, HCO$_3$, Ca, Mg and Fe at 25 m distance from the injection well were similar to the levels in the BWRO concentrate. Only PO$_4$ levels clearly decreased during aquifer passage, for all well screens and all PFs considered, while Si was lower at some occasions, but not always (Table 6). The lower levels of Ba and Sr recorded later on in the experiment, did not result from sorption or precipitation, but merely mimicked the gradual decrease of these parameters in the pumped BWRO feed water. Likewise, the declines and increases in fluoride levels resulted from the spiky fluoride pattern recorded in the feed water.

Phosphate removal was either due to sorption to the aquifer matrix (hydroxides, clay minerals, organic matter) or due to precipitation as hydroxyapatite and/or vivianite (the concentrate is supersaturated towards these minerals). Precipitation of hydroxyapatite and vivianite would have led to a (minor) decline in Ca and Fe levels, but this would remain unnoticed due to the high Ca and Fe concentrations in the BWRO concentrate. Sorption of silica on iron(hydr)oxides or other phases probably explains the decline in Si during aquifer passage. Precipitation of silica is an alternative explanation, but seems unlikely given the sluggishness of quartz crystallization.

Table 6. Water quality changes following injection of BWRO concentrate at Noardburgum. Water qualities are listed for the BWRO concentrate (time averaged) and for observation well N25 (3 depths), after flushing the disposal aquifer with 3 to 12 pore volumes (PFs) of injectate.

Sample		concentrate	B06D1114-f4		B06D1114-f5			B06D1114-f6	
Label			N25-172		N25-180			N25-191	
Depth	[m]		172		180			191	
t50	[d]		40		18			47	
PF			3.5	5.7	4.4	8.6	11.9	3.0	4.9
pH lab		6.97	6.96	7.02	6.91	6.96	6.99	6.95	7.01
EC lab	[mS/m]	473	461	442	485	455	440	463	440
CH4	[mg/L]	15.7	15.7	16.0	**14.0**	16.0	15.3	15.3	15.0
Cl	[mg/L]	1409	1400	1350	1500	1400	1300	1400	1300
Br	[mg/L]	5.54	**4.90**	6.00	5.29	**4.79**	5.73	**4.80**	**6.14**
F	[mg/L]	0.12	**0.06**	**0.14**	**0.14**	**0.08**	**0.21**	**0.06**	**0.16**
HCO3	[mg/L]	671	651	677	639	662	669	656	676
SO4	[mg SO4/l]	<2	<2	<2	<2	<2	<2	<2	<2
PO4-total	[mg P/L]	0.70	**0.30**	**0.39**	**0.25**	**0.32**	**0.22**	**0.30**	**0.26**
TOC	[mg/L]	9.60	8.93	9.10	8.65	9.30	9.23	9.07	9.05
Na	[mg/L]	174	176	158	188	170	163	178	162
K	[mg/L]	6.53	6.44	6.26	6.25	6.26	6.20	6.47	6.39
NH4	[mg N/L]	1.45	1.47	1.50	1.45	1.50	1.50	1.47	1.50
Ca	[mg/L]	754	712	695	758	702	727	730	684
Mg	[mg/L]	60.7	61.6	55.7	61.1	59.6	56.0	63.2	56.2
Sr	[ug/L]	2516	2433	**2235**	2560	2410	**2243**	2463	**2245**
Ba	[ug/L]	533	525	**454**	566	517	**469**	**460**	**460**
Fe	[mg/L]	78.5	77.2	71.8	82.7	73.6	75.9	77.1	**69.1**
Mn	[mg/L]	1.68	1.62	1.57	1.70	1.64	1.57	1.66	1.57
Si	[mg Si/L]	30.0	27.7	**25.5**	**26.0**	30.0	**27.0**	**26.3**	**26.5**
As	[ug/L]	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
B	[ug/L]	24.6	25.5	26.3	22.4	25.1	24.9	26.9	25.6
Ni	[ug/L]	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Saturation index									
Barite		n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Calcite		0.7	0.7	0.8	0.6	0.7	0.7	0.7	0.7
Dolomite		0.5	0.5	0.6	0.4	0.5	0.5	0.5	0.6
Fluorite		-2.2	**-2.8**	-2.0	-2.0	-2.5	**-1.7**	**-2.8**	-2.0
Gypsum		n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Hydroxyapatite		2.3	**1.3**	**1.9**	**0.8**	**1.3**	**0.5**	**1.2**	**1.3**
Quartz		1.2	1.2	1.1	1.1	1.2	1.2	1.2	1.2
Rhodochrosite		0.4	0.4	0.5	0.4	0.4	0.4	0.4	0.5
Siderite		1.8	1.8	1.9	1.8	1.8	1.8	1.8	1.8
SiO2(a)		-0.1	-0.2	-0.2	-0.2	-0.1	-0.2	-0.2	-0.2
Strontianite		-1.2	-1.3	-1.2	-1.3	-1.3	-1.3	-1.3	-1.2
Talc		-1.8	-2.0	-1.9	**-2.4**	-1.9	-2.0	**-2.1**	-1.9
Vivianite		3.3	**2.7**	**3.0**	**2.5**	**2.7**	**2.1**	**2.7**	**2.6**
Witherite		-2.8	-2.8	-2.8	-2.8	-2.8	-2.8	-2.9	-2.8

blue bold = >10% decrease compared to the BWRO concentrate, indicating sorption and/or precipitation
blue bold SI = >0.3 decrease compared to the BWRO concentrate, indicating sorption and/or precipitation
red bold = 10% or 15% (SI) increase compared to the BWRO concentrate, indicating desorption and/or dissolution
red bold SI = >0.3 increase compared to the BWRO concentrate, indicating desorption and/or dissolution

3.2.2 Zevenbergen

At Zevenbergen, injection of the BWRO concentrate resulted in a complex pattern of hydrochemical interactions. Figure 5 shows the breakthrough curves for a selection of parameters at the first (25 m distance) and second (43 m distance) observation wells, at a depth of 176 and 173 meters, respectively.

Again, EC and chloride were good indicators of injectate breakthrough, though EC levels in the observation wells did not fully increase to the levels of the concentrate. This also applies to HCO_3. pH values, which were higher for the native groundwater than for the BWRO concentrate, dropped and stabilized at levels lower than the BWRO concentrate after breakthrough. Ca and Fe, lower in the initial groundwater than in the concentrate, increased after breakthrough, but both stabilized at levels well below the concentrate. Contrary, magnesium peaked to levels well above the concentrate after breakthrough, to stabilize at a level of about twice the concentrate.
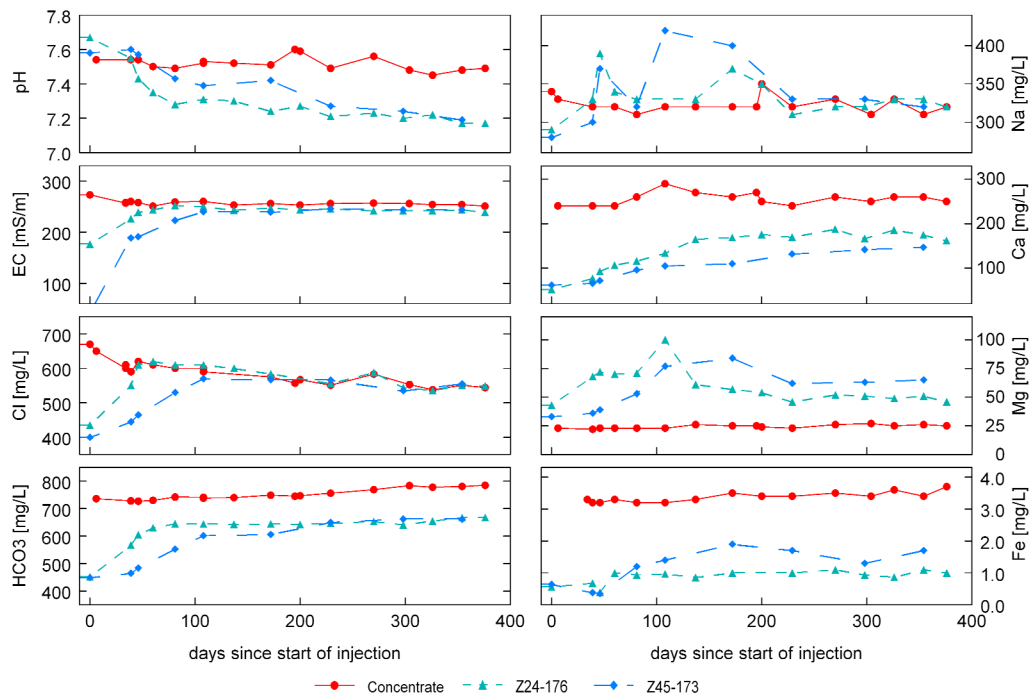

Figure 5. Breakthrough patterns at Zevenbergen for a selection of parameters at 24 (Z24-176, t_{50} = 37 days) and 45 meters (Z45-173, t_{50} = 72 days) distance from the injection well. Also shown is the water quality of the injected BWRO concentrate.

The observed patterns in macro chemistry can be explained by a combination of cation exchange, and precipitation and dissolution reactions. The magnesium peak is a clear example of cation exchange. At breakthrough, Mg was released from the exchange complex and replaced by Ca and Fe, which were present in the injectate at concentrations higher than the native groundwater. After depletion of adsorbed Mg, levels dropped again, but remained elevated. Loss through adsorption only partly explains why levels of Ca and Fe did not mimic the concentrate after breakthrough; precipitation as calcite and siderite is a more likely cause. Other indicators of precipitation were EC and HCO_3, which, after breakthrough, did not rise to the same levels as in the concentrate. Finally, the drop in pH was explained by precipitation of carbonates, which induced a shift from HCO_3 to CO_3 thereby releasing protons (H^+). Hydrochemical modeling (Phreeqc; Parkhurst and Appelo, 1999) confirmed the above reasoning. Observed patterns of pH, HCO_3, Ca and Fe could be modeled only when including precipitation of calcite and siderite in the model (Fig. 6). The temporary peak in Mg was modeled by including cation exchange as a process, but the model failed to correctly simulate the end level of Mg, after depletion of adsorbed Mg. This indicates that, next to adsorbed Mg, there is a second source of Mg, which was not included in the model. A "candidate" for this second Mg source is the dissolution of a magnesium rich mineral, which is discussed in further detail below.
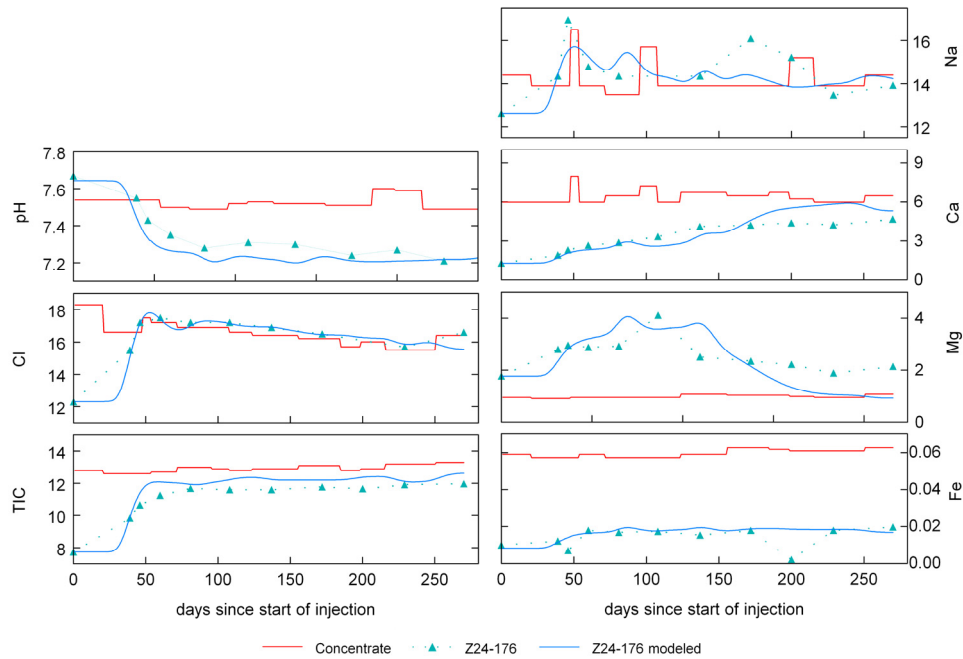
Figure 6. Modeled and observed water quality of the disposal aquifer at Zevenbergen, at 24 m distance from the injection well. All concentrations in mmol/L. Also shown are the model input concentrations of the BWRO concentrate. TIC = total inorganic carbon.

The various hydrochemical interactions following injection are also reflected in Table 7, which compares the (average) water quality of the Zevenbergen concentrate and the water quality in the three well screens of Z24 (B44C0801), after flushing the aquifer with 3 and 9 pore flushes of injectate, respectively. Like Figure 5, the table indicates that Ca, Fe and HCO_3 were removed from the solution, while Mg was released. Other clear hydrogeochemical reactions include the removal from the injectate of phosphate, ammonium, manganese, arsenic and nickel, and the (strong) release from the aquifer of strontium and barium. Phosphate removal was either due to sorption to the aquifer matrix or precipitation as hydroxyapatite. Processes that could have accounted for the removal of manganese, arsenic and nickel, include co-precipitation with calcite and siderite (manganese!) and sorption to (hydr)oxide minerals. Precipitation of $NiCO_3$ was not relevant, as the concentrate was (strongly) undersaturated towards this mineral. The removal of NH_4 was probably accounted for by cation exchange, as was the release of barium. Note that although barium levels of the injectate increased during aquifer passage, they remained below the initial levels of the disposal aquifer (cf. Tables 5 and 7), and were still (very) low compared to Noardburgum.

Table 7. Water quality changes following injection of BWRO concentrate at Zevenbergen. Water qualities are listed for the BWRO concentrate (time averaged) and for observation well Z24 (3 depths), after flushing the disposal aquifer with 2.8 to 8.8 pore volumes (PFs) of injectate.

Sample		Concentrate	B44C0801-f06		B44C0801-f07		B44C0801-f08	
Label			Z24-168		Z24-176		Z24-182	
Depth	[m]		168		176		182	
t50	[d]		44		37		44	
PF			2.8	8.6	3.3	8.8	2.8	8.6
pH lab		7.52	7.27	7.22	7.31	7.20	7.36	7.17
EC lab	[mS/m]	256	247	245	247	243	247	242
CH4	[mg/L]	1.4						
Cl	[mg/L]	583	605	556	605	543	600	558
Br	[mg/L]	1.82	**1.62**	1.93	1.65	1.90	**1.60**	1.97
F	[mg/L]	0.27	**0.51**	0.28	**0.55**	**0.33**	**0.55**	0.29
HCO3	[mg/L]	752	**642**	691	**644**	**654**	**656**	**662**
SO4	[mg SO4/l]	7.77	**9.00**	7.33	**9.00**	**6.67**	**9.00**	**6.67**
PO4-total	[mg P/L]	0.20	**0.10**	**0.06**	**0.06**	**0.07**	**0.11**	**0.08**
TOC	[mg/L]	7.78		7.83		7.67		7.13
Na	[mg/L]	328	**395**	327	**430**	327	340	317
K	[mg/L]	12.4	**18.0**	13.3	**25.0**	**22.7**	**32.5**	**30.0**
NH4	[mg N/L]	1.7	**1.0**	**1.6**	**1.1**	**1.2**	1.8	**1.4**
Ca	[mg/L]	259	**181**	**216**	**150**	**176**	**108**	**180**
Mg	[mg/L]	24.2	**35.0**	**29.3**	**80.5**	**50.3**	**96.5**	**44.3**
Sr	[ug/L]	2106	**10800**	**3733**	**12550**	**5833**	**7900**	**5367**
Ba	[ug/L]	2.92	**8.80**	**4.33**	**19.00**	**11.20**	**15.00**	**8.17**
Fe	[mg/L]	3.36	**0.83**	**0.97**	**0.92**	**0.97**	**0.80**	**0.75**
Mn	[mg/L]	0.09	**0.04**	**0.01**	0.09	**0.04**	0.08	**0.03**
Si	[mg Si/L]	19.9	**16.7**	19.9	**15.1**	18.2	**14.4**	19.6
As	[ug/L]	2.0	**1.1**	**0.9**	**0.9**	**0.5**	**0.9**	**0.2**
B	[ug/L]	1239	**1400**		**1700**		1350	
Ni	[ug/L]	2.6	**0.85**	**0.41**	**0.95**	**0.65**	**0.65**	**0.36**
Saturation index								
Barite		-2.2	**-1.7**	-2.1	**-1.4**	**-1.7**	**-1.5**	**-1.8**
Calcite		1.0	**0.5**	**0.5**	**0.4**	**0.4**	**0.4**	**0.4**
Dolomite		1.1	**0.4**	**0.3**	**0.7**	**0.5**	0.8	**0.3**
Fluorite		-1.7	**-1.2**	-1.6	**-1.3**	-1.6	-1.4	-1.7
Gypsum		-2.4	-2.5	-2.5	-2.6	-2.6	-2.7	-2.6
Hydroxyapatite		2.2	**-0.7**	**-1.3**	**-1.9**	**-1.4**	**-1.3**	**-1.5**
Quartz		1.0	1.0	1.1	0.9	1.0	0.9	1.1
Rhodochrosite		-0.3	**-0.9**	**-1.4**	-0.5	**-0.9**	-0.5	**-1.1**
Siderite		1.1	**0.2**	**0.1**	**0.3**	**0.2**	**0.3**	**0.0**
SiO2(a)		-0.3	-0.4	-0.3	-0.4	-0.4	-0.5	-0.3
Strontianite		-0.6	**-0.2**	-0.7	**-0.1**	-0.5	**-0.2**	-0.6
Talc		-0.3	**-1.7**	**-2.2**	**-0.6**	**-1.4**	-0.1	**-1.9**
Vivianite		0.1	**-2.9**	**-3.4**	**-2.9**	**-3.0**	**-2.6**	**-3.4**
Witherite		-4.1	-4.1	**-4.5**	**-3.8**	-4.1	-3.8	-4.3

blue bold = >10% decrease compared to the BWRO concentrate, indicating sorption and/or precipitation
blue bold SI = >0.3 decrease compared to the BWRO concentrate, indicating sorption and/or precipitation
red bold = 10% or 15% (SI) increase compared to the BWRO concentrate, indicating desorption and/or dissolution
red bold SI = >0.3 increase compared to the BWRO concentrate, indicating desorption and/or dissolution

Very striking was the strong increase in strontium following injection. The concentrate itself was already high in strontium, with an average concentration of around 2 mg/L, but levels in the injectate rose to as much as 12 mg/L after breakthrough (Table 7). Figure 7 shows the breakthrough patterns of magnesium and strontium (and barium) at 25 and 43 m distance from the injection well, at a depth of 176 and 173 meters, respectively. Clearly, the observed patterns in strontium and magnesium are identical, peaking after breakthrough (cation exchange) to stabilize later on at a level well above the concentrate. We already mentioned that the high magnesium levels may have resulted from dissolution of a magnesium rich mineral, and we may now add that (given the identical patterns in Mg and Sr) this mineral should also be rich in strontium. Dolomite ($CaMg(CO_3)_2$) is often rich in strontium, and seems a logical candidate, yet the BWRO concentrate was already supersaturated towards dolomite, making it illogical for dolomite to dissolve. Irrespective of the exact mineral source of strontium (and magnesium), note that the Sr release corresponds to the geochemistry of the Zevenbergen disposal aquifer, which contained relatively large amounts of strontium (Table 1). Also, note that dissolution of Sr and Mg

minerals continued during aquifer passage, as indicated by the higher end concentrations at Z45 than at Z24 (Fig. 7).
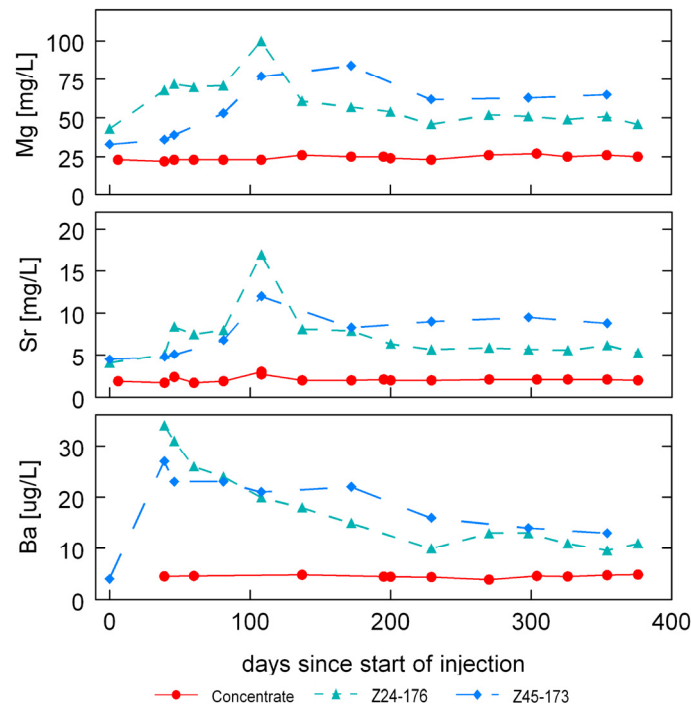

Figure 7. Breakthrough patterns at Zevenbergen for magnesium, strontium and barium, at 24 (Z24-176) and 45 meters (Z45-173) distance from the injection well. Also shown is the concentrations in the BWRO concentrate. Note that Sr concentrations are in milligrams per liter (mg/L).

In summary, at Noardburgum, injected BWRO concentrate passed through the aquifer unaltered, while at Zevenbergen there were many hydrogeochemical interactions between injectate and aquifer. This resulted in a complex pattern of water quality changes, including precipitation and dissolution of various minerals. Note that this difference between both pilots was reflected in the geochemistry of the disposal aquifers, as depicted in Table 1. The Zevenbergen disposal aquifer was finer in texture, higher in CEC, and contained vast amounts of reactive constituents like calcite (18 weight%!), FeS_2 and (hydr)oxides, making this aquifer highly reactive. Contrary, the Noardburgum disposal aquifer was virtually free of calcite, much lower in CEC, and contained only traces of FeS_2 and (hydr)oxides. This low geochemical reactivity explained the (near) absence of interactions between aquifer and injectate at Noardburgum, yet it remained remarkable that precipitates did not form from Noardburgum's highly supersaturated BWRO concentrate. The difference in mineral precipitation at both locations is discussed further in the next section.

3.3   Mineral precipitation and injection well clogging

The previous sections made clear that despite the comparable levels of supersaturation in the BWRO concentrates (cf. Tables 4 and 5), there was a large difference in mineral precipitation between both pilots. At Noardburgum, calcite and siderite precipitates did not form, even though SIs for these minerals amounted to 0.7 and 1.8, respectively. At Zevenbergen, precipitation of these minerals did occur, while the SI levels were in the same range as at Noardburgum, namely 1.0 and 1.1, respectively. At this point it should be noticed that at neither one of the pilots scaling of the RO membranes occurred, as indicated by the stable membrane pressure drops and normalized flux values. At Noardburgum, there were no signs of clogging of the injection well, *i.e.* the injection pressures remained stable. At Zevenbergen, after one year of injection, some mild clogging of injection well and/or aquifer had occurred, indicated by an estimated 10% increase in the injection pressure. The equal end levels of bicarbonate at the first (Z24) and second (Z45) observation well (Fig. 5), indicated that no precipitation

occurred beyond Z24 or, in other words, that all precipitates formed (somewhere) between the injection well and the first observation well at 24 m distance. An estimated 35 tons or 13m³of $CaCO_3$ must have been deposited there during the first year of injection, and as such it is not surprising that some increase in injection pressure occurred. Moreover, this indicates that, at Zevenbergen, a recovery level of 50% is not (technically) sustainable in the long run, as aquifer and injection well clogging will become problematic.

The Noardburgum results indicate that mineral supersaturation towards calcite and siderite (and many other minerals) does not necessarily mean that equilibrium will be attained by mineral deposition. Dissolved organic matter (DOC) is often recognized as an inhibitor of crystallization, by forming complexes with cations like Ca and Fe. However, TOC concentrations in both pilots were similar (9.6 and 7.8 mg/L for Noardburgum and Zevenbergen, respectively; Table 4 and 5), and thus did not explain the differences in mineral precipitation. Also, note that TOC levels were very low compared to the extremely high Fe and Ca levels in the Noardburgum concentrate. PO_4 and Mg are two other well-known inhibitors of calcite precipitation. PO_4 levels were indeed higher at Noardburgum, yet still low relative to Ca and HCO_3. Also, PO_4 levels decreased at Noardburgum during aquifer passage, owing to PO_4 sorption or precipitation as hydroxyapatite and/or vivianite. Mg concentrations were higher in the Noardburgum BWRO concentrate (61 mg/L versus 24 mg/L at Zevenbergen), yet relative to Ca and HCO_3 higher levels were found at Zevenbergen. Also, note that Mg peaked to levels of near 100 mg/L in the Zevenbergen injectate during aquifer passage (Table 7), without blocking the precipitation of calcite. Finally, kinetic hindrances are listed in the literature (*e.g.*, Jensen et al. 2002) to slow down precipitation. Indeed, at Zevenbergen precipitation did not occur until the injectate reached the aquifer, and kinetics could play a role here. At Noardburgum, travel times from injection well to the second observation well (N25) were up to 50 days, and no precipitation occurred in this time span. Though kinetics could be involved here as well, this still does not clarify the observed differences with Zevenbergen.

Three factors remain that could explain why precipitation of calcite and siderite took place at Zevenbergen and not at Noardburgum. First is the geochemistry of the disposal aquifers. The disposal aquifer at Zevenbergen has a finer texture than Noardburgum, and while calcite contents were very high at Zevenbergen (18 weight%), the Noardburgum disposal aquifer is virtually free of calcite (Table 3). Both the presence of calcite and the finer texture are beneficial for carbonate precipitation, as they provide potential nucleation sites (Lebron and Suarez, 1996). This would also explain why precipitation at Zevenbergen occurred in the disposal aquifer, and not in the RO. Also, this provides a warning for the operation of ROs and injection wells: once the first precipitates have formed, they may catalyze and thus accelerate further precipitation, leading to scaling and/or clogging. A second possible factor explaining differences in mineral precipitation is the carbonate chemistry of both BWRO concentrates. Even though calcium and iron(II) levels were much lower in the Zevenbergen concentrate, supersaturation towards calcite and siderite was comparable to Noardburgum. The reason is the higher pH of the Zevenbergen concentrate, resulting in higher carbonate (CO_3) levels (note that bicarbonate concentrations are comparable at both locations). This could indicate that precipitation of carbonate minerals is governed more by carbonate levels in the solution than by metals, but this is still speculative. Finally, the high iron(II) levels at Noardburgum may explain why calcite precipitation did not occur here. In lab experiments with "synthetic" solutions mimicking the Noardburgum concentrate, with and without Fe^{2+} present, calcite precipitates did not form in presence of Fe^{2+}, but precipitation did occur in solutions free of Fe^{2+} (Jack Gilron, Ben-Gurion University of the Negev, personal communication). Herzog et al. (1989) drew similar conclusions in a study on magnetic water treatment: Fe^{2+} inhibits calcite precipitation.

The above results were obtained while operating the RO installations at 50% recovery, at both pilot locations. Operation of the ROs and injection wells was successful, despite some mild increase in injection pressure at Zevenbergen after one year of injection. A question is whether it is technically possible to further increase the RO recovery. At higher recoveries, the RO efficiency increases, leading to a decrease in energy needed to produce permeate (drinking) water from brackish groundwater. After operating the RO at 50% recovery for 13 months, the recovery at Zevenbergen was increased to 65%. Water quality data for this concentrate are presented in Table 8. At this level of recovery, scaling of the RO membranes started to occur. Moreover, the injection pressure increased rapidly, some 20% in two months, and the experiment had to be stopped. The clogged injection well was subsequently

Table 8. Quality of the Zevenbergen and Noardburgum BWRO concentrates, after increasing the RO recoveries to 65 (Zevenbergen) and 70% (Noardburgum). Also shown is the water quality at observation well N12 (2 depths), after flushing this well with 14.4 (N12-179) and 4.3 (N12-190) pore volumes of injectate (70% recovery).

Location		Zevenbergen	Noardburgum		
Sample		concentrate	concentrate	B06D1087-f3	B06D1087-f4
RO recovery		65%	70%		
Label		Zconc	Nconc	N12-179	N12-190
Depth	[m]			179	190
t50	[d]			2.5	8.3
PF				14.4	4.3
pH lab		7.54	7.12	7.10	7.09
EC lab	[mS/m]	350	670	661	662
CH4	[mg/L]	n.d.	16.8	17.0	15.5
Cl	[mg/L]	771	2067	2000	2050
Br	[mg/L]	2.70	8.06	7.42	7.73
F	[mg/L]	0.36	0.11	**0.13**	0.11
HCO3	[mg/L]	1140	1100	1100	1100
SO4	[mg SO4/l]	n.d.	<2.0	<2.0	<2.0
PO4-total	[mg P/L]	0.62	0.54	**0.47**	0.52
TOC	[mg/L]	12.0	15.0	15.0	15.0
Na	[mg/L]	465	222	**188**	**190**
K	[mg/L]	15.0	9.8	9.4	9.4
NH4	[mg N/L]	2.4	2.32	2.4	2.5
Ca	[mg/L]	365	1107	1060	1065
Mg	[mg/L]	35.5	83.90	89.8	91.3
Sr	[ug/L]	3150	3730	3765	3755
Ba	[ug/L]	7.0	740	759	757
Fe	[mg/L]	5.2	116	109	108
Mn	[mg/L]	0.14	2.5	2.4	2.4
Si	[mg Si/L]	29.4	40.8	**36.0**	**17.0**
As	[ug/L]	2.2	<1.0	<1.0	<1.0
B	[ug/L]	n.d.	n.d.	n.d.	n.d.
Ni	[ug/L]	<1.0	<1.0	<1.0	<1.0
Saturation index					
Barite		n.a.	n.a.	n.a.	n.a.
Calcite		**1.3**	**1.2**	1.1	1.1
Dolomite		**1.7**	**1.4**	1.4	1.4
Fluorite		-1.3	-2.1	-2.0	-2.1
Gypsum		n.a.	n.a.	n.a.	n.a.
Hydroxyapatite		**3.2**	**3.1**	2.9	3.0
Quartz		**1.2**	**1.3**	1.3	**0.9**
Rhodochrosite		0.0	**0.8**	0.8	0.8
Siderite		**1.4**	**2.2**	2.2	2.2
SiO2(a)		-0.2	0.0	-0.1	**-0.5**
Strontianite		-0.3	-0.8	-0.8	-0.8
Talc		**0.9**	-0.1	**-0.4**	**-2.1**
Vivianite		**0.7**	**3.6**	3.4	3.5
Witherite		-3.8	-2.3	-2.3	-2.4

black bold = SI concentrate >0.3

blue bold = >10% decrease compared to the BWRO concentrate, indicating sorption and/or precipitation

blue bold SI = >0.3 decrease compared to the BWRO concentrate, indicating sorption and/or precipitation

red bold = 10% or 15% (SI) increase compared to the BWRO concentrate, indicating desorption and/or dissolution

red bold SI = >0.3 increase compared to the BWRO concentrate, indicating desorption and/or dissolution

rehabilitated using HCl to dissolve the carbonates that caused the clogging. At Noardburgum, the RO recovery was increased to 70%, 9 months after start of the experiment. Like at 50% recovery, and despite the high levels of supersaturation of the concentrate, RO operation and concentrate injection were without problems. In addition, water quality data from the first observation well (N12; Table 8) indicated that no precipitation or other reactions occurred in the subsoil, except for some sorption of silica (as also occurred at 50% recovery, cf. Table 6). In the final month of the Noardburgum pilot, the recovery was increased even further, to 75%. Data from the subsoil are lacking for this experiment, yet the RO and injection well operated without problems, indicating that precipitation still did not occur.

In summary, the maximum attainable RO recovery level differs considerably between both pilot locations. At Zevenbergen, even a recovery level of 50% is not (technically) sustainable, as aquifer and injection well clogging will become problematic in the long run. At Noardburgum, the RO can be operated at 75% recovery, without introducing any technical problems. This difference between both pilot locations is due to differences in water quality of the BWRO concentrate (pH, Fe^{2+}) and the geochemistry of the disposal aquifers (texture, calcite content). A simple means to maintain a (sustainable) 50% recovery at Zevenbergen is to lower the pH by adding HCl or CO_2 to the concentrate. This will be tested in the near future.

3.4 Synthesis: evaluation of water quality changes

The previous sections made clear that the effect of BWRO concentrate injection on water quality in the disposal aquifer was a function of both the injectate quality as well as interactions with the aquifer matrix. Hydrogeochemical interactions included sorption of phosphate, silica (both pilots), arsenic and nickel (Zevenbergen), precipitation of calcite and siderite (Zevenbergen), and coupled dissolution of strontium and magnesium (Zevenbergen). The net effect of concentrate injection on water quality in the disposal aquifer is presented in Table 9. This table lists the initial water quality of the disposal aquifer as well as the water quality at the end of the field tests at approximately 25 m distance from the injection wells, after flushing both the aquifers with several pore volumes of injectate. At Noardburgum, the end concentrations of most elements fell within the water quality ranges of the native groundwater, except for fluoride, bicarbonate, phosphate, TOC, iron and silica. Of these, most were in close range of the native groundwater and / or their environmental relevance is limited, i.e. (concentrations of) these elements do not form an environmental or health risk. For example, although PO4 increased following injection, the end levels were still low for brackish groundwater (Stuyfzand and Stuurman, 2006; Verweij et al., 2008). The only exception perhaps was iron, with end concentrations of about 70 mg/L. Although this level is exceptionally high, even for brackish waters, the environmental relevance of high Fe levels is limited.

Table 9. Comparison of the initial (native) groundwater of the disposal aquifers and the end concentrations after 7 (Noardburgum) and 12 months of injection of BWRO concentrate (50% recovery).

Location		Noardburgum		Zevenbergen	
Observation well		B06D1114		B44C0801	
Label		N25		Z24	
Depth	[m]	172 - 191		168 - 182	
		initial	end	initial	end
pH lab		6.70 - 6.85	7.01	7.59 - 7.75	7.20
EC lab	[mS/m]	153 - 1026	441	164 - 191	243
CH4	[mg/L]	0.09 - 12.00	15.4	0.04 - 0.06	
Cl	[mg/L]	370 - 4500	1317	385 - 465	552
Br	[mg/L]	1.3 - 15.1	5.96	1.18 - 1.49	1.93
F	[mg/L]	0.03 - 0.08	0.17	0.9 - 1	0.30
HCO3	[mg/L]	227 - 331	674	444 - 452	669
SO4	[mg SO4 / l]	<2 - 160	<2	1.77 - 3	6.89
PO4-total	[mg P/L]	0.13 - 0.20	0.29	0.02 - 0.04	0.07
TOC	[mg/L]	2.7 - 4.7	9.13	2.85 - 3.93	7.54
Na	[mg/L]	47 - 849	161	270 - 300	323
K	[mg/L]	2.9 - 14.6	6.28	14 - 26	13.0 - 30
NH4	[mg N/L]	0.7 - 4.4	1.50	0.7 - 1.4	1.4
Ca	[mg/L]	222 - 1370	702	42 - 64	176 - 216
Mg	[mg/L]	21 - 157	56.0	28 - 52	29 - 50
Sr	[ug/L]	777 - 5980	2241	3000 - 4600	3733 - 5833
Ba	[ug/L]	128 - 1660	461	18 - 34	4.3 - 11.2
Fe	[mg/L]	16 - 34	72.2	0.5 - 0.69	0.90
Mn	[mg/L]	0.6 - 1.5	1.57	<0.01 - 0.01	0.03
Si	[mg Si/L]	13 - 14	26.3	9.1 - 10.0	19.2
As	[ug/L]	<1.0 - 3.1	<1.0	<1.0	<1.0
B	[ug/L]	14 - 33	25.6	1000	
Ni	[ug/L]	<1.0 - 2.4	<1.0	<1.0	<1.0

At Zevenbergen, similar conclusions were drawn with respect to macro chemistry: injection led to an increase in concentrations for some elements, but the environmental relevance was limited or absent. Even the end levels of strontium, which was released from the aquifer, were in the same range as the levels in the native groundwater, and did not result in a deterioration of water quality. We thus conclude that injection had no negative effects on groundwater quality of the disposal aquifer at Zevenbergen. Apart from the water quality changes, injection also led to minor changes in the geochemistry of the Zevenbergen disposal aquifer, mainly the build-up of calcite contents and some sorption of arsenic and nickel. However, we would like to pinpoint that injection took place at very large depths, and that geochemical changes are not much relevant from an environmental viewpoint.

The above discussion points to an important issue in policy development and permitting of deep well injection of BWRO concentrate: how to evaluate (mild) changes in water quality (and geochemistry), of confined aquifers, at large depths. When strictly applying the stand-still principle, injection should not result in an increase of any of the relevant WFD parameters and trace elements. We advocate a different approach, and believe the effects of concentrate injection should be evaluated in a wider context, including associated environmental and health risks. We mentioned already that different (WFD) threshold values should be defined for fresh and brackish/salt groundwater bodies, respectively, as was also concluded by Stuyfzand (1991, 1992), Passier et al. (2006) and Verweij et al. (2008). Defining these thresholds may not be that simple, as we currently lack a good overview of water quality of (deeper) brackish groundwater, especially concerning trace elements (although a first overview has been provided by Stuyfzand and Stuurman, 2008). Moreover, the water quality may vary considerably with depth, as was the case for the Noardburgum disposal aquifer (Tables 1 and 4).

At both pilot locations, injection of the BWRO concentrate was in a deep aquifer, separated from the overlying source aquifer by a confining clay layer. There was, as such, little chance on short-circuiting of the injectate into the source aquifer, and it is foreseen that the injectate will reside in the disposal aquifers for decennia and longer, unused. The injectate will thus not interfere with, for example, public functions like drinking water supply, nor will it exfiltrate to surface water environments within a period of hundreds to thousands of years. In our opinion, this should be incorporated in a risk evaluation. Moreover, the social and environmental benefits of brackish water abstraction for drinking water supply may outweigh the (minor) negative effects of BWRO concentrate injection. In the Noardburgum pilot, salinization of the fresh water abstraction well was reversed effectively by simultaneous abstraction of upper fresh and lower brackish groundwater (Fig. 2; also see Oosterhof and Raat, 2010). It is foreseen that the abandoned (salinized) Noardburgum well field can be re-opened when the fresh keeper concept is applied at full scale, producing 3 Mm³ of drinking water yearly.

In summary, we conclude that at both pilot locations, injection of BWRO concentrate has no negative impact on water quality of the disposal aquifers. For a limited number of chemical (WFD) parameters, injection did lead to minor increases in concentration, yet from an environmental viewpoint this was not relevant. Moreover, we advocate the idea that the effects of BWRO injection should be evaluated in a wider, risk based context. Such an evaluation should also include possible benefits of applying BWRO and deep well injection, like counteracting salinization of fresh water wells.

4 Conclusions

The effects of BWRO concentrate injection on the hydrochemistry of the disposal aquifer were studied at the BWRO pilot plants near Noardburgum (water supply company Vitens) and Zevenbergen (water supply company Brabant Water). The main, overall conclusion is that deep well injection indeed provides a sustainable solution for disposal of BWRO membrane concentrate, being environmentally safe and technically feasible. More specifically, from the pilots we learned the following:

Effects on water quality in the disposal aquifer
- The BWRO concentrate fitted neatly into the natural chemical environment of the disposal aquifer, at both locations, both for macro as well as trace elements. The only exception was the exceptionally high Fe concentration in the Noardburgum concentrate, but from an environmental viewpoint this is of not much relevance.
- Injected BWRO concentrate passed through the disposal aquifer of Noardburgum almost unaltered, despite supersaturation towards several carbonate and phosphate minerals.
- At Zevenbergen, injection induced a series of hydrochemical reactions with the aquifer, including precipitation of calcite and siderite, dissolution of minerals rich in magnesium and strontium, and sorption of phosphate, silica, arsenic and nickel from the injected solution.
- Injection had no negative effects on water quality of the disposal aquifer at both sites. The only relevant concentration increases (compared to the native groundwater) were the very mild increase in phosphate at Zevenbergen, and the strong increase in iron at Noardburgum.

Membrane scaling and injection well clogging
- Membrane scaling and injection well clogging due to mineral precipitation were a problem at Zevenbergen, but did not occur at Noardburgum. This difference was due to differences in water quality of the BWRO concentrate (pH, Fe^{2+}) and the geochemistry of the disposal aquifers (texture, calcite content).
- At Noardburgum, the RO could be operated at 75% recovery, without introducing any operational problems.
- In the long run, aquifer and injection well clogging will become problematic at Zevenbergen, already at a RO recovery level of 50%. Lowering the pH of the RO feed water by dosing HCl or CO_2 could be a sustainable solution here.

Policy and legislation
- We believe that current legislation and policy towards deep well injection are too rigid, focusing too much on the "standstill principle". We advocate the idea that the effects of BWRO injection on groundwater quality of the disposal aquifer should be evaluated in a wider context, and weighted against societal and environmental benefits of applying BWRO like counteracting salinization of fresh water wells.

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