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Assessment Reverse Osmosis membrane clogging by varying redox conditions of feed water

Part 2: Assessment Reverse Osmosis membrane clogging (period: 2013-2015)

KWR Watercycle Research Institute, Bruine de Bruin, December 2015

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 619039

ASRO: an innovative solution for sustainable freshwater supply from brackish/saline aquifers

D22.3: Assessment Reverse Osmosis membrane clogging by varying redox conditions of feed water
Part II: Assessment Reverse Osmosis membrane clogging

SUMMARY

When combining aquifer storage and recovery and brackish water reverse osmosis in one integrated ASRO-system, espially formation of suspended fine particles forms a

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D22.3	WP22.2
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List of Acronyms and Abbreviations

ASR	*Aquifer storage and recovery*
RO	*Reverse osmosis*
RE	*Recovery Efficiency*
K	*Hydraulic conductivity*
n	*Porosity*
ASRO	*Aquifer Storage and recovery and Reverse Osmosis*
BWRO	*Brackish Water Reverse Osmosis*
MFI	*Modified Fouling Index (also: membrane fouling index*
SDI_{15}	*Silt Density Index*
m-ASL	*meters above sea level*
m-BSL	*meters below sea level*
MPPW	*Multiple partially penetrating wells*
MW	*Monitoring well*
ATES	*Aquifer thermal energy storage*
EC	*Electrical conductivity*
ICP-OES	*Inductively-Coupled Plasma – Optic Emission Spectrometry*
ΔP	*Pressure difference (between feed side and reject side of RO-feed channel)*

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Executive summary

Rainwater is injected into a brackish aquifer (23-37 m below sea level; 3700 – 4700 mg Cl/l) at the Westland demosite, using two multiple partially penetrating wells (MPPWs). The water is recovered at the aquifer top for direct use as high-quality irrigation water. This technique is called aquifer storage and recovery (ASR). The deep wells of the MPPWs are used as 'Freshkeepers' and intercept brackish groundwater below the zone of freshwater recovery. This intercepted water is desalinated via reverse osmosis (RO). This combination of ASR and RO is called 'ASRO'. The complete field system (including wells, pumps, infrastructure) is called an 'ASRO'-system and the RO-treatment system is called 'ASRO-plant'). At the Westland demosite, brackish water is also recovered from the whole aquifer thickness at the fringe of the injected freshwater body to feed a second RO-plant. This is complete system called brackish water RO ('BWRO') and contains a 'BWRO-plant'.

Since both plants had similar design characteristics, any clogging must have been caused by the water type feeding the plants. Both water types showed primarily dilution with rainwater, as well as enrichment with Al, Fe, Mn, and SO_4. Sorption led to a relative decrease for especially SiO_2, PO_4, Ba, and B. These non-conservative, chemical effects were most distinct at the ASRO abstraction wells. However, it was the BWRO-plant showing a significant linear decrease in freshwater production. Around 50% of the permeate production capacity (recovery decrease: 48 to 25%) was left after two months of operation. This recovery decrease was accompanied by an increase in feed and reject pressures, and later also an increasing ΔP. Treatment with Genesol703 for removal of cake layers was very successful in restoring the BWRO-plant's capacity. On the other hand, the ASRO-plant's operation remained very constant.

The operational data supported membrane fouling by particles as the clogging mechanism at the BWRO-plant, where clogging was not observed before rainwater was injected (2012 and before). Clay mobilization during aquifer freshening and the formation of Fe (and Al) colloids during injection of oxic rainwater were found as the most likely sources for the formation of suspended particles in the groundwater. Their transport is dominated by both an upward flux (buoyancy) and a lateral flux away from the ASRO wells. This may be the reason that the particles were primarily present around the BWRO well, and not at the Freshkeeper wells of the ASRO system. Location of feed water abstraction is therefore a vital design parameter for the success of ASRO.

Means to reduce the particle mobilization and/or prevent subsequent the particle clogging observed at the BWRO-plant were evaluated. Addition of Ca^{2+} to the first injection water can reduce clay mobilization and remove adsorbed Fe around the ASR well (in-situ treatment). Secondly, suspended particles from the abstracted water can be removed prior to feeding the RO-plant (ex-situ treatment). Both will, however, lead to a larger operational complexity and higher costs. Regular and automated flushing of the BWRO-membranes to remove the cake layer is a low-cost solution and its efficiency will be tested in 2016. Abandonment of the BWRO abstraction well and a full transition to ASRO is another interesting future mitigation strategy.

1 Introduction

1.1 Westland: horticultural capital of The Netherlands

The Westland area in The Netherlands (Figure 1) is the Dutch largest intensive greenhouse horticultural area. Its second name is therefore 'the glass city'. Glasshouses cover about 2,500 ha of this 10,000 ha large municipality (population: 104,000 inhabitants). For this reason, the horticultural sector, including related companies/suppliers, forms a very relevant contribution to the local and even national economy.

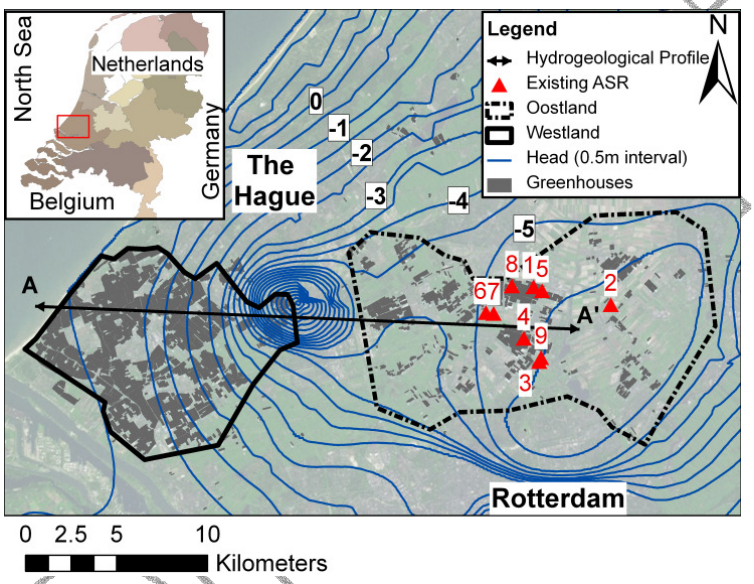

Figure 1: Location of the Westland and neighbouring Oostland greenhouse area.

1.2 The need for additional freshwater in summer

The salinity requirements of the irrigation water in this area (generally measured using electrical conductivity (EC)) are exceptionally strict; drinking water is already too saline for many of the crops (predominantly tomatoes, cucumbers, peppers) and flowers cultivated. Low salinities allow greenhouse owners to reuse drained water from artificial substrates multiple times, without reaching critical sodium concentrations. Fresh irrigation water supply is realized primarily by storing low-EC rainwater from greenhouse roofs in basins or tanks, complemented by the use of surface water in periods of low salinity and by desalination of brackish groundwater (Stuyfzand and Raat, 2010).

A mismatch in precipitation and water demand results in a large winter freshwater surplus (see Part I), which is discharged to sea, as only a small part can be stored in basins or tanks. Surface water is generally unsuitable as a source of freshwater during summer droughts, as they are fed by brackish seepage water (de Louw et al., 2010). Fresh surface water can be brought in from major rivers, but the inlets suffer increasingly from salinization caused by seawater intrusion during summer

droughts, which is exacerbated by sea level rise (Barends et al., 1995; Kooi, 2000; Kwadijk et al., 2010; Oude Essink et al., 2010; Post, 2003; Schothorst, 1977). Wintertime precipitation is expected to increase, whereas summer droughts may become more intense and prolonged (Intergovernmental Panel on Climate Change (IPCC), 2007; Royal Netherlands Meteorological Institute, 2014). Freshwater availability for irrigation during summer will likely be reduced due to the changing temporal precipitation distribution in combination with a predicted rise in temperature. Up to now, desalination by reverse osmosis is the only proven technology to ensure additional freshwater supply. Major disadvantages of this technique are the high energy consumption, the required maintenance, and especially the disposal of leftover concentrate in deeper aquifers. Discharge of this concentrate to sewage systems or surface waters is not allowed and its disposal in deeper aquifers can conflict with the goals set in the EU Water Framework Directive.

1.3 Aquifer storage and recovery (ASR) as a sustainable but yet too vulnerable freshwater source via ecosystem services

A more sustainable use of the precipitation surplus collected by greenhouse roofs will improve freshwater availability in the area. ASR is a cost-effective, readily applicable technique to store large water volumes, without the need for large surface areas. In the study area, ASR has been applied on a small scale since the 1980s in the upper, relatively shallow aquifer (10 - 50 m below sea level (m-BSL)), which is the thinnest and least saline aquifer found in the area. The performance of ASR (i.e., the percentage of freshwater that can be recovered upon storage) using this target aquifer, even though it is the least saline aquifer available, is limited especially in the Westland area (Zuurbier et al., 2013). The main causes for the reduced performance are the buoyancy effects induced by the difference in density of the native groundwater (high density), and the injected freshwater (low density), which leads to early salinization at the bottom of the ASR well (Figure 2).

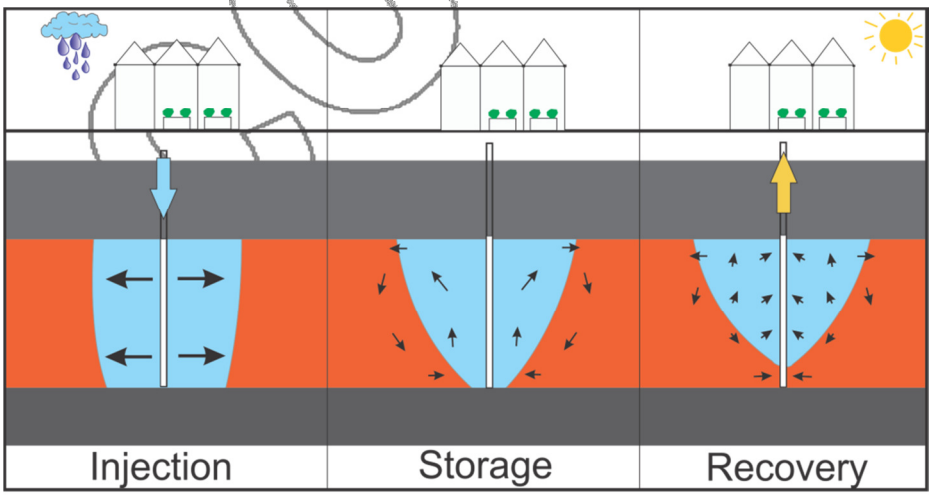

Figure 2: **Freshwater loss during ASR in brackish and saline aquifers due to buoyancy effects.**

1.4 Aquifer storage and recovery combined with reverse osmosis (ASRO) to provide a robust and sustainable freshwater solution

An innovative ASR solution, combined with a Freshkeeper and RO, is proposed to maximize the recovery of injected freshwater surpluses. Multiple partially penetrating wells (MPPW) allow for deep injection and shallow abstraction, postponing the salinization during recovery to attain higher recovery efficiencies. By simultaneously abstracting upper fresh and lower brackish groundwater, salinization of the fresh water well is prevented even longer (Figure 3). The abstracted brackish water is used as additional and reliable freshwater source after desalination. The hybrid aquifer storage and recovery and reverse osmosis (ASRO) system thus combines the best of two techniques and it contributes to optimal durable use of 'free' natural sources as (rain)water and soil, saving expensive aboveground space, and mitigating salinization. The potential is high in coastal areas facing water shortages for drinking water, agricultural, and industrial applications, and/or salinization.

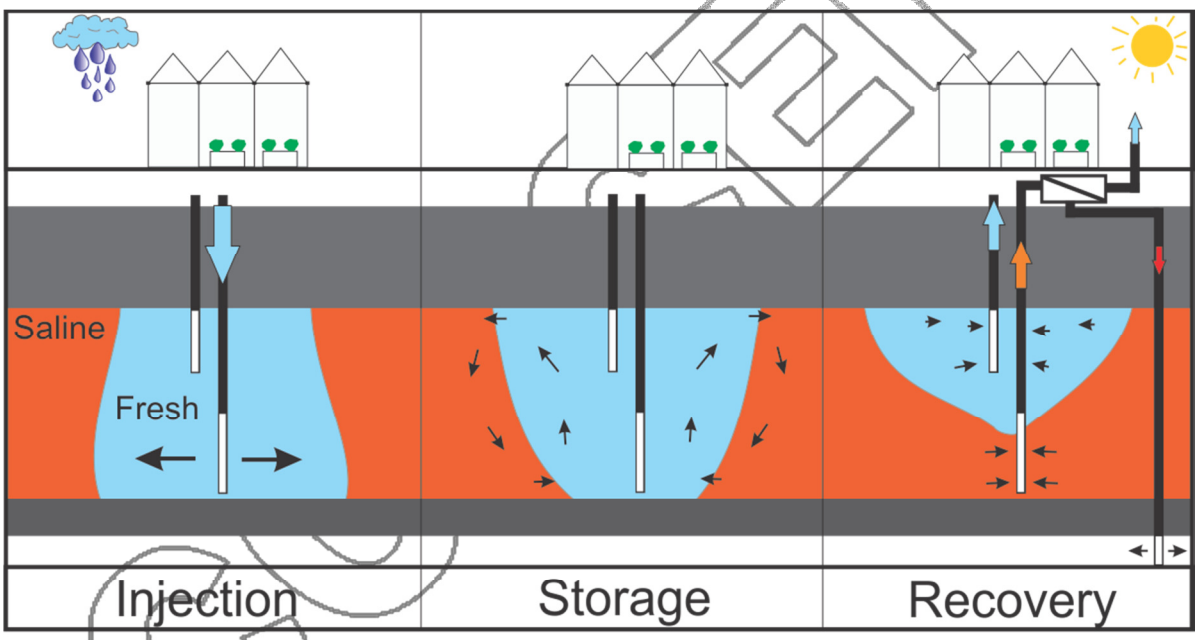

Figure 3: **The introduction of the MPPW for deep injection and shallow recovery in combination with a Freshkeeper and RO-treatment for a maximal recovery of freshwater (together: ASRO).**

1.5 Research aims during first application of ASRO

The task descriptions and accompanying research aims in this report are listed in Table 1.

Table 1: Tasks within WP22.2

Task	Task description	Research aim	Time
22.1	Quantification of the freshwater recovery increase by an innovative well design: In this task the freshwater recovery increase by Multiple Partially Penetrating Wells (MPPW), injection/recovery schemes, and the use of the Freshkeeper at the base of the freshwater bubble is quantified.	To assess the optimal well configuration and potential increase in freshwater recovery in the Westland case and in differing hydrogeological settings.	M1-12 (Part I)
22.2	Assessment of membrane clogging by varying redox conditions of the feed water. Reverse Osmosis (RO) membrane clogging due to varying redox conditions of the feed water from Freshkeeper is quantified and potential in-situ (e.g., subsurface iron removal) and ex-situ (e.g., pre-treatment of membrane feed water) techniques to prevent membrane clogging are evaluated.	To quantify and cope with potential negative effects on the RO-feed water quality induced by introduction of oxic rainwater in the anoxic, saline target aquifer.	M1-24 (Part II)

2 Research approach and methods

2.1 General approach/methods

In order to complete the defined tasks (Table 2), a multiphase approach with specific methodologies was set up. These approaches and methods are listed in Table 2 and visualized in Figure 4.

Table 2: The approaches and methods applied to fulfill the defined tasks.

Task	Task description	Approach	Methods
22.1 (Part I)	Quantification of the freshwater recovery increase by an innovative well design	1. Field testing ASR-cycle 2012/2013: use of MPPW only; 2. Field testing ASR-cycle 2013/2014: addition of the Freshkeeper (no RO); 3. Modelling the performance of a conventional (fully-penetrating) ASR-well instead of an MPPW; 4. Modelling and evaluation of the MPPW-benefits in various hydrogeological settings.	1. Recording of injected/recovered volumes and EC; 2. Lab analysis on (ground)water samples; 3. SEAWAT[1] groundwater transport modelling; 4. SEAWAT groundwater transport modelling.
22.2 (Part II)	Assessment of membrane clogging by varying redox conditions of the feed water. Reverse Osmosis (RO) membrane clogging due to varying redox conditions of the feed water from Freshkeeper is quantified and potential in-situ (e.g., subsurface iron removal) and ex-situ (e.g., pre-treatment of membrane feed water) techniques to prevent membrane clogging are evaluated. (BdB, KWR, M1-24)	1. Field testing of the Freshkeeper including desalination of saltwater recovered by the Freshkeeper (below injected freshwater). 2.Testing of RO using feed water from BWRO well (from fringe of injected freshwater)	1. Analysis of the data obtained during 'BWRO' cycle on mixed rainwater / groundwater in 2013. 2. Analysis of the operational data in 2015 during the use of 'BWRO' and 'ASRO' 3. Hydrochemical analyses on the (ground)water samples obtained 4. Geochemical analyses on filter residues.

[1] SEAWAT Version 4: A computer program for simulation of multi-species solute and heat transport (Langevin et al., 2007)

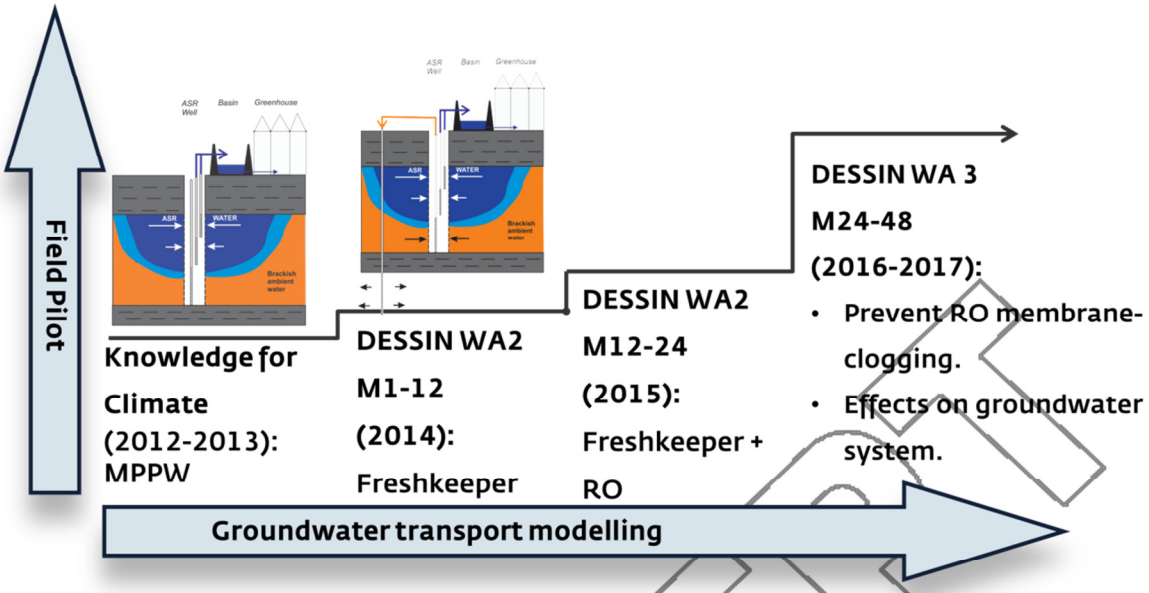

Figure 4: Visualisation of the approach and methods applied in the Westland ASRO study

2.2 Westland ASRO field pilot

The ASRO study takes place at the world's first ASRO-system. This pilot system was initially funded by Knowledge for Climate national research program to test the performance of ASR using MPPWs in coastal (brackish, saline) aquifers. Within the DESSIN project, the ASR-system was converted stepwise to an ASRO-system. The system was realized at a cluster of tomato growers with a total greenhouse roof area of 270.000 m^2. At the location, brackish groundwater was previously desalinated via RO (BWRO) to produce supplementary freshwater, without injection of rainwater surpluses.

2.2.1 Set-up of the Westland ASR system and hydrogeological setting

The Westland ASRO system is installed to inject the rainwater of the greenhouse roofs in a local, shallow aquifer (23 to 37 m below sea level (m-BSL); surface level = 0.5 m above sea level (m-ASL)) for recovery in times of demand. For this purpose, two multiple partially penetrating wells (MPPWs) were installed (Figure 5, Figure 6), so that water could be injected preferably at the aquifer base, and recovered at the aquifer's top in order to increase the recovery efficiency of ASR (Zuurbier et al., 2014). All ASR wells (AW1 and AW2, installed in 2012) and the nearby aquifer thermal energy storage (ATES) well (K3, installed in 2006 and replaced nearby in 2008) were installed using reverse-circulation rotary drilling, while the monitoring wells (MW1-5, Figure 6) were installed using bailer drillings. Bentonite clay was applied to seal the ASR wells (type: Micolite300) and ATES well K3 (Micolite000 and Micolite300). The ASR wells used a 3.2 m high standpipe to provide injection pressure, whereas the ATES well used a pump to meet the designed injection rate of 75 m^3/h. Water abstracted by the ASR-system or membrane concentrate produced

during RO-treatment can be injected in Aquifer 2 via a disposal well, which is installed approximately 250 m downstream from the ASR-site.

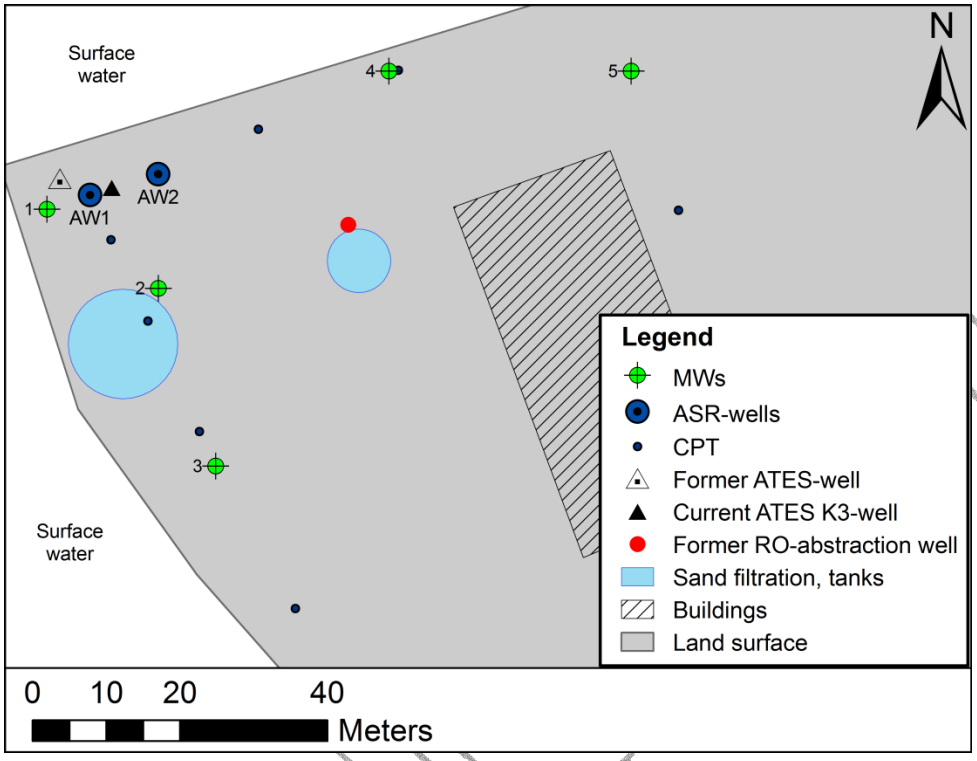

Figure 5: **Overview of the Westland ASR site, including the locations of the ASRO wells (AW) and the well of the 'BWRO' plant (coded as 'Former RO-abstraction well').**

The target aquifer for ASR (Aquifer 1) is 14 m thick and consists of coarse fluvial sands (average grain size: 400 µm) with a hydraulic conductivity (K) of 30-100 m/d (see D22.3, Part I), which was derived from the head response in MW1 and MW2 upon pumping. Approximately 1% of the aquifer sediment consists of clay (Figure 7). The groundwater is typically brackish, with Cl concentrations ranging from 3,793 to 4,651 mg/l in Aquifer 1 and approximately 5,000 mg/l in Aquifer 2 (Figure 6). A fine sand layer in Aquitard 2 contains residual fresher water (Cl = 3,270 mg/l). SO_4 is a useful tracer at the field site to separate the brackish water in Aquifer 1 and 2, as it is typically virtually absent in Aquifer 1 (presumably younger groundwater, infiltrated when the Holocene cover was already thick, which caused SO_4-reduction), whereas it is high in Aquifer 2: 300 to 400 mg/l SO_4 (older, infiltrated through a thinner clay cover which limited SO_4-reduction, see Stuyfzand (1993) for more details). The lateral displacement of the groundwater based on regional hydraulic heads is limited to only a few m per year (Zuurbier et al., 2013).

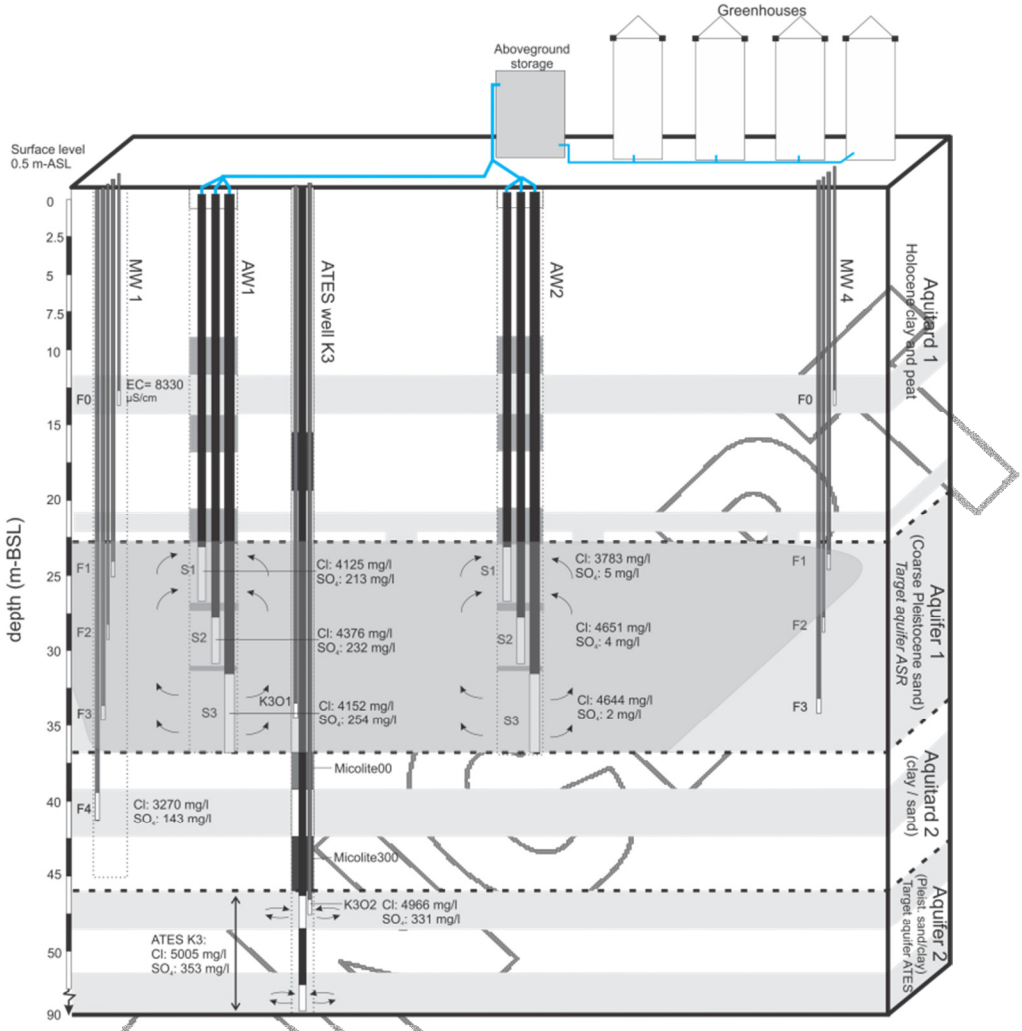

Figure 6: **Cross-section of the Westland ASR-pilot, including the ambient groundwater quality observed prior to the ASR operation.**

The targeted water quality during recovery is again rainwater (low salinity, Na<0.5 mmol/l), which means that the water should be recovered by the ASR-system practically unmixed.

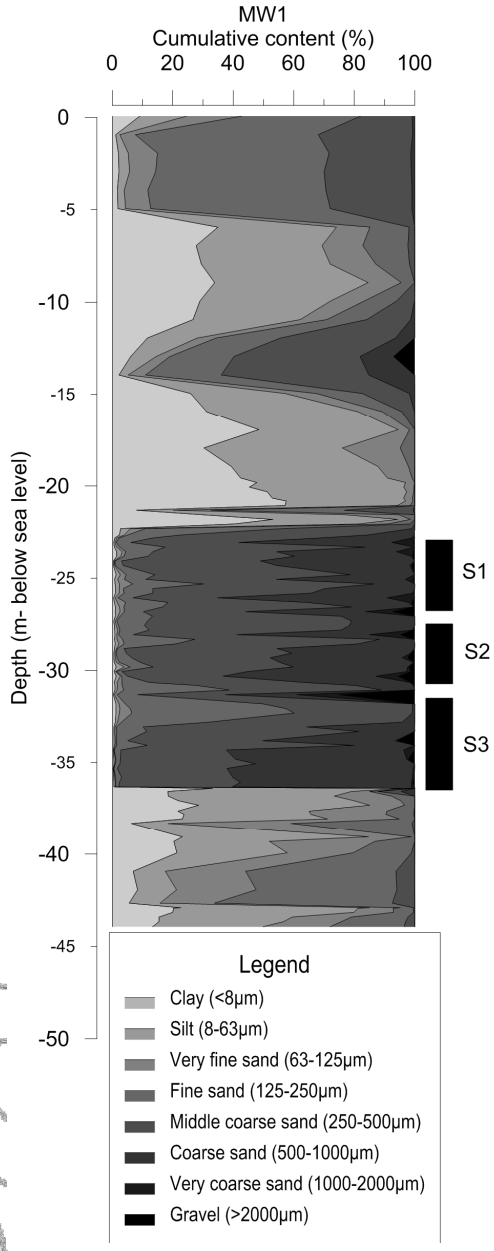

Figure 7: **Cumulative grain size contents observed at MW1 (at 5 m from ASR well 1). S1-S3 mark the depth intervals of the ASR well screens.**

2.3 RO-treatment of recovered water

2.3.1 RO-plants

When recovery of unmixed water becomes unattainable due to admixing of brackish groundwater with the injected rainwater, treatment via reverse osmosis is applied to maintain the production of fresh irrigation water. Two wells are used to feed two separate RO-facilities. One is the original brackish water RO-plant present at the site (coded BWRO), which was formerly used to abstract

brackish groundwater for RO (without rainwater admixed). This BWRO-system has been active since 2006, and forms the original supplementary freshwater supply of the local greenhouse. The BWRO-well now abstracts water from the whole aquifer thickness at the fringe of the injected freshwater body. The BWRO-plant is therefore fed by a mixture of water qualities present at this fringe (Figure 8).

The wells of the ASR-system were connected to a new RO-plant, realized in the DESSIN project to test the desalination of mixed injected water / brackish groundwater from below the freshwater bubble. This will simultaneously enable longer shallow recovery of unmixed injected water for direct use (Freshkeeper, Figure 8). This system is coded 'ASRO' (Figure 8) and the treatment part is coded ASRO-plant.

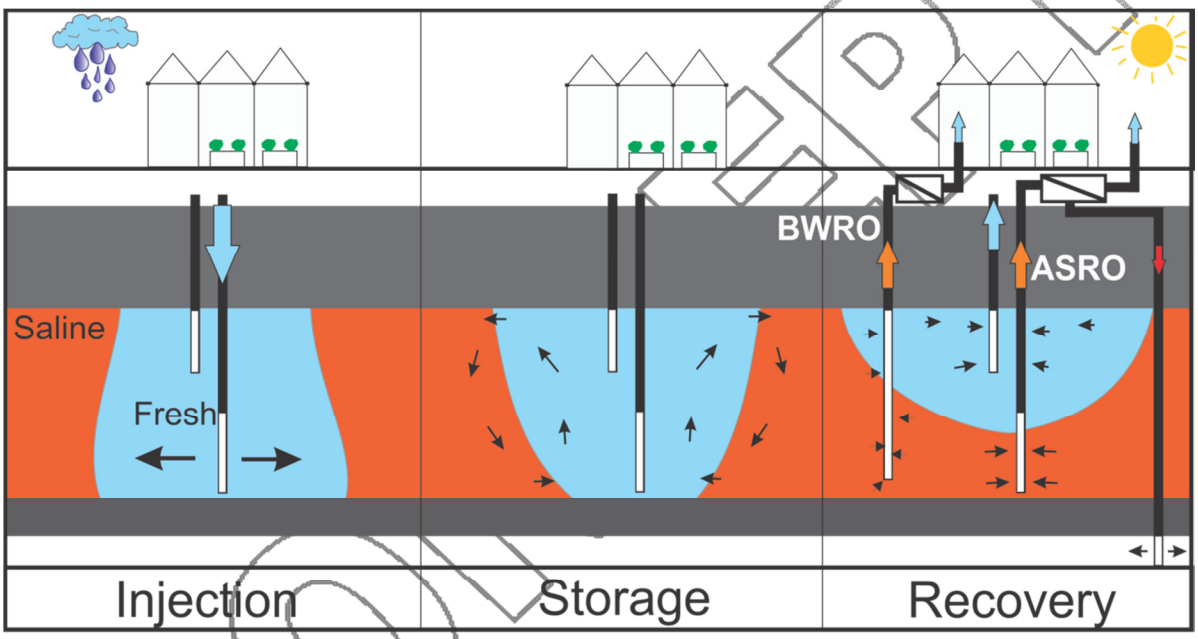

Figure 8: **Locations of the groundwater abstractions for desalination: BWRO at the (lateral) fringe of the injected freshwater bubble, ASRO below the injected freshwater bubble.**

The main difference between the feed water of ASRO and BWRO consists of the location of abstraction. The water for the BWRO-plant is abstracted via a long, fully penetrating well screen at approximately 20 m from AW2. This well is in the unmixed freshwater bubble at the end of the winter, but that deeper segments of the well completely salinizes as recovery proceeds. The abstracted water will therefore be a mixture of unmixed rainwater, mixed rainwater/groundwater, and unmixed brackish groundwater. This BWRO-plant was designed to be fed by 40 m^3/h of brackish groundwater to produce 20 m^3/h (480 m^3/d) of freshwater, which should result in an equal stream of concentrate at an RO-recovery of 50%.

The ASRO-plant is fed by the much shorter well screens of only 4 to 5 m length of the two MPPWs (AW1, AW2). For this reason it is possible to have more control on the composition of the ASRO

feed water. The same well screens are used for infiltration of rainwater in wet periods. This ASRO-plant was designed to be fed by 10 m^3/h of brackish groundwater to produce 5 m^3/h (120 m^3/d) of freshwater, which should result in an equal stream of concentrate at an RO-efficiency of 50%.

2.3.2 Characteristics of the RO-membranes

The BWRO plant uses a two-step design to guarantee low-salinity production water. The second step is a polishing step to remove remnant salts, while the bulk of the salts and all particles are removed by the first RO-step. The membrane concentrates from the polishing step is added to the feed water of the first RO-step, diluting the abstracted brackish water which forms the rest of the feed water.

The ASRO-plant uses a one-step approach using high-rejection membranes. The typical characteristics are summarized in Table 3. All membranes have a maximum operating pressure of 41 bar and a maximum feed water SDI_{15} of 5. In order to prevent clogging of membranes by precipitations in the concentrate, Flocon 260 was dosed to the feed water of the BWRO-plant with 250 ml/min. No dosing was applied at the ASRO-plant. The plants were both equipped with a cartridge filter (5 micron (nominal) at BWRO in 2013/2014; 1 micron (nominal) at both plants in 2015). The starting feed pressure of BWRO was 26 bar, while ASRO started operating at around 21 bar. The design permeate flux rate at both plants was 31 l/m^2/h.

Table 3: Typical characteristics of BWRO and ASRO membranes

Plant	Type	Membrane composite	Membrane area (m^2)	Feed spacer thickness (mil (mm))	Salt rejection (%)	Installation date (dd-mm-yy)
BWRO (step 1)	Low-fouling spiral wound	Composite Polyamide	37.1	34 (0.864)	99.7	18-6-2012
BWRO (step 2)	Spiral wound	Composite Polyamide	40.8	?	99.6	18-6-2012
ASRO	Cross Linked	Fully Aromatic Polyamide Composite	40.8	28 (0.711)	99.8	29-05-2015

2.4 Monitoring of water quality and RO-performance during ASR Cycle 1 and 3

All ASR and monitoring well screens were sampled prior to ASR operation (November and December, 2012). MW1 and 2 were sampled with a high frequency during the first breakthrough of the injection water at MW1 (December 2012, January 2013), while all wells were sampled on a

monthly basis until March 2014. Three times the volume of each well casing was removed prior to sampling. The injection water was sampled regularly during injection phases.

In Cycle 1 (December 2012 – Augustus 2013), the abstracted feed water to feed the BWRO-plant was frequently sampled, while also the performance of the BWRO-membranes was analysed based on operational parameters (production, recovery based on chemical analyses, feed and reject pressures). In Cycle 1, there was no ASRO-plant yet. The ASRO treatment plant was operational in Cycle 3 (October 2014 – July 2015) and the abstracted feed water, produced water, and the performance of both the ASRO and BWRO-membranes were monitored more extensively (

Table 4).

Table 4: Measurement at RO-treatment plants in Cycle 3

Location	Measurements
BWRO, ASRO	~Weekly • Date, time, hours of operation • Produced permeate and concentrate (m^3) • Conductivity, temperature, and pressure via CTD –divers (every 15 min) at MW1.1, MW1.3, MW2.1, MW2.3, K3O1. • Flow permeate, flow concentrate • Membrane: Pressure (feed), pressure (reject) • Pre-filter: Pressure (inlet), pressure (outlet) • EC(feed water), EC (concentrate), EC (permeate) • Temperature feed water • Samples of feed water and membrane concentrate Regularly: MFI, SDI measurement (Con-vergence MFI-inspector, Convergence, NL)

All samples were analyzed in the field for EC (GMH 3410, Greisinger, Germany), pH and temperature (Hanna 9126, Hanna Instruments, USA), and dissolved oxygen (Odeon Optod, Neotek-Ponsel, France). Samples for alkalinity determination within one day after sampling on the Titralab 840 (Radiometer Analytical, France) were stored in a 250 ml container. Samples for further hydrochemical analysis were passed over a 0.45 µm cellulose acetate membrane (Whatman FP-30, UK) in the field and stored in two 10-ml plastic vials, of which one was acidified with 100 µl 65% HNO_3 (Suprapur, Merck International) for analysis of cations and other elements (Na, K, Ca, Mg, Mn, Fe, S, Si, P, and trace elements) using ICP-OES (Varian 730-ES ICP OES, Agilent Technologies, U.S.A.). The second 10 ml vial was used for analysis of F, Cl, NO_2, Br, NO_3, PO_4, and SO_4 using the Dionex DX-120 IC (Thermo Fischer Scientific Inc., USA), and NH_4 using the LabMedics Aquakem 250 (Stockport, UK). All samples were cooled to 4 ^oC and stored dark immediately after sampling.

Calibrated, electronic water meters were coupled to the programmable logic controller (PLC) of the ASR-system to record its operation per well screen.

2.5 Chemical analyses on filtration residue's

Water samples were filtered in the field using 0.45 µm pre-filters for reliable sampling (Whatmann acetate membranes FP-30) and MFI/SDI measurements (0.45 µm Mixed Cellulose Ester by Convergence, NL). The filter membranes were conserved at room temperature for geochemical analyses. The 1 micron pre-filter of the BWRO-plant was replaced on June 24, 2015 (halfway Cycle 3) and a 3x3 cm piece was taken from this pre-filter for further analysis. On July 9, 2015, the samples mentioned in Table 5, were sent for semi-quantitative micro-XRF analyses on the EDAX "Orbis" micro XRF analyser at 'Philips Innovation Services' in Eindhoven (NL).

Table 5: Samples for XRF analyses

Sample nr.	Sample code	Sample type	Sampling date
1	MW2.2_27-12-12	0.45 um filter	12/27/2012
2	Reference_Whatmann	0.45 um filter	no sample
3	MW2.2_24-12-12	0.45 um filter	12/24/2012
4	Reference_Convergence	0.45 um filter	no sample
5	RO-feed_19-6-15	0.45 um filter	19-Jun
6	RO-feed_5-6-15	0.45 um filter	5-Jun
7	ASRO-feed_19-6-15	0.45 um filter	19-Jun
8	Pre-filter_24-6-15	1 um filter	24-Jun

The Edax "Orbis" XRF-analyser is an energy dispersive (EDX) X-Ray-Fluorescence device. The equipment can be used for point measurements, using a measuring spot of 30 µm, 1 mm or 2 mm. Besides the spot measurements the "Orbis" is equipped with a special software tool for screening purposes. Using this tool a surface of maximum 10 x 10 cm can be screened step by step for pre-defined elements, using the measuring spot of 30 µm, 1 mm, or 2 mm, with a mapping of the

elements involved as a result. The Edax “Orbis” XRF-analyser is a fast analysis method for determining the type of material and the presence of elements from sodium to uranium. Quantification of these elements is done using a “standard less” semi-quantitative analysis method, highly effective for analysing (screening) unknown samples for which no standards are available.

The residue samples were analysed using a 2 mm measurement spot with 30kV and 100µA under a vacuum. Each sample was measured on 5 different spots for 50 seconds, each to derive the ratio Al-Si-Fe. This way, it could be derived if the filtered residue consisted of mainly clay-silt (marked by large contributions of Al and Si) or Fe-precipitates (marked by a large contribution of Fe). Other elements which were found to have a significant contribution to the residue composition were noted.

Figure 9: **The Convergence MFI/SDI 0.45 micron filters used to derive the MFI/SDI of the ASRO feed water (left) and the BWRO feed water (right) (date: June 19, 2015).**

Figure 10: Pre-filters (1 micron, red-brown-coloured) of 'RO' on June 24, 2013. The white filters indicate the colour of unused pre-filters.

3 RESULTS

3.1 Cycle 1 (2012/2013): treatment of brackish water abstracted at the fringe of the ASR bubble via the BWRO-plant

3.1.1 Performance of the RO-membranes

In the Summer of 2013, the injected freshwater, which was injected in the preceding winter (15,518 m^3), was only partly recovered unmixed for direct use (3,110 m^3). The other 80% was recovered via the existing BWRO-plant. This way, the additional water demand was supplied. The BWRO-plant was continuously operated in 5 phases of 10 to 60 days. At the start of the BWRO operation, the brackish water consisted for more than 30% of rainwater, indicating that almost 70% of the feed water was already native groundwater. The contribution of rainwater consequently decreased. Only as a consequence of the injection of 2,824 m^3 of rainwater in a wet period (end of May, 2013), a short increase in rainwater contribution was observed. Membrane cleaning using citric acid was performed on June 11, after recovering a total of almost 47,000 m^3 of feed water.

The monitoring data indicates that the recovery of the BWRO-plant decreased upon the start of the desalination of mixed rainwater/brackish groundwater (Figure 11). As a consequence, less feed water was desalinated, and the plant required more operating hours to produce sufficient irrigation water, while the concentrations in the concentrate became as more water was send to the concentrates stream due to the recovery decrease (**Error! Reference source not found.**). The recovery of the BWRO-plant decreased from 45 to 34%. The treatment with citric acid slightly improved the plant's recovery (back to 36%), yet it was not brought back to its initial level.

During the BWRO operation, the feed pressure increased from 29 to 32.5 bar. An increase in pressure difference over the BWRO-membranes from 0.5 to 1.7 bar was observed.

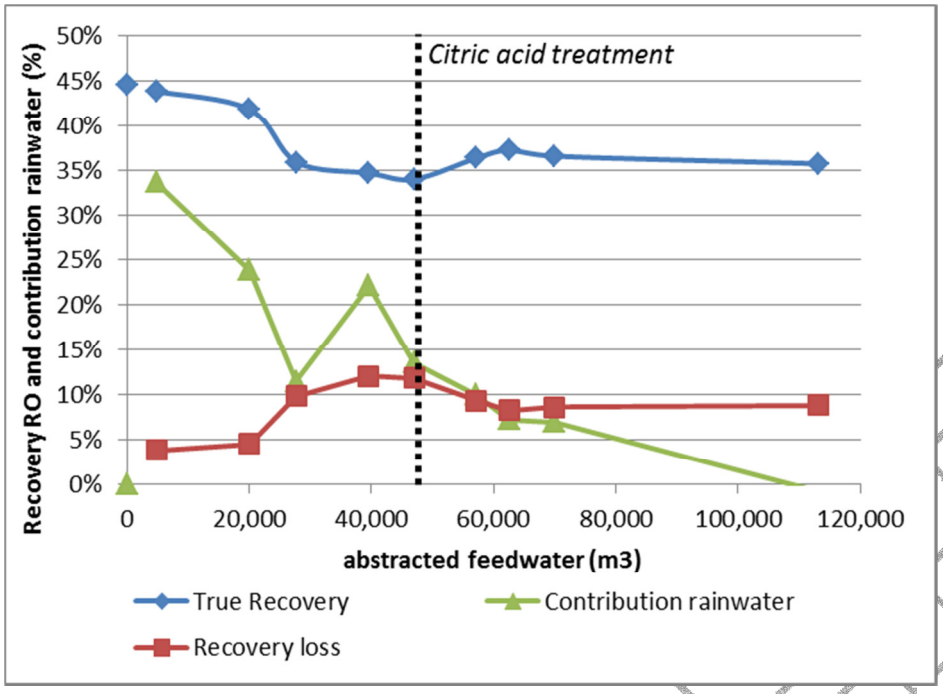

Figure 11: **Recovery achieved by the BWRO-plant ('true recovery'), contribution of rainwater to the feed water. At abstracted feed water = 0 m3, the operational data of the last servicing round (June 20, 2012) is shown. At this time, the installation had his normal design capacity.**

3.1.2 Feed water composition

The BWRO feed water quality was marked by a slow salinization due to a decreasing contribution of injected rainwater to the abstracted feed water. The resulting chemical composition is shown in Table 6. Concentration changes during recovery can be induced by dilution with rainwater (virtually free of solutes) and the relatively fresh concentrate from the polishing step, or by geochemical process. In

Table 7, the relative changes with respect to the ambient brackish water (the original feed water for BWRO) are shown, as well as the changes induced by other processes than dilution.

The measurements indicate that with respect to the native brackish water, the abstracted feed water is enriched in Mn, SO_4, Al, and Br. On the other hand, Fe, SiO_2 and B show decreasing concentrations, while PO_4 is initially increased, but decreases later on with respect to the native brackish water. Especially Al and SO_4 show a significant and absolute increase in feed water concentrations. The high Al concentrations are possibly caused by relatively high Al-concentrations in the injection water (average: 46 ug/L).

The resulting, most prominent water quality changes are summarized as follows:

- Dilution by the infiltration of rainwater and the addition of the rejected concentrate stream of BWRO-step 2 to the feed water of BWRO-step 1: generally lower concentrations, for some species complying with the dilution factor (mainly Cl, Na, Mg);
- Absolute enrichment of Al;
- Absolute enrichment by pyrite oxidation (SO_4);
- Relatively (with respect to the dilution) increasing Mn and decreasing Fe concentrations by redox processes;
- Relative enrichment (initially) and retardation (later) by resp. desorption and adsorption (SiO_2, PO_4);
- Relative enrichment by dissolution (Ca).

Table 6: **Water quality parameters of the feed water at BWRO in 2013. At the end (August 30, 2013), native brackish groundwater is abstracted. The reference brackish water quality is taken from MW3 (most reliable indicator for the brackish groundwater quality in Aquifer 1)**

Parameter	*Unit*	**brackish water MW3** *05/12/2012*	**start** *08/04/2015*	**intermediate** *13/06/2015*	**end** *30/08/2015*	**average** *12 samples*
Temp	C	11.8	11.5	12.6	12.6	12.1
pH		7	7	7	7.1	7.1
Cl	mg/L	4398	2757	3369	4086	3422
Na	mg/L	2145	1376	1630	2020	1663
K	mg/L	87	52	58	79	61
Ca	mg/L	403	274	318	383	331
Mg	mg/L	312	199	234	289	241
Fe	mg/L	12	6	7	10	7
Mn	mg/L	1	0.5	0.8	0.9	0.8
SiO_2	mg SiO_2/L	36	24	24	28	25
SO_4	mg/L	3	11	13	19	17

HCO_3	mg/L	1242	782	na	1060	914
NO_3	mg NO_3/L	0	0	0	2	1
PO_4-t	mg PO_4/L	10	7.0	5.7	5.9	5.6
Al	ug/L	7	33	34	26	36
As	ug/L	0	1	4	6	4
B	ug/L	759	415	492	712	504
Ba	ug/L	1340	793	932	1160	960
Br	ug/L	13954	12128	12292	14401	11805

Table 7: **Water quality changes in feed water at BWRO in 2013 caused by rainwater injection. Changes in percentages with respect to the native brackish groundwater composition and the changes induced by other processes than dilution with rainwater and concentrate from RO-step 2, assuming rainwater contains no solutes. Decreased concentrations are marked green, increased concentrations are marked red.**

	Total changes			***Changes by reactions***		
Parameter	*08-Apr*	*13-Jun*	*30-Aug*	*08-Apr*	*13-Jun*	*30-Aug*
Cl	63%	77%	93%	0%	0%	0%
Na	64%	76%	94%	2%	-1%	1%
K	60%	67%	90%	-4%	-12%	-3%
Ca	68%	79%	95%	9%	3%	2%
Mg	64%	75%	93%	2%	-2%	0%
Fe	53%	56%	82%	-16%	-27%	-12%
Mn	71%	102%	117%	13%	33%	25%
SiO_2	67%	67%	78%	8%	-13%	-16%
SO_4	399%	463%	672%	536%	504%	623%
HCO_3	63%		85%	0%		-8%
NO_3						
PO_4-t	74%	60%	62%	18%	-22%	-34%
Al	471%	487%	379%	652%	536%	308%
As						
B	55%	65%	94%	-13%	-15%	1%
Ba	59%	70%	87%	-6%	-9%	-7%
Br	87%	88%	103%	39%	15%	11%

Based on the hydrochemical compositions, saturation indices (SI) were calculated by PHREEQC Version 3 (Parkhurst and Appelo, 2013). Most relevant changes in SI were observed for Al-containing minerals ($Al(OH)_3$ (amorphous), Alunite, and Gibbsite) and Barite (Figure 12).

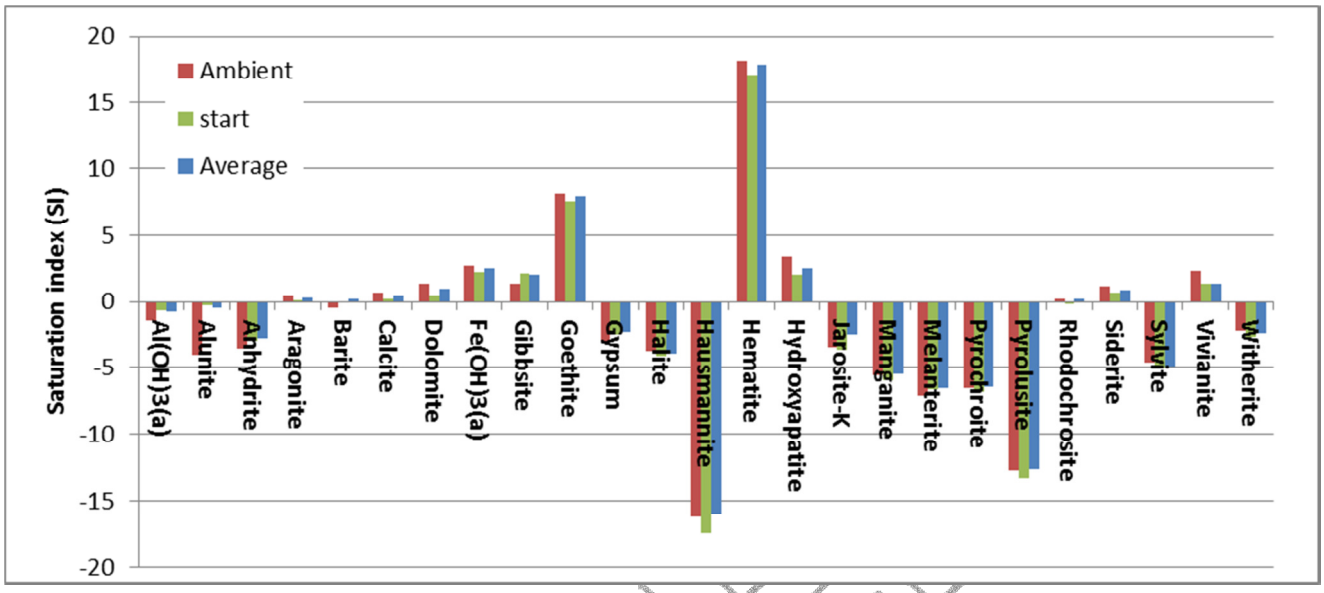

Figure 12: Saturation indices of minerals in the BWRO feed water based on the composition of the brackish water and the feed water composition at the start of abstraction and the average composition in 2013.

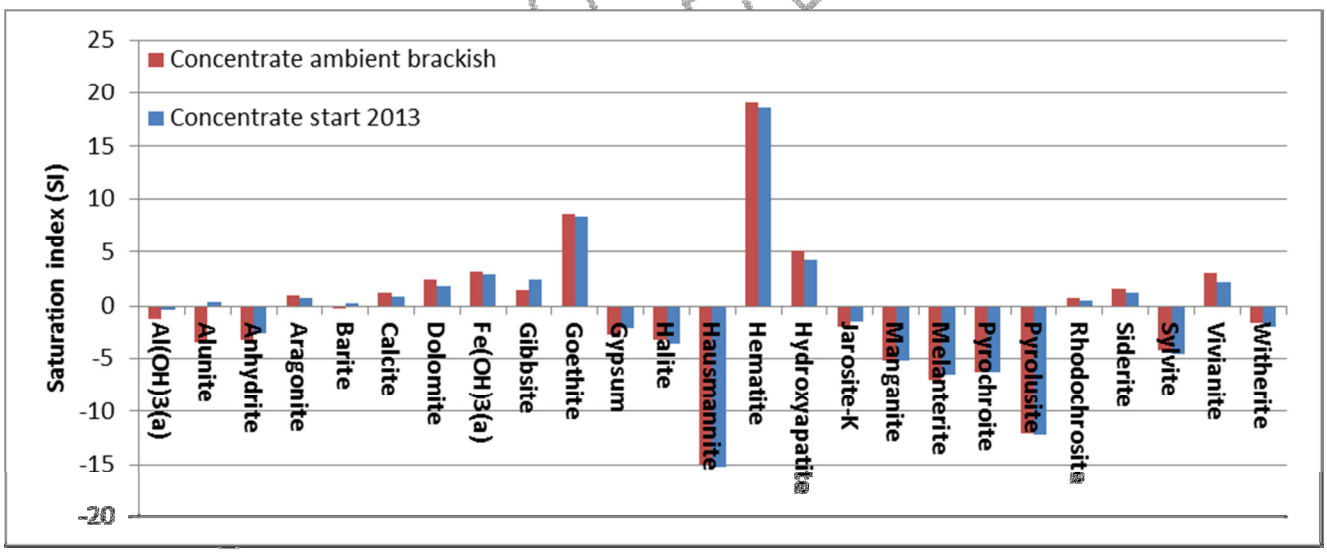

Figure 13: Saturation indices of minerals in the BWRO concentrate based on the composition of the brackish water and a 50% RO recovery and the observed composition of the membrane concentrate at the start of abstraction in 2013.

3.2 Cycle 3 (2014/2015): treatment of brackish water via BWRO and ASRO

3.2.1 Performance of the membranes

Performance of the BWRO membranes

The recovery of the BWRO-plant decreased from 48% to a minimum of 25%. In the same period, the rainwater contribution to the feed water decreased from 62 to 25%. Most of the recovery decrease was observed in the first period of operation, when the highest contribution of injected rainwater to the BWRO feed water was present (Figure 14). The recovery decrease in this phase was linear. During the last phase of production, the recovery increased upon standstill periods, when the membranes were flushed daily with fresh permeate. The initial recovery efficiency was not achieved, however, and the recovery decreased during longer periods of continuous operation.

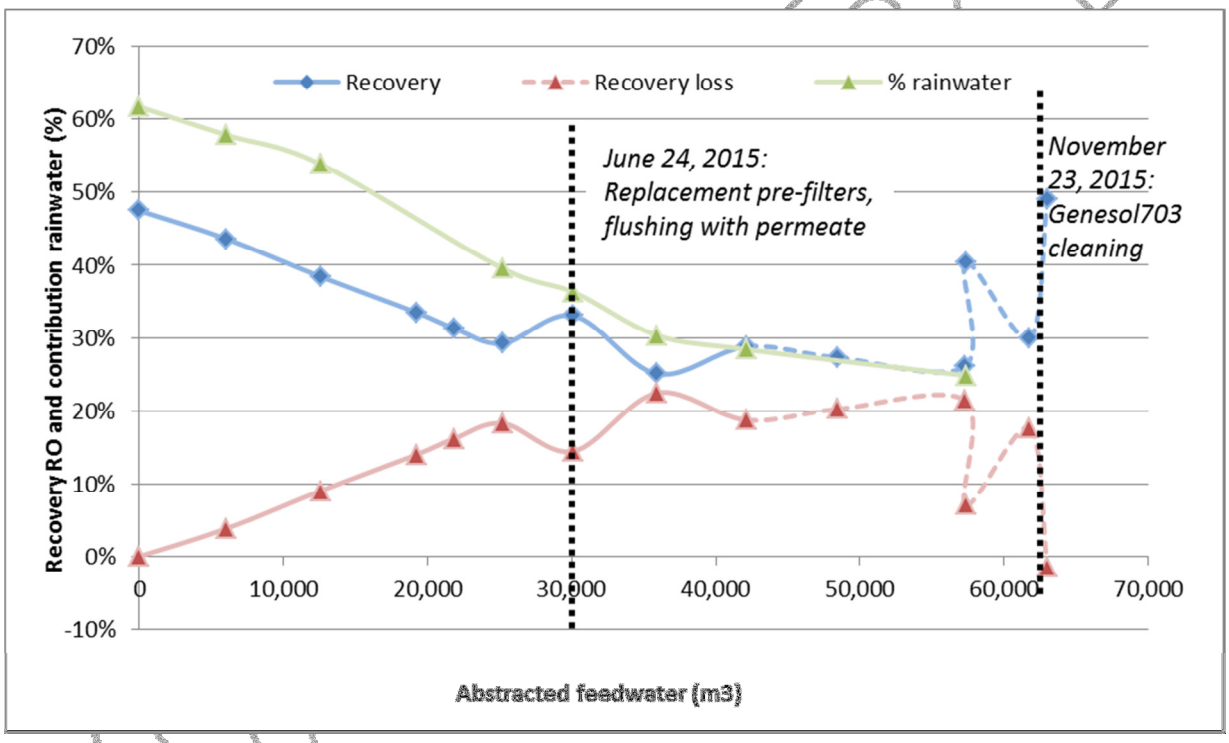

Figure 14: **Recovery and recovery loss of the BWRO membranes, and the contribution of rainwater to the RO-feed water in 2015. Solid lines indicate continuous operation, dashed lines indicate frequent periods of standstill and flushing alternating with irregular operation.**

The feed pressure applied on the membranes significantly increased during the first period of production (26 to 32 bar). The pressure difference (ΔP) remained stable in the first phase, but showed a later increase from around 1.1 bar to 1.5 bar. These observations suggest that first the membrane surfaces were clogged (increasing the feed pressure), while later also the feed channels were blocked (increasing ΔP). Standstill periods in the final phase of production led to a decrease of the feed pressure and the pressure difference, although the initial feed pressure was not attained.

Upon cleaning of the RO-membranes with GENESOL-703 in November 2015, the membranes were brought back to their original capacity.

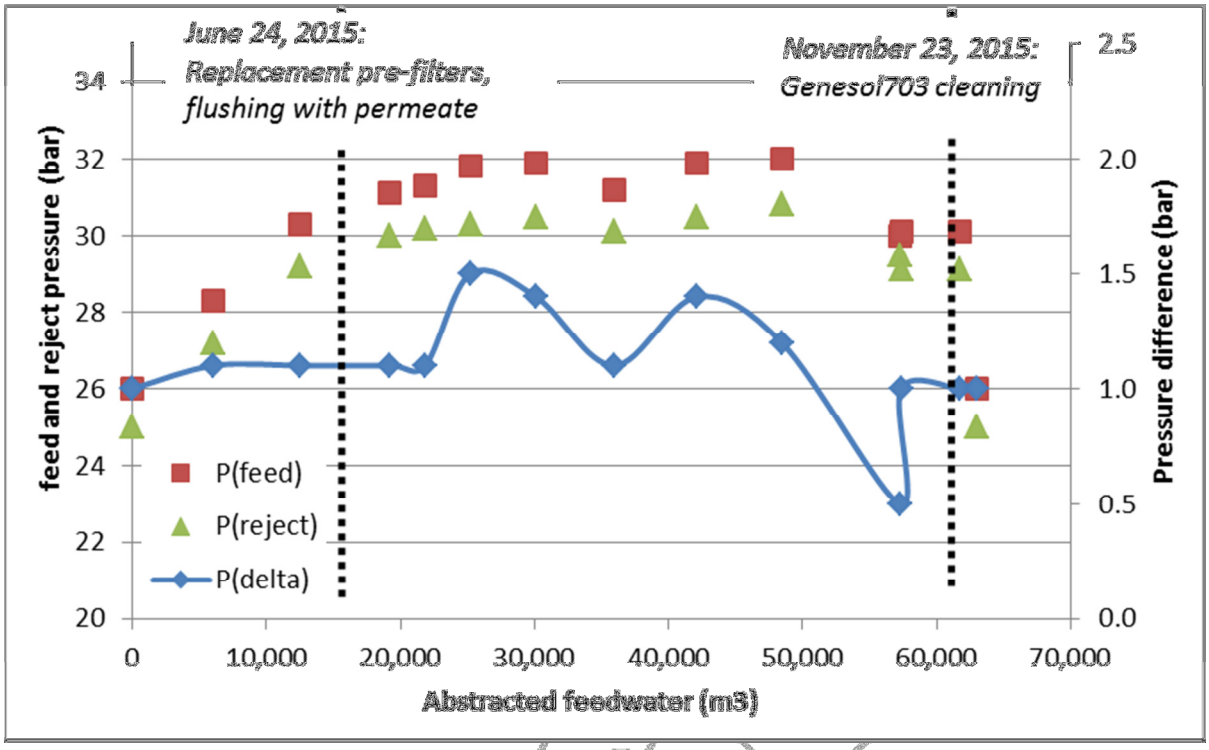

Figure 15: Feed and reject pressures and ΔP at the BWRO membranes in 2015.

Performance of the ASRO membranes

The ASRO-plant showed virtually no decrease in recovery during an almost 3 months runtime. The contribution of rainwater to the injected water varied between 28 and 47%, depending on which combination of specific ASR wells (AW2.1, 2.2, and 2.3) was feeding the ASRO-plant: during the runtime of the pilot, the abstraction was shifted from the basal part of the aquifer (AW2.2 and AW2.3) to the upper part of the target aquifer (AW2.1 and AW2.2), in order to maintain a lower salinity. The feed and reject pressures remained virtually constant throughout the pilot runtime. In total, 6,841 m^3 of permeate was produced.

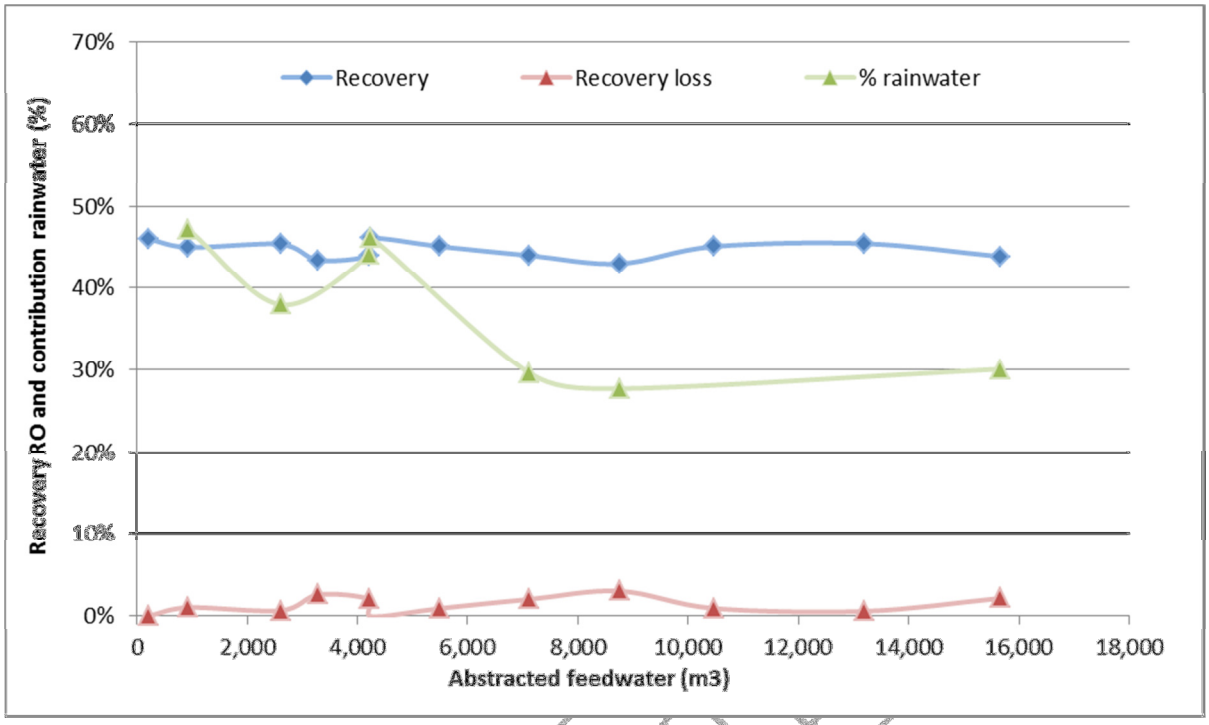

Figure 16: Recovery and recovery loss of the ASRO-plant and the contribution of rainwater to the ASRO-feed water in 2015.

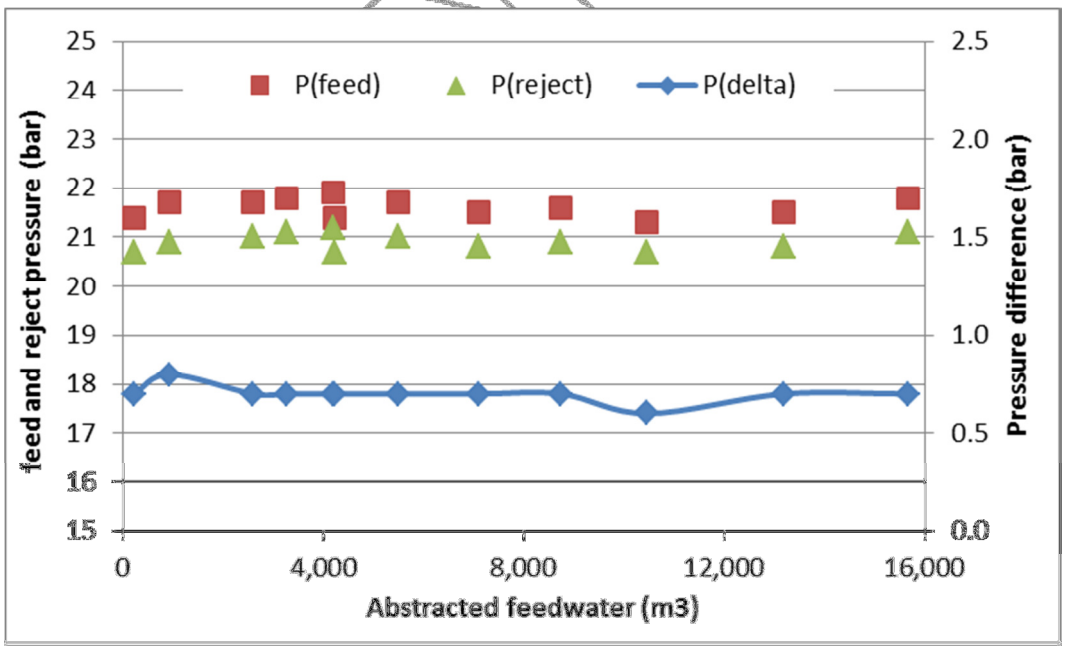

Figure 17: Feed and reject pressures at the ASRO-plant in 2015.

3.2.2 Analyses on the feed water

BWRO feed water

The BWRO feed water was again diluted by rainwater and showed a similar alternation comparable with 2013. Most elements showed again primarily dilution, whereas particularly Al, SO_4, Fe, and Mn showed a significant relative increase.

Analysis of the Modified Fouling Index (MFI) and the Silt Density Index (SDI) using an automated MFI/SDI Inspector (Convergence, The Netherlands) indicated an MFI of 2.2 l/s^2 (SDI: 3.5) at the start of operation (June), and 1.3 l/s^2 (SDI: 3.3) during later operation (July).

Table 8: **Water quality parameters of the BWRO-plant's feed water in 2015. The reference brackish water quality is taken from MW3 (most reliable indicator for the brackish groundwater quality in Aquifer 1).**

		brackish water			
		MW3	**start**	**intermediate**	**end**
Parameter	*Unit*	*05/12/2012*	*26/05/2015*	*05/06/2015*	*07/08/2015*
Temp	C	11.8	12.5	12.5	12.6
pH		7	7.1	7.1	7.1
Cl	mg/L	4398	1687	1923	3251
Na	mg/L	2145	848	991	1525
K	mg/L	87	30	37	58
Ca	mg/L	403	179	120	220
Mg	mg/L	312	120	138	220
Fe	mg/L	12	5	6	10
Mn	mg/L	0.8	0.6	0.7	1.3
SiO_2	mg SiO_2/L	36	14	16	21
SO4	mg/L	3	17	18	12
HCO_3	mg/L	1242	490	539	893
NO_3	mg NO_3/L	0	0	0	0
PO_4-t	mg PO_4/L	10	3	4	5
Al	ug/L	7	26	37	29
As	ug/L	0	4	1	0
B	ug/L	759	239	293	438
Ba	ug/L	1340	467	549	879
Br	ug/L	13954	6110	6933	11063

Table 9: **Water quality changes in BWRO-plant's feed water in 2015 caused by rainwater injection. Changes in percentages with respect to the native brackish groundwater composition and the changes induced by other processes than dilution with rainwater and concentrate from RO-step 2, assuming rainwater contains no solutes. Decreased concentrations are marked green, increased concentrations are marked red.**

	Total changes			*Changes by reactions*		
	26-May	*05-Jun*	*07-Aug*	*26-May*	*05-Jun*	*07-Aug*
Cl	38%	44%	74%	0%	0%	0%
Na	40%	46%	71%	3%	6%	-4%
K	35%	43%	66%	-9%	-3%	-10%
Ca	44%	30%	55%	16%	-32%	-26%
Mg	39%	44%	71%	1%	1%	-4%
Fe	45%	50%	84%	17%	14%	14%
Mn	74%	86%	162%	92%	97%	119%
SiO_2	39%	44%	59%	0%	1%	-20%
SO_4	574%	628%	403%	1396%	1337%	446%
HCO_3	39%	43%	72%	3%	-1%	-3%
NO_3						
PO_4-t	30%	39%	49%	-21%	-10%	-34%
Al	369%	537%	419%	863%	1128%	467%
As						
B	31%	39%	58%	-18%	-12%	-22%
Ba	35%	41%	66%	-9%	-6%	-11%
Br	44%	50%	79%	14%	14%	7%

ASRO Feed water

The composition of the brackish water abstracted for desalination by the ASRO-plant shows a similar alternation as the water feeding the BWRO-plant. All dilution must be due to admixing with rainwater in this case, there is no addition of permeate from a second BWRO-step.

The observed concentrations of SiO_2, K, Ca, PO_4, B, Ba were significantly lower than predicted via the dilution factor. Mn and SO_4 increased even more significantly than observed at BWRO. However, where Mn showed an increase during the pilot, SO_4 decreased. There was less enrichment with Al. HCO_3 was relatively low in the first part of the pilot. Fe concentrations were low at the start of the pilot, but increased to concentrations which were twice the background concentrations in the brackish water.

Analysis of the Modified Fouling Index (MFI) and the Silt Density Index (SDI) using an automated MFI/SDI Inspector (Convergence, The Netherlands) indicated and MFI of 1.9 l/s^2 (SDI: 3.5) at the start of operation (June), and 1.2 l/s^2 (SDI: 3.1) during later operation (July).

Table 10: **Water quality parameters of the ASRO-feed water at ASRO in 2015. The reference brackish water quality is taken from MW3 (most reliable indicator for the brackish groundwater quality in Aquifer 1).**

Parameter	*Unit*	**brackish water MW3** *05/12/2012*	**start** *15/06/2015*	**intermediate** *01/07/2015*	**end** *07/08/2015*
Temp	C	11.8	11.7	12.0	12.5
pH		7	7.2	7.1	7.1
Cl	mg/L	4398	3472	3095	3074
Na	mg/L	2145	1725	1533	1472
K	mg/L	87	57	51	52
Ca	mg/L	403	355	216	213
Mg	mg/L	312	246	216	213
Fe	mg/L	12	9	11	24
Mn	mg/L	0.8	2.7	2.4	5.2
SiO_2	mg SiO_2/L	36	16	17	16
SO_4	mg/L	3	103	69	42
HCO_3	mg/L	1242	787	733	864
NO_3	mg NO_3/L	0	0	0	0
PO4-t	mg PO_4/L	10	1	1	2
Al	ug/L	7	40	37	36
As	ug/L	0	5	7	12
B	ug/L	759	390	352	385
Ba	ug/L	1340	741	630	656
Br	ug/L	13954	10335	10335	10551

Table 11: **Water quality changes in ASRO-feed water at ASRO in 2015 caused by rainwater injection. Changes in percentages with respect to the native brackish groundwater composition and the changes induced by other processes than dilution, assuming rainwater contains no solutes. Decreased concentrations are marked green, increased concentrations are marked red.**

	Total changes			*Changes by reactions*		
	15-Jun	*01-Jul*	*07-Aug*	*15-Jun*	*01-Jul*	*07-Aug*
Cl	79%	70%	70%	0%	0%	0%
Na	80%	71%	69%	2%	2%	-2%
K	65%	59%	60%	-17%	-16%	-14%
Ca	88%	54%	53%	12%	-24%	-24%
Mg	79%	69%	68%	0%	-1%	-2%
Fe	71%	90%	201%	-10%	28%	188%
Mn	352%	309%	678%	346%	339%	870%
SiO_2	45%	47%	44%	-43%	-33%	-36%
SO_4	3585%	2411%	1450%	4441%	3327%	1974%
HCO_3	63%	59%	70%	-20%	-16%	-1%
NO_3						
PO_4-t	7%	14%	20%	-91%	-80%	-71%
Al	578%	525%	520%	632%	646%	644%
As						
B	51%	46%	51%	-35%	-34%	-27%
Ba	55%	47%	49%	-30%	-33%	-30%
Br	74%	74%	76%	-6%	5%	8%

3.3 Analyses on the filter residues

Eight samples of filter residues were sent for lab analysis on chemical composition using micro-XRF. Two reference samples of the filters were analysed to exclude possible background contributions of the filter material.

3.3.1 Mobilized material during freshening in target aquifer

Two samples contained material collected during filtration of abstracted groundwater from the fringe of the injected water body. It was found that this high-turbidity water was transporting fines primarily consisting of Al and Si, suggesting clay dispersion (i.e. mobilization) during freshening.

3.3.2 Suspended material reaching the ASR feed water

Despite the different filtration steps (gravel pack, 1 µm pre-filter), suspended solids were present in the BWRO and ASRO feed water. The residue on the 0.45 µm obtained during MFI/SDI measurements at BWRO and ASRO showed that Al and Si again dominated the filter residue. Compared to the mobilized solids at the fringe of the injected freshwater body, there was a slightly higher contribution of Fe in the suspended material reaching the abstraction wells, however.

3.3.3 Suspended material captured by the BWRO pre-filter

The material on the BWRO-pre-filter indicated a presence of significantly more Fe than observed in all other samples. Fe dominated over Si and Al, while also Ti and Mn were found.

Table 12: Measured chemistry by micro-XRF on filter residues (by Philips Innovation Services, project 2015.3271/XF150055).

Sample nr.	Sample code	Al-Si-Fe ratio on molar basis	Other elements
1	MW2.2_27-12-12 (high turbidity injected water, fringe)	19-79-2	P, S, K, Ca, Ti, Mn
2	Reference_Whatman filter	-	
3	MW2.2_24-12-12 (high turbidity injected water, fringe)	21-78-1	P, S, K, Ca, Ti
4	Reference_convergence filter	-	
5	RO-feed_19-6-15	21-69-10	Na, P, S, K, Ca
6	RO-feed_5-6-15	25-63-12	Na, P, S, K, Ca
7	ASRO-feed_19-6-15	21-71-8	Na, P, S, K, Ca
8	RO_Pre-filter_24-6-15	9-27-64	P, S, K, Ca, Ti, Mn

4 Interpretation of the observations

4.1 Brief summary of observations

Based on the observations, the following relevant statements can be made:

- The characteristics and designs of both RO-plants (ASRO and BWRO) are more or less similar. The main differences are a higher design capacity and a second RO-step at BWRO, compared to the low-capacity one-step RO at ASRO;
- Both plants recover a diluted brackish, anoxic water type. Relative enrichment in Al, SO_4, Fe, and Mn is observed. Higher Al concentrations may originate from the injection water. SO_4, Fe, and Mn are more enriched at ASRO;
- A relative decrease of K, PO_4, B, Ba, and SiO_2 was observed and was most explicit at ASRO;
- Slightly higher MFIs / SDIs were observed in the feed water at BWRO;
- BWRO showed a rapid and severe linear capacity decrease (and pressure increase) in the first stage of production. The capacity stabilized during periods with frequent standstills and flushing with fresh permeate. The capacity was completely restored upon cleaning with Genesol703;
- No capacity decrease nor pressure increase was observed at ASRO, which showed a very constant operation throughout the three months runtime;
- In the target aquifer, clay mobilization was suspected at the fringe of the freshwater body during freshening, based on the observed turbidity and geochemical composition and colour (grey) of residues upon filtration of turbid water from this zone. A similar geochemical composition was found on residues from filtrated feed water at the RO-plants, although a higher contribution of Fe was observed in suspended material in the feed waters. At the pre-filter, the residue primarily consisted of Fe, which showed a more red-brown color.

4.2 Driving processes for changes in the chemical water quality

The processes observed at the Westland ASR site are regularly observed during ASR (Stuyfzand, 1998). The most relevant processes are discussed below:

- The initial increase in SO_4 was observed in combination with a decrease in dissolved oxygen and nitrate concentrations in the injected water, suggesting oxidation of pyrite (FeS_2) to produce SO_4. Additionally, and predominantly during the end of the abstraction period, leakage of deeper saltwater via the borehole of ATES K3 may introduce the additional SO_4 in the last phase of abstraction. The latter also occurred before ASR was applied;
- Introduction of oxygen (dissolved in the injection water; see Part I) will have led to precipitation of desorbing Fe^{2+} to Fe-hydroxides (and subsequent sorption of Fe^{2+} on these hydroxides) and Mn^{2+} to MnO_2 (and subsequent sorption of Mn^{2+}) around the

ASR wells. Subsequently, reduction of MnO_2 by oxidation of Fe^{2+} and/or desorption of Mn^{2+} has probably occurred, as Fe concentrations reaching the BWRO abstraction well are relatively low with respect to the Mn-concentrations. During later abstraction phases, relatively high Fe and Mn concentrations were observed;

- Dissolution of calcite in the target aquifer, in the unsaturated injected rainwater and as a consequence of proton-buffering upon pyrite oxidation, explains the Ca increase in the injected water, which was relatively strong especially for the initial feed waters. During later abstraction, relatively low Ca concentrations were observed, which can be related to cation exchange of Na for Ca;
- The observed concentrations of SiO_2 and PO_4 show that sorption processes affect their presence in the feed waters. Desorption processes during freshwater injection first led to enrichment in the injected water (which was, for instance, abstracted at the start of the BWRO operation in Cycle 1, sample April 8, 2013), and retardation during salinization induced by abstraction of the feed waters, leading to relatively low concentrations during the later phases of abstraction (June – August 2013 at BWRO, and continuously at ASRO in 2015). Precipitation of Fe-hydroxides in the vicinity of the ASR wells will have enhanced the sorption of PO_4 and SiO_2 in the aquifer;
- The increase in Al-concentrations may be explained by infiltration of the rainwater, as relatively high Al-concentrations were observed in the infiltration water (>50 ug/l), while very low concentrations were found in the groundwater samples preceding ASR operation (Aquifer 1 and 2). Based on the relatively higher concentrations in the feed water at the end of the Cycle 1 at BWRO, sorption of Al in the target aquifer can be suspected. This is however not underlined by the observations in Cycle 3. One difficulty in the interpretation of Al is that the injected concentration varied over time (10 to 100 µg/l) and the potential presence of clay particles <0.45 µm bearing Al in the groundwater samples (Kennedy et al., 1974; Stuyfzand, 1993). It is therefore uncertain if Al in the injection water, groundwater, and feed water was dissolved, or (partly) present as fine clay particles.

The water quality changes were most distinct at ASRO, indicating that most water quality changes occur in the surrounding of the injecting ASR wells. The qualitative changes are summarized in

Table 13.

Table 13: General water quality change and presumed chemical processes.

RO-plant	Increased	Decreased	Driving process(es)
BWRO	Al SO_4 Fe, Mn		Injection water Pyrite oxidation Desorption / cation exchange, reduction
BWRO		PO_4, B later: Ba, SiO_2, Ca	Sorption / cation exchange
ASRO	Al SO_4 Fe, Mn		Injection water Pyrite oxidation Desorption / cation exchange, reduction
ASRO		SiO_2, PO_4, B, Ba, K later: Ca	Sorption / cation exchange

4.3 Potential sources of the membrane clogging observed at the BWRO-plant

Potential sources for the observed clogging at the BWRO-plant (and the absent clogging at ASRO) were evaluated using the operational and chemical data derived.

4.3.1 Membrane scaling by oversaturation

Scaling of membranes can occur when the RO feed water is significantly concentrated during the desalination process, which is the case at the Westland ASRO site. As concentrations at the reject-side of the membrane rise as a consequence of freshwater passing the membranes, oversaturation of soluble salts (like carbonates and barium sulphate) can result. Precipitating minerals can then get deposited on the membrane, causing plugging and a reduced freshwater production.

An increasing scaling sensitivity would be marked by increasing saturation indices (SI). In Figure 12 and Figure 13, these SIs in the RO feed water and concentrate were shown for the most common minerals. The results show that for most minerals, a decrease in SI is calculated when admixing with the injected rainwater occurs. This would reduce the risk of membrane scaling. Only minerals related to Al (which was present in relatively high concentrations in the injection water) and SO_4 (released in the aquifer) such as Alunite (change in SI: -3.5 to 0.4) and Barite ($BaSO_4$, change in SI: from -0.3 to 0.3) showed an increased risk of precipitation, although the SIs stayed relatively low. Other important minerals for scaling, like carbonates, actually showed a decreasing tendency to precipitate. The SIs in the ASRO feed water and membrane concentrate were similar. Together with the low SIs, this suggests scaling was not a major factor for the reduced BWRO performance.

4.3.2 Reduced membrane performance by biofouling

Biofouling involves clogging of the membranes by biological contamination. This biological contamination is caused by biological growth ('biofilms') on the RO-membranes. Available nutrients are the most dominant factor for biofouling (Flemming, 1997). In the BWRO and ASRO feed water however, nutrient concentrations did not show a significant increase due to the admixing of rainwater. Nitrate and oxygen in the rainwater were consumed during aquifer transport, and other species were primarily diluted. AOC levels of the injection water (rainwater after sand filtration) were presumably low. This was observed at ASR-systems nearby (Zuurbier et al., Submitted), where the AOC concentration was approximately 10 µg/l. No significant difference in nutrient loads were observed between the BWRO and ASRO feed water. The results suggest biofouling will not play a major role in the clogging of the BWRO-plant.

Biofouling will result in an decreased permeate production, an increased pressure difference (ΔP), and a decrease in salt retention. The first two were observed at the BWRO plant. However, in general an exponential development of the biological clogging is observed. The BWRO plants showed a clear linear clogging trend, as marked by the linear decrease in capacity and linear increase of the feed pressure. The operational aspects do therefore not support the occurrence of biofouling at the BWRO-plant.

4.3.3 Precipitation of Fe-hydroxide and / or Mn-oxide during well abstraction

The injected freshwater is recovered by the shallow parts of the BWRO abstraction well, while native brackish water is abstracted at the deeper parts. The injection water contains oxygen at the moment it is injected, while the native groundwater is rich in Fe and Mn. Mixing of both water types in one abstraction well would lead to precipitation of Fe-hydroxide and Mn-oxide, which may then plug the membranes. Field measurements at the various monitoring wells however indicated that the oxygen is quickly consumed in the injected water by pyrite (FeS_2) oxidation (producing SO_4) and oxidation of soil organic matter (producing CO_2). Complete oxygen consumption is observed within 15 meters from the injection well. All abstracted water at the BWRO well at 20 m from the injection wells was therefore expected to be anoxic. The absence of nitrate in the feed water, which is the next oxidator consumed after the dissolved oxygen, confirmed these findings. The only injected water containing still some low concentrations of oxygen was recovered unmixed for direct use via the ASR wells in the first periods of freshwater recovery. Despite the high contents of Fe (and some Mn) on the BWRO pre-filter, indicating that Fe particles were present in the abstracted water, mixing of Fe/Mn-rich and oxygen containing water was not a very likely source.

4.3.4 Particle clogging

Another source for membrane clogging can be small particles (colloids, clay, silt) present in the abstracted water, which feeds the BWRO membranes. Especially the smallest particles may not be hampered by the borehole wall, the gravel pack, or the pre-treatment (1 micron filters in the Westland), and can therefore reach the membranes. In brackish water, however, their concentrations are generally low, as clay particles tend to flocculate in solution with a high ionic strength, like brackish water (Appelo and Postma, 2005; Brown and Silvey, 1977). However, the injected rainwater had an exceptionally low ionic strength, which may actually promote clay

swelling and dispersion (or: mobilization) during freshening of the target aquifer during injection. This was observed during the initial freshening of the aquifer in 2013, but also during the later cycles. Groundwater samples obtained at the fringe of the injected freshwater body showed a high turbidity, often too high to measure a MFI/SDI or to filtrate large volumes over the 0.45 micron pre-filter during groundwater sampling. Geochemical analyses on the filtrated residues from this fringe and from BWRO feed water confirmed that the material causing the turbidity consists mainly of clay (high Si and Al-content). After passing of the freshwater front, low-turbid water was again observed, despite the very low salinity.

The contamination of feed water with mobilized clay should be marked by elevated MFIs and/or SDIs. However, the MFI/SDI measured in 2015 at the BWRO plant was only slightly higher than at the ASRO plant. Perhaps slight differences are sufficient to cause clogging. On the other hand, 2015 was the first year that the MFI and SDI were measured with the new MFI inspector, and some start-up problems with this device prohibited extensive, frequent measurements.

The operational data supports the theory of particulate clogging: linearly decreasing permeate production, increasing feed and reject pressures, an increasing pressure difference (ΔP), and restoration of the operational performance upon flushing with permeate and cleaning with Genesol703 (Genesys International, U.K.). During the flushing with and subsequent standstill in the permeate, similar clay dispersion as observed in the target aquifer can be expected. Upon restarting the RO-plant, this material is removed during initial flushing with approximately 9 Bar). The Genesol703 membrane cleaner is particularly effective against clogging by cake layers of aluminium silicates (clays), and its success also supports the finding that clay particles were responsible for a large part of the clogging. Fe colloids have presumably contributed to the cake layer, but did probably not dominate this layer based on the successful Genesol703 cleaning and the significantly less successful cleaning with citric acid in 2013, which should have removed (more of the) Fe-deposition.

The residue at the BWRO pre-filter and to a lesser extent on the 0.45 micron filters contained significantly more Fe than the water observed at the fringe of the freshwater body. With respect to the samples from the fringe of the freshwater body, Al was increased with respect to Si. Apparently, a second source of particles (presumably Fe and Al-colloids) besides the clay was present and contaminated the water at the BWRO well. A potential candidate is the formation of Fe (and Al)-colloids upon injection of the oxygen-containing rainwater in the aquifer containing Fe-rich native groundwater. Part of the Fe^{2+} oxidizing to Fe^{3+} can then remain mobile in the form of colloids (e.g., Wolthoorn, 2003).

4.4 Implication for desalination of (diluted) brackish water upon freshwater infiltration

With clay mobilization and potential formation of Fe-colloids resulting in particulate fouling as the most important candidate for the reduced performance at the BWRO-plant, the question arises why the ASRO-plant did not suffer from similar problems.

The locations of the abstraction wells that feed the BWRO and ASRO-plant are the most presumable cause: the BWRO well is located at the fringe of the injected freshwater body and abstracts water from the whole aquifer thickness. This well is situated 20 m from the injection wells. At the upper part of this well, unmixed freshwater is recovered. The lower part of the well abstracts unmixed native groundwater. A mixing zone will be situated in between (Figure 18). This system acts more like an aquifer storage transfer and recovery system (Maliva and Missimer, 2010). The ASRO well, on the other hand, primarily and selectively attracts unmixed native groundwater and water from the mixing zone, but hardly any unmixed rainwater, even though the same wells are used for injection of rainwater in times of surplus. This complies with a normal ASR strategy (Stuyfzand and Doomen, 2005), where injected water moves more or less the same route through the aquifer: away from the ASR well and back again.

Any colloids mobilized in the first water that is injected upon freshening and/or by Fe oxidation at the start of injection, will be transported to the fringe of the injected freshwater body. Thus, the water with the highest turbidity will be transported as far as possible from the ASRO wells. During transport, (a part of) the colloids may become immobilized as a consequence of decreasing flow velocities (Zheng et al., 2014). During storage, the turbid water will be transported as a consequence of buoyancy effects: water from the bottom will move upwards in the aquifer, while at the top of the aquifer lateral displacement occurs (Figure 18). The bottom of the aquifer will be washed with native groundwater (low turbidity, high ionic strength), stimulating clay flocculation.

Consequently, a part of the zone where colloids may be present in suspension will presumably be located in the area where the BWRO well is abstracting its water from. This may also be the zone were mobilized particles settled in the aquifer sediments as a consequence of low flow velocities. Once the BWRO abstraction well is switched on (with 40 m^3/h), this induces high flow velocities in the vicinity of the BWRO well, which may remobilize previously settled particles (van Beek et al., 2009; van Beek et al., 2010; Zheng et al., 2014). Instead, the ASRO well is primarily fed by native brackish groundwater travelling through the basal parts of the aquifer, while abstraction rates are low (10 m^3/h). Any admixed rainwater recovered together with this brackish water will be relatively 'young': this rainwater was injected in the later phases of the injection period, when particle mobilization around the ASRO wells was limited as this zone was already freshened. Additionally, most of the absorbed Fe^{2+} and Mn^{2+} in the vicinity of the ASRO wells was presumably already exchanged or oxidized when this younger freshwater was injected. Most of the oxygen was therefore consumed by pyrite oxidation (consuming approximately 50% of the oxygen, based on the SO_4-production) and oxidation of sedimentary organic matter (based on the Ca-production), potentially limiting the formation of Fe colloids. This transition from oxidation of adsorbed Fe (and Mn) to oxidation of pyrite and organic matter is supported by findings at an extensively monitored MPPW-ASR pilot in the same target aquifer at approximately 15 km from the Westland demosite (Zuurbier et al., Submitted).

An alternative hypothesis is that the upper part of the aquifer has a higher potential for mobilization of clay or Fe-colloids. The higher turbidity during freshening was however observed at all aquifer intervals. Additionally, the ASRO plant was also fed by abstracted water from the top of

the aquifer during the last weeks of operation, in which no decrease in operational performance was observed. The higher abstraction rate at the BWRO well can also explain the higher load of inflowing particles (van Beek et al., 2010). As abstraction wells tend to have a decreasing inflow of particles upon longer operation (van Beek et al., 2010), one would naturally expect a very low inflow of particles here. Again, an increase in particle mobilization must have taken place first.

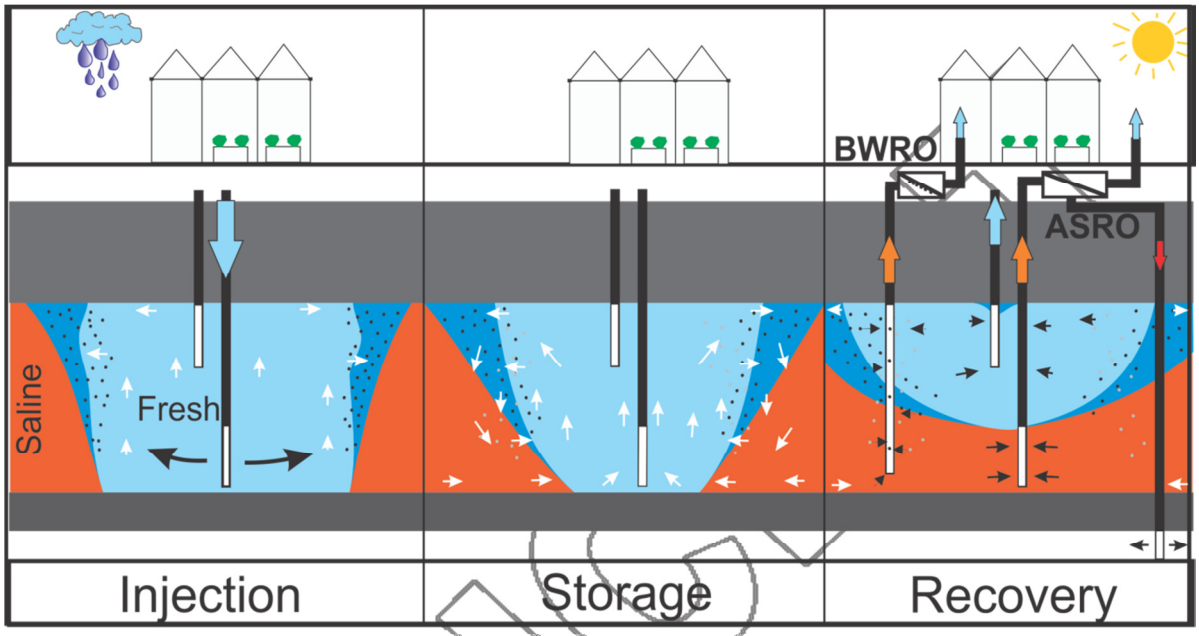

Figure 18: **Schematic of the hypothesized groundwater and colloid transport in the target aquifer.**

4.5 Evaluation of countermeasures

4.5.1 Ex-situ treatment

One logical direction of solving the membrane clogging at BWRO is the removal of the particles before the water feeds the RO-membranes. Two possible pre-treatment steps are:

- Ultrafiltration (UF): a type of membrane filtration to remove solids, not solutes;
- Normal cartridge filtration (e.g. a 1 micron, absolute pre-filter, followed by a 0.45 or 0.2 micron filter).

The addition of an additional UF in front of the BWRO-plant requires an investment of around 120 kE, and will raise the cost price per produced m^3 of freshwater with around €0,44. This will also require backwashing and disposal of the backwashed material to a sewage system (additional infrastructure). The more conventional treatment consisting of cartridge filtration can be realized at significantly lower costs (9 kE), but will also require regular replacement of the filter cartridges upon clogging with the suspended particles. This will lead to regular downtime and additional costs of around 6.5 kE per year. The cost price will then be raised with around 0.11 euro per m^3 of produced water. A drawback is that particles <0.45 or 0.2 micron may still pass this pre-filter.

4.5.2 In-situ treatment or prevention

Instead of correcting the feed water of the BWRO plant after contamination with suspended particles, it may be more interesting to try to limit the mobilization of particles. This can be realized by Ca-dosing during the first injection phase to counteract clay swelling / dispersion by rapid exchange of Na for Ca, after which the clay particles tend to remain flocculated (Brown and Silvey, 1977; Konikow et al., 2001). Additionally, this may also speed-up the removal of adsorbed Fe (and Mn) from exchanger sites in the vicinity of the ASR wells in the first stage of injection. This could reduce their oxidation and the accompanying formation of Fe-colloids. As a result, the load of suspended particles may be significantly decreased, which will prevent cake formation on the BWRO-membranes.

In order to realize an immediate exchange of all exchangeable Ca during infiltration of the targeted 60.000 m^3, it is required to pre-flush with more than 200 m^3 of $CaCl_2$ (35%) each year. With a current cost-price of around 2 kE/m^3 of $CaCl_2$, the costs will be unacceptable, even if only the lower half of the aquifer is treated with the required volume of $CaCl_2$.

It is relevant to study if a significant part of the mobilization of clay and the exchange of the abundant Fe (and Mn) around the ASR well can be sufficiently reduced by injecting a relatively small volume of $CaCl_2$ before the freshwater is injected. The additional costs to dose around 3 m^3 of 33% $CaCl_2$ (around 15 L per m^3) are 2 kE for the installation, while yearly operational costs are 7 kE to supply the $CaCl_2$. The cost price will then be raised with around 0.07 euro per m^3 of produced water.

4.5.3 Regular flushing at the BWRO-plant

Instead of preventing clogging of the BWRO-plant, it may be feasible to 'cure' the plant by regular flushing during long operations. This flushing should remove the cake layer and includes a standstill period after the feed channel is filled with fresh permeate. Subsequently, the feed channel is flushed abruptly with a high flux using feed water from the abstraction well. The standstill in permeate should induce remobilization of the suspended material in the cake layer, similar to the clay mobilisation during freshening of the target aquifer. If this weakens the cake layer sufficiently, it will be merely removed during subsequent flushing with feed water. The advantage is that this doesn't require significant investments or operational costs. The downsides are the operational downtime and the discharge of the flushed material. In the current set-up, this water is discharged towards the concentrate injection well, which becomes more vulnerable for clogging. This low-cost 'cure' will be studied in the Summer of 2016.

4.5.4 Feed also the BWRO-plant with water from the ASRO wells (i.e. complete transition to ASRO)

A final option to prevent or limit the clogging at the BWRO-plant is to feed it with water from the deep ASRO wells, instead of the older BWRO abstraction well at the fringe of the freshwater body. The ASRO plant can then be used to treat water from shallow ASRO-wells. A boosterpump or a lower production capacity at the BWRO-plant may than be required when feeding, since the

submersible pumps from the ASRO system have a limited capacity. Once this is realized, the BWRO well is abandoned and an up-scaled ASRO-system remains.

5 CONCLUSIONS

The observations at the Westland ASRO site indicate that especially particle clogging may occur during desalination of injected rainwater mixed with brackish groundwater via RO after aquifer storage. Chemical alteration appears to be less relevant for clogging and accompanying RO recovery decrease as a consequence of the complete oxygen consumption and lowering of saturation indices. However, clay mobilization during freshening at the fringe of the injected freshwater body during the injection stage was also observed. Secondly, formation of Fe-colloids upon oxidation of primarily Fe(II) in the aquifer by oxygen in the rainwater seems to occur. Both processes lead to formation of a groundwater type with a high turbidity, especially at the fringe of the injected freshwater body, relatively far (>20 m) from the ASRO wells.

The formation of water with a high-turbidity (i.e. high concentration of particles) appears to be crucial in successfully combining aquifer storage and recovery and reverse osmosis (ASRO). The prevention of RO-membrane clogging by the particles from this water type is a key element for the future success of ASRO. This study shows that the location of the abstraction of mixed rainwater / brackish groundwater is a critical aspect: the worst water type will be abstracted in the upper part of the aquifer at the fringe of the injected freshwater body when an aquifer storage transfer and recovery (ASTR) strategy is applied. (at the Westland demosite: the abstraction at the existing BWRO well). This led to a 50% reduction of the RO-performance in approximately two months due to the formation of a cake layer on the membrane surface. A more suitable water type fed the ASRO-plant and was abstracted from below the centre of the freshwater body, like it was designed at the Westland ASRO-system. Here, no performance reduction was observed. This set-up simultaneously improved the direct recovery of freshwater via shallow wells of the MPPW, as planned (Part I).

A relevant question is whether the mobilized particles have the chance of reaching the ASRO abstraction well, for instance after prolonged recovery or when an increased abstraction rate at the ASRO well is applied. Means to reduce the particle mobilization and/or prevent subsequent the particle clogging observed at the BWRO-plant were evaluated. One approach is to prevent colloid mobilization via addition of Ca^{2+} to the first injection water (in-situ treatment). This has been successfully applied elsewhere to reduce clay mobilization due to rapid exchange of Na for Ca during freshening, after which the rainwater can safely flush the aquifer. It may also limit the formation of Fe-colloids as a result of the faster removal of adsorbed Fe around the ASR well by cation exchange. This aspect needs to be investigated further, however, as pre-flushing the aquifer can bring significant costs. Another option is to remove the suspended particles from the abstracted water prior to feeding the membranes (ex-situ treatment). This may, however, lead to a higher operational complexity and higher costs. Regular flushing of the BWRO-membranes is a low-cost solution and its efficiency will be tested in 2016.

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