DANMARKS OG GRØNLANDS GEOLOGISKE UNDERSØGELSE RAPPORT 2015/93

Water4Coast

Evaluation of water quality issues before application of managed aquifer recharge in a coastal chalk aquifer

Klaus Hinsby, Anders R. Johnsen, Sebastian R. Sørensen
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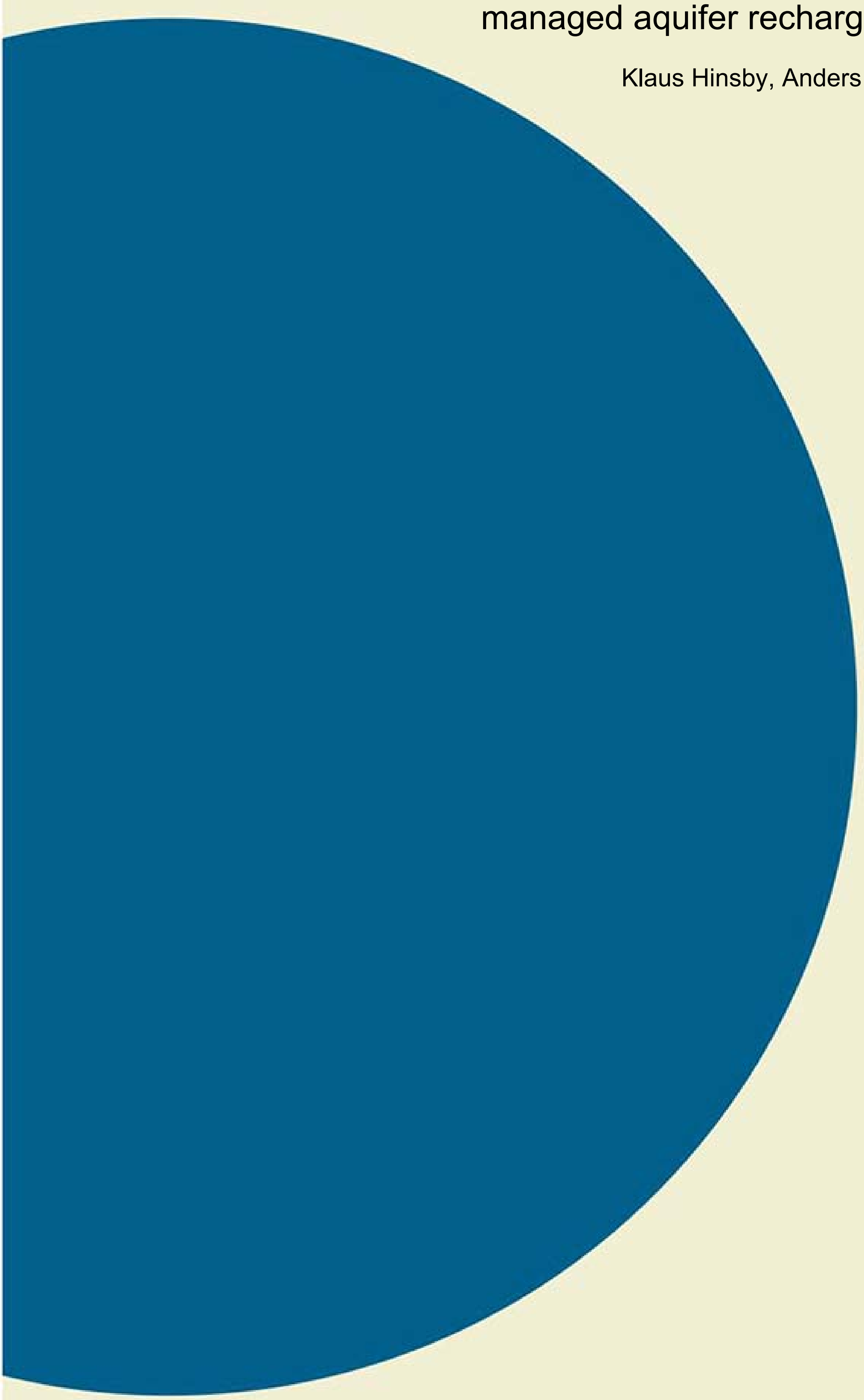

GEOLOGICAL SURVEY OF DENMARK AND GREENLAND
DANISH MINISTRY OF CLIMATE, ENERGY AND BUILDING

GEUS

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1. Summary

This report is one out of three reports assessing the potential for application of managed aquifer recharge to control salt water intrusion on the Southern part of the Falster Island, Denmark. The two other reports by Rasmussen et al., 2015 and Hinsby et al. 2015 consider the model simulations of injection into the Chalk aquifer and efficient data acquisition, transfer and management for the development of advanced Supervisory Control and Data Acquisition (SCADA) systems, respectively. This report considers water quality issues related to aquifer storage and recovery e.g. by using either groundwater or treated surface water (drainage water) for e.g. injection during the wet wintertime and retrieval again in the dryer summer period in order to reduce and control salt water intrusion in the region and protect subsurface drinking water resources. The report evaluates the risks of using aerobic and anaerobic groundwater as well as aerobic drainage water for injection into the Chalk aquifer.

It is concluded that anaerobic groundwater from the water works connected pipelines may be used for injection without any treatment. Analyses from all the water supply wells show that they generally contain very similar anaerobic groundwater older than 75 years without any measurable human impact or contamination. Hence, this water type can be infiltrated without initiating problematic geochemical reactions and jeopardizing the quality of the high quality groundwater in the Chalk aquifer.

In contrast the drainage waters in the drainage canals contain elevated concentrations of both pesticides (MCPA-), industrial chemicals (PFOS), and at one point also high numbers of faecal bacteria (E.coli). Furthermore, a wide range of pharmaceuticals used for a variety of diseases have been found in rather high concentrations in the effluent from a waste water treatment plant discharging to the drainage canal. Hence, if these waters have to be used for injection, strict quality control and/or an intensive treatment and dilution e.g. with pristine groundwater pumped from the Chalk aquifer, will be required to ensure that contamination is not introduced at unacceptable levels into the pristine high quality groundwater of the Chalk aquifer in the area.

Furthermore, the injection of aerobic water containing oxygen and/or nitrate into the anaerobic groundwater will induce oxidation of reduced minerals (Iron sulphides) and organic matter, which may lead to on one hand both technical problems with clogging of wells screens by iron oxides and water quality issues with elevated concentrations of some trace elements and metals, but on the other hand also positive side effects such as removal of nitrate in the subsurface and reduced nitrogen loadings to the coastal waters of the western Baltic Sea.

The results from the preliminary investigations and assessments clearly show that further investigations of the geochemistry and the hydraulics of the Chalk aquifer are required in order to better assess positive and negative effects and the feasibility of injecting anaerobic groundwater or treated aerobic drainage water into the fractured Chalk aquifer to protect subsurface water resources used for water supply on Southern Falster.

2. Background

Coastal aquifers are affected by saltwater intrusion globally, and have been under pressure for many decades especially in densely populated areas with significant groundwater abstraction for water supply (Post and Abarca, 2010; Hinsby et al., 2011, da Silva and Montenegro, 2012). Such problems are especially known and managed (controlled) in aquifer systems along coastlines of U.S.A. and Northern Spain (Sheahan, 1977; Iribar et al., 1997; Misut and Voss, 2007; Custodio, 2010), but problems appear in an increasing number of coastal aquifers in different climate zones, globally, including many coastal aquifers in northeastern Brazil (Bocanegra et al, 2010; da Silva et al., 2010) , China (Wu et al., 1993; Xue et al., 2000, Liu et al., 2001; Han et al., 2011) and Denmark (Andersen et al., 2005; Jørgensen et al, 2008; 2012, Thorn, 2011; Rasmussen et al., 2013), and measures need to be implemented in order to ensure freshwater supplies in these regions in the future.

Climate change is projected to affect precipitation patterns and increase sea levels globally and thereby increasing the risk of saltwater intrusion and deterioration of coastal water resources (Kundzewicz et al., 2007; Hinsby et al., 2011; Loaiciga et al., 2012). Although the extend of the saltwater intrusion highly depends on the geological setting (Werner and Simmons, 2009; Chang et al. 2011), and also may stem from other sources than recent seawater such as old connate waters in former marine sediments (Buckley et al., 2001; Bonnesen et al., 2009; Tran et al., 2012) and even may include highly saline brines (Xue et al., 2000; Han et al., 2011). Especially low-lying areas and areas that receive less precipitation, and experience falling water tables, will be under severe pressure (Essink et al., 2010).

Hence, salt water intrusion due to climate change, sea level rise and increasing demands Is becoming an increasing challenge for many water supply companies in coastal regions, globally, and calls for the development of new adaptive and innovative solutions to prevent salt water intrusion, monitor the development and ensure sustainable and high quality water supply in the future (Essink, 2001; Post, 2005; Post and Abarca, 2010; Hinsby et al., 2011, Thorn and Mortensen, 2012; Sulzbacher et al., 2012, Rasmussen et al., 2013). Managed aquifer recharge through basins in phreatic aquifers or injection wells in artesian aquifers are both possible solutions, which have been applied and operated at large scales for decades mainly around large cities such as Los Angeles (since the early 1950's) (http://dpw.lacounty.gov/wrd/barriers/historical.cfm), and Barcelona; where treated wastewater are injected to avoid saltwater intrusion and ensure water supply for the city (Hernandez et al., 2011). Freshwater injection and aquifer storage and recovery is furthermore considered for emergency water supply of New York City (Misut and Voss, 2007). It is foreseen that managed aquifer recharge will be a cost-efficient way to protect water resources globally in the future (Megdal and Dillon, 2014).

Besides the salt water intrusion problem coastal catchments often face other important problems that are expected to become more severe due to climate change and its impact on the hydrological cycle, water tables and sea level.

The problems vary between regions and climatological settings, but include:

1) Increased flooding risks (Sonnenborg et al., 2012),
2) Increased nutrient loadings to rivers, lakes and coastal marine waters in wet temperate regions (Hinsby et al., 2008, 2012; Sonnenborg et al., 2012; Wikner and Andersson, 2012)
3) Droughts, overabstraction and declining water tables in arid and semi-arid regions (Ragab and Prudhomme, 2002; Montenegro and Ragab, 2012), which in some regions lead to severe land subsidence, a phenomenon known or antipicated for many overabstracted aquifers around the world including Europe (e.g. Boni et al., 2015; Ruiz-Constan et al, 2016), Brazil (e.g. dos Santos et al., 2012) and China (eg. Wu et al., 2010; Shi et al, 2016).

Re 1) The study area on Southern Falster have experienced several floods from rising groundwater tables and drainage canals during the past 10 years. The latest significant flood in 2011 resulted in the broadening of the North canal by up to 50 % along several kilometers as a meaure to more efficiently handle and discharge excess precipitation to the coastal waters via the drainage canals. The extension of the drainage canals are believed to efficiently control and avoid future floods in the area, but injection of drainage waters directly to the Chalk aquifer could support the drainage system and decrease the risk of flooding even further.

Re 2) Nitrogen loadings to ecosystems and resulting effects is currently considered to be one of the most severe environmental problems on a global scale (Steffen et al. 2015) by e.g. increasing the risk of eutrophication, harmful algal blooms, hypoxia, fish kills and acidification in many coastal waters (Diaz and Rosenberg, 2008; Rabalais et al., 2009; O´Neill et al., 2011; Paerl and Paul, 2012) including coastal waters in Brazil, China and Denmark (Diaz and Rosenberg, 2008; Cai et al., 2011; Hinsby et al., 2012).

The Baltic Sea and it’s coastal waters most probably exhibits the largest problems at present with oxygen depletion and hypoxia due to excessive nutrient loading, even in a global perspective (Diaz and Rosenberg, 2008; Conley, 2012). Partly for that reason the status of the major part of shallow oxic groundwater in Denmark (located in the Western Baltic Sea) is of poor status and does not comply with EU directives as groundwater threshold values for total nitrogen (“nitrate”), which have been established according to the EU Water Framework and Groundwater Directives to protect associated aquatic ecosystems, are breached (Hinsby et al., 2008, 2012). This puts a strong pressure on Denmark to reduce nutrient loadings to coastal waters in Denmark and the Western Baltic Sea, and to find new innovative and cost-efficient ways for this purpose. The coastal waters of Falster is currently not considered to receive excess loadings of nutrients, but considering the general status of the Baltic Sea, and the increasing pressure and vulnerability of the Baltic Sea and coastal waters in general due to climate change (O’Neill et al., 2011), it is worth exploring measures to decrease nutrient loadings from agricultural catchments to coastal waters.

Re 3) Overabstraction and land subsidence is not an issue of concern on Southern Falster. Hence, MAR will not be studied as a means of avoiding or reducing land subsidence. However, it is worth noticing that MAR is relevant for mitigating or avoiding land subsidence in other coastal aquifers around the world, and in the longer perspective it may also be relevant for other coastal aquifers in Denmark.

3. Introduction

The WATER4COASTS project seeks to assess, test and developed new and efficient solutions for integrated, sustainable and adaptive management of groundwater and surface water that take into account both surface and subsurface water quantity and quality aspects and the protection of water resources and ecosystems in coastal regions. By injecting water from other water supply wells with lower salinity or waste water treatment plants and drainage canals into for instance artesian anaerobic aquifers by managed aquifer recharge the hydraulic pressure increase and reduce the risk of saltwater intrusion (Misut and Voss, 2007; Hernandez et al., 2011).

Furthermore, any nitrate in the injected water and the stage in drainage canals are reduced, and hence the risk of eutrophication and flooding.

The main objective of WATER4COASTS is to develop and demonstrate new efficient tools for sustainable and adaptive water management in coastal aquifers and catchments based on artificial recharge to coastal aquifers to ensure good status of water resources and coastal ecosystems in order to:

1) Prevent salt water intrusion towards coastal well fields
2) Reduce nitrogen loads from coastal catchments to marine waters
3) Reduce the risk of flooding in the hinterland from e.g. drainage canals and Groundwater and
4) Develop efficient monitoring systems

This report describes the current organic (incl. pathogens) and inorganic quality of groundwater, drainage and waste water, discuss the treatment needs before injection of oxic drainage water into an anoxic confined chalk aquifer, and negative and positive effects and the cost-efficiency of different potential water treatment technologies.

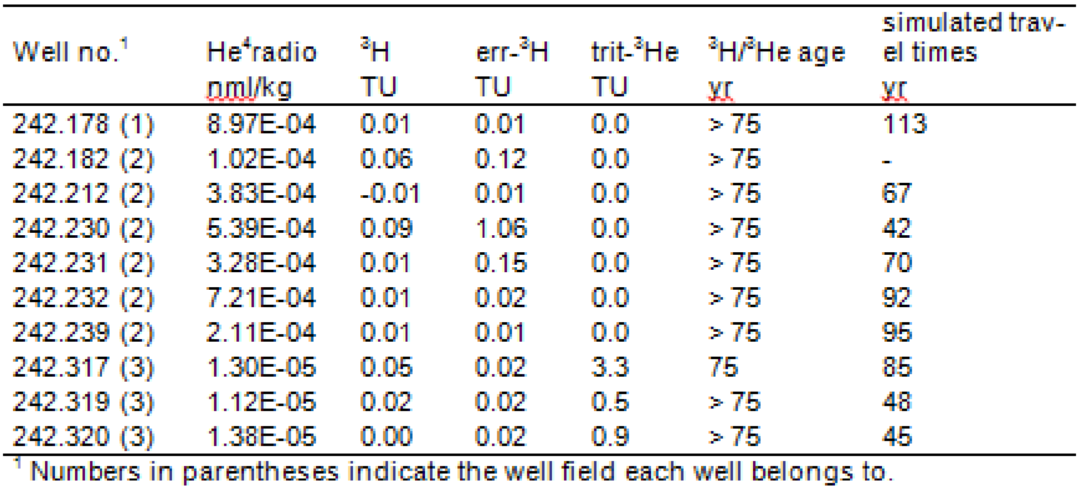
As described in the background section (section 2) and indicated above MAR may be a relevant measure for mitigating different types of negative climate change impacts on water resources, ecosystems and the built environment in coastal regions. For the case of Southern Falster it is the protection of the coastal groundwater resources against both lateral salt water intrusion from the Baltic Sea and vertical salt water intrusion from old seawater in the deeper part of the Chalk aquifer, which is the main concern, and hence will be the main focus and topic for this and future studies on the protection of water resources on Southern Falster.

4. Water quality assessment

4.1 Groundwater quality and age

Analyses of groundwater sampled in water supply wells of the Marielyst Water Works show that the sampled groundwater in the Chalk aquifer are relatively old (> 75 yr) as they contain no Tritium (^{3}H) and no tritiogenic Helium (trit-^{3}He, table 4.1) as described in Rasmussen et al. (2013). In accordance with this no other human impacts and contamination are found in the Chalk aquifer in the national groundwater monitoring program as expected (Hinsby et al., 2001).

Table 4.1. Measured 3H/3He values and estimated 3H/3He groundwater ages in water supply wells of Marielyst waterworks compared to model simulated travel times.



Well no.[1]	He^{4}radio	^{3}H	err-^{3}H	trit-^{3}He	^{3}H/^{3}He age	simulated travel times
	nml/kg	TU	TU	TU	yr	yr
242.178 (1)	8.97E-04	0.01	0.01	0.0	> 75	113
242.182 (2)	1.02E-04	0.06	0.12	0.0	> 75	-
242.212 (2)	3.83E-04	-0.01	0.01	0.0	> 75	67
242.230 (2)	5.39E-04	0.09	1.06	0.0	> 75	42
242.231 (2)	3.28E-04	0.01	0.15	0.0	> 75	70
242.232 (2)	7.21E-04	0.01	0.02	0.0	> 75	92
242.239 (2)	2.11E-04	0.01	0.01	0.0	> 75	95
242.317 (3)	1.30E-05	0.05	0.02	3.3	75	85
242.319 (3)	1.12E-05	0.02	0.02	0.5	> 75	48
242.320 (3)	1.38E-05	0.00	0.02	0.9	> 75	45

[1] Numbers in parentheses indicate the well field each well belongs to.

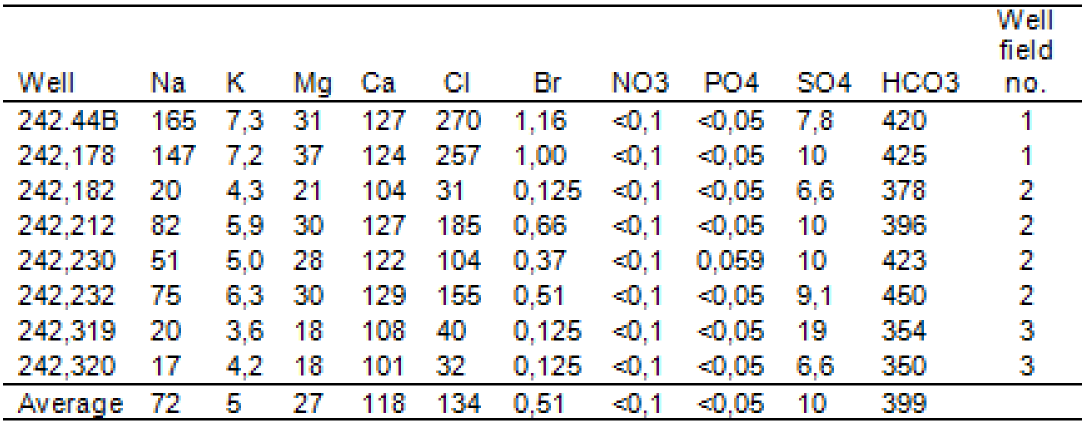
Hence, the only known groundwater quality issue in the Chalk aquifer is elevated chloride concentrations due to salt water intrusion from three natural sources (marine Holocene sediments, fossil seawater in the deeper part of the Chalk, the Baltic Sea), which have increased due to water abstraction for water supply and drainage pumping. This result in increasing salt (chloride) concentrations in water supply wells to an extent where the chloride concentrations have breached the WHO and EU drinking water standard of 250 mg/L in two water supply wells (242.44B and 242.178) in well field one closest to the Baltic Sea (Table 4.2, Figure 4.1, Rasmussen et al., 2013).

If it is ensured that groundwater in the pipelines of the water supply company does not contain groundwater with chloride concentrations above 250 mg/l and it is anaerobic (groundwater from the Chalk aquifer is anaerobic i.e. with oxygen and nitrate concentrations below detection limits) groundwater can be re-injected into the aquifer by managed aquifer recharge without any concern of salinization, pollution or problematic reactions in the aquifer around the injection well.

Continuous pumping from the water supply wells and the drainage canals will result in continuously increasing chloride concentrations unless effective countermeasures such as subsurface water solutions that include managed aquifer recharge e.g. in combination with remediation pumping are introduced. Such solutions have shown promising results in e.g. the Netherlands (Zuurbier, et al., 2014, 2015).

Recharge of groundwater by injection of anaerobic fresh groundwater into more saline groundwater wells during the rainy winter season e.g. using the ASR coastal solution (Zuurbier et al., 2014) to sustain continuous abstraction of freshwater in Marielyst on Southern Falster seems to be a potential and highly relevant solution for the protection of the coastal water resources in the area.

Table 4.2. Concentrations of major cations and anions in groundwater samples collected from water supply wells of Marielyst water works. The water supply wells of well field 1 is located closest to the Baltic sea coast line have the highest chloride (Cl) concentrations breaching the WHO and EU drinking water standard of 250 mg/l.(well 242.44b and 242.178). Unit = mg/l.



Well	Na	K	Mg	Ca	Cl	Br	NO3	PO4	SO4	HCO3	Well field no.
242.44B	165	7,3	31	127	270	1,16	<0,1	<0,05	7,8	420	1
242,178	147	7,2	37	124	257	1,00	<0,1	<0,05	10	425	1
242,182	20	4,3	21	104	31	0,125	<0,1	<0,05	6,6	378	2
242,212	82	5,9	30	127	185	0,66	<0,1	<0,05	10	396	2
242,230	51	5,0	28	122	104	0,37	<0,1	0,059	10	423	2
242,232	75	6,3	30	129	155	0,51	<0,1	<0,05	9,1	450	2
242,319	20	3,6	18	108	40	0,125	<0,1	<0,05	19	354	3
242,320	17	4,2	18	101	32	0,125	<0,1	<0,05	6,6	350	3
Average	72	5	27	118	134	0,51	<0,1	<0,05	10	399	

4.2 Drainage water and discharge from waste water treatment plant (WWTP)

Water from drainage canals draining the area and ensuring dry farm lands and summer housing areas would be another source for injection waters to control salt water intrusion. A study on the quality of these was therefore conducted in order to assess the need for water treatment of the drainage waters before these are injected.

The studies on the quality of the drainage waters in drain canals and pipes focused on the area between the most upstream sampling site W4C-3 located approximately 100 m upstream the waste water treatment plant (WWTP) andW4C-6 located approximately 150 m upstream the pumping station. All sampling sites are located between well field two and three of the water works (Figure 4.1). This part of the drainage system seems to be the most relevant potential source for injection into the groundwater system after required treatment. If water for injection was collected upstream the WWTP it would contain less pharmaceutical contaminants, but it would then reduce the flow in the canal at the WWTP and hence reduce the dilution of the contaminants from the WWPT. Using waters from the canal between the WWTP and the pumping station for injection is therefore considered the best option as long as the water is treated properly and it is ensured that only pure water is injected into the pristine high quality groundwater of the Chalk aquifer.

4.2.1 Drainage canal and WWTP sampling sites.

For the chemical analyses, we sampled water from Marrebæk Kanal (or the “North Canal”), a canal that drains an agricultural area west of the town of Marielyst (Fig. 1). The elevation of the water surface in the canal is typically 1-2 meters below sea level. The canal receives water from smaller side canals and drain pipes that drains the agricultural fields, and from the discharge of water from Marielyst Waste Water Treatment Plant (WWTP). The water in the main drainage canal runs in the direction from the WWTP (north-east) towards the pumping station (south-west). The upstream part of the canal is on the fringe of the town and therefore might also receive some water directly from private housings, either as run off or as non-intentional leaching.

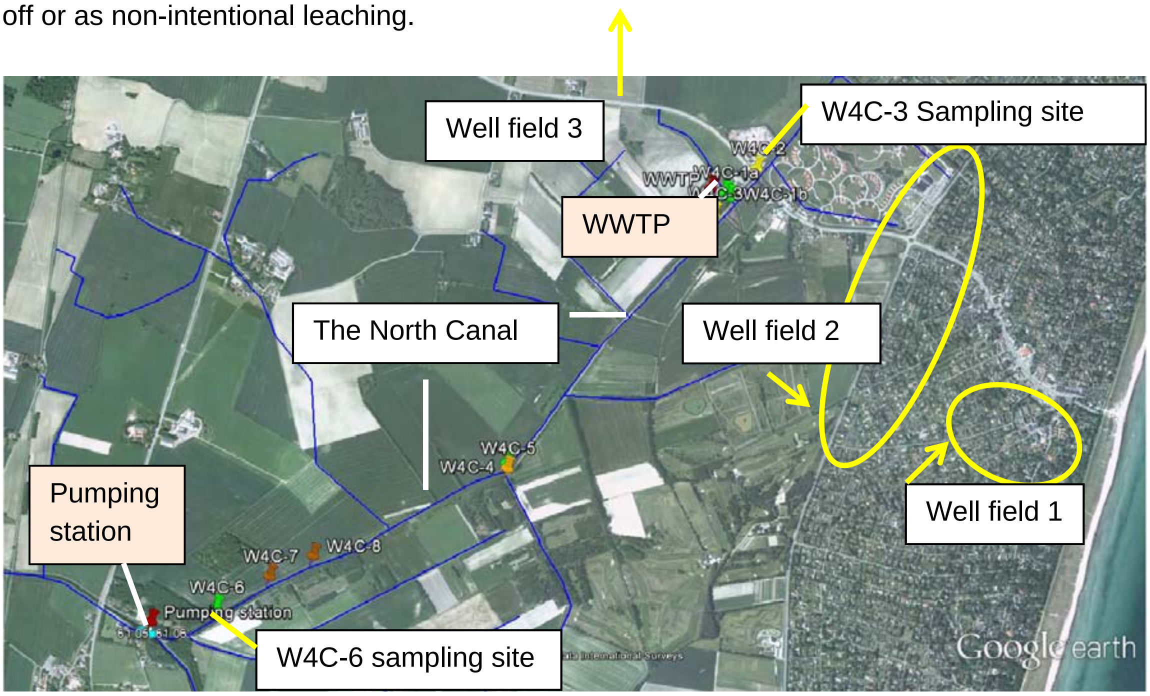


Fig. 4.1. **Overview of the Marrebæk Kanal and the positions where water was sampled for chemical and microbial analyses.**

The town of Marielyst is a center for tourism with a permanent population of approximately 700 persons. During the summer months, however, the population may approach 50.000 persons. This means that the treatment plant during the dry summer months may provide a significant proportion of the water in the drainage canal. The use of pesticides, chemicals and pharmaceuticals may vary over the year. Two sampling times therefore does not give a full screening of the composition of the water, but should rather be seen a snapshot examples of types and levels of compounds that may be present in the water. The two sampling dates were chosen so that they represented a spring scenario with a small population (24.04.2013) as well as a summer scenario with tourists (14.08.2013).

To cover most sources of pollution, we sampled water both from the main canal, from a side canal, from tile drains and directly from the outlet of the WWTP. All samples were sampled directly into flasks provided by the analytical laboratories and treated as recommended by these laboratories with respect to storage and transport. Samples were collected from below the surface of the canal to avoid the surface slick and always upstream of the person who carried out the sampling. Four types of analyses were applied to the samples: content of industrial chemicals, content of pharmaceutical compounds, content of pesticides and content of faecal bacteria. Chemical analyses were carried out by Eurofins, whereas the microbial analyses were done by Amphe-Bac Aps. The samples were prioritized so that the most expensive analyses were carried out only for the most important samples. The locations of the sampling sites and the specific analyses were as follows:

W4C-1: Samples taken directly in the discharge pipe from the wastewater treatment plant, analysed for industrial chemicals, pharmaceutical compounds and faecal bacteria.
W4C-2: Main drainage canal approximately 80 meters downstream of the waste water treatment plant, analysed for pesticides and faecal bacteria.
W4C-3: Main drainage canal approximately 100 meters upstream of the waste water treatment plant, analysed for faecal bacteria.
W4C-4: Main drainage canal downstream of the waste water treatment plant half way to the pumping station , analysed for industrial chemicals and faecal bacteria.
W4C-5: A small side-canal approximately 10 meters downstream of W4C-4, the canal receives water only from agricultural land, analysed for pesticides and faecal bacteria.
W4C-6. Main drainage canal 150 meters upstream of the pumping station, analysed for pesticides and faecal bacteria.
W4C-7: Samples taken directly in a mall drain pipe 400 meters upstream of the pumping station, analysed for faecal bacteria.
W4C- 8: Samples taken directly in a large drain pipe 600 meters upstream of the pumping station, analysed for faecal bacteria.

The results from the different sites and analyses are provided in the following sections.

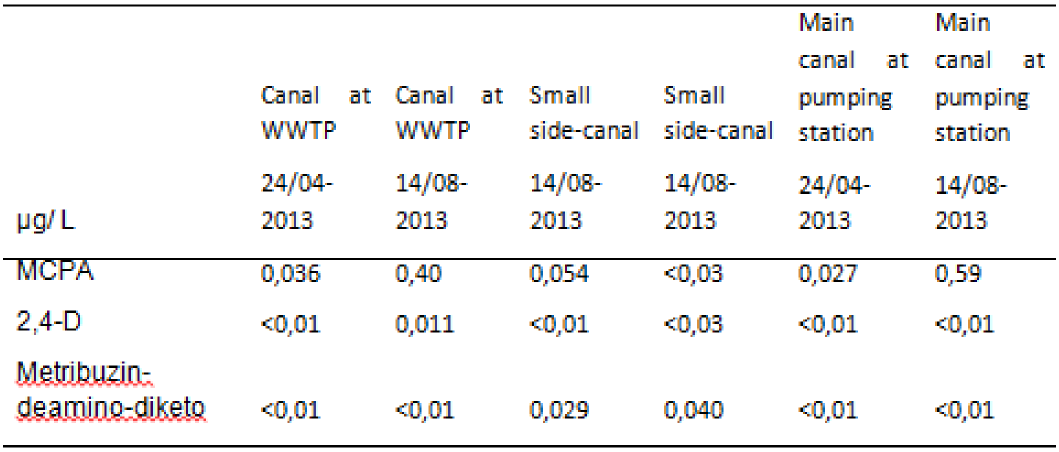
4.2.2 Pesticides in drainage water

Many different pesticides have been used over the years in Denmark in agriculture and private households. It was therefore important to prioritize which pesticides to look for since the economy did not allow an extensive screening for a large number of compounds. We therefore selected the prioritized pesticides on the basis of results from the Danish Pesticide Leaching Assessment Program (Brüsh et al., 2012) and the Danish Groundwater Monitoring Program (Thorling et al., 2012), i.e., we analysed for many of the compounds that are most likely to leach from agricultural fields.

The prioritized pesticides covered one fungicide (Fenpropimorph), one insecticide (Pirimicarb) and 12 herbicides (2,4-D; Atrazine; Bentazon; Bromoxynil; Ethofumesat; Fluazifop-P-butyl; Ioxynil; MCPA; Metamitron; Metribuzine; Propyzamide; Terbutylazine) and 7 herbicide degradation products (2-hydroxy-terbutylazine; Deethyl-atrazine; Deethyl-terbutylazine; Deisopropyl-atrazine; Metribuzine-deamino; Metribuzine-deamino-diketo; Metribuzine-diketo).

Two phenoxyalcanoic acid herbicides (MCPA and 2,4-D) and one degradation product (metribuzin-deamino-diketo) was detected (table xx). MCPA was found both upstream (W4C-2) and downstream (W4C-6) in the main canal and in the spring sample also in the small side canal. The MCPA concentrations in the main canal in the summer samples exceeded the drinking water threshold limit with 400% at the upstream location and 600% at the downstream location. 2,4-D was found only upstream and only in the summer sample. MCPA and 2,4-D are marketed both for agricultural use and for private use on lawns; the sources therefore may be both leaching from the agricultural fields and from the private gardens upstream of the waste water treatment plant. Metribuzin, on the other hand, has only been approved for use on potato fields in Denmark. The presence of the metribuzin degradation product metribuzin-deamino-diketo in water from the small side canal (W4C-5) at both sampling times, suggests leaching from potato fields in the area drained by the side canal.

Table 4.3. Pesticides detected in water samples from the main canal and a side-canal (analysed by Eurofins).



µg/ L	Canal at WWTP 24/04-2013	Canal at WWTP 14/08-2013	Small side-canal 14/08-2013	Small side-canal 14/08-2013	Main canal at pumping station 24/04-2013	Main canal at pumping station 14/08-2013
MCPA	0,036	0,40	0,054	<0,03	0,027	0,59
2,4-D	<0,01	0,011	<0,01	<0,03	<0,01	<0,01
Metribuzin-deamino-diketo	<0,01	<0,01	0,029	0,040	<0,01	<0,01

4.2.3 Industrial chemicals in effluent from WWTP and drainage water

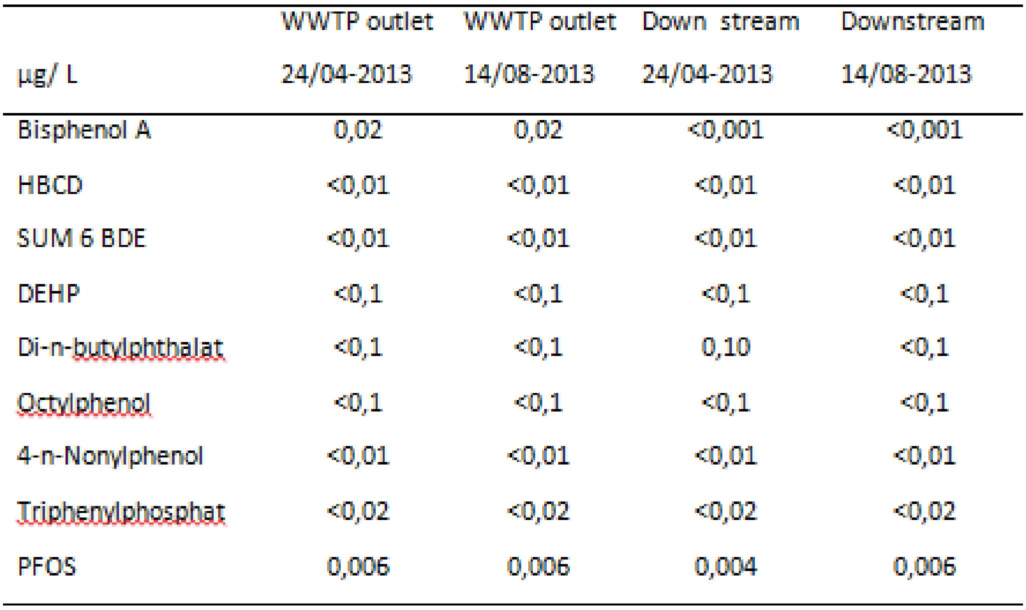
The major waste water treatment plants in the Copenhagen area have carried out a large screening of industrial and pharmaceutical compounds in the discharge water and in sludge (Madsen 2011). A number of focus compounds have been selected as important compounds to monitor since these compounds exceeded the acceptable environmental quality standards (EQS) for surface waters. We screened discharge water from the Marielyst WWTP (W4C-1) and water from the canal half way to the pumping station (W4C-4) for the presence of these industrial focus chemicals (Table 4.3) and compared the levels with EQS limits. It should be noted that most of the EQSs reported below are annual averages for rivers and lakes, not maximum concentrations. This parameter was chosen since we cannot calculate reliable averages from only two time points. Annual average EQSs for other inland waters are often lower than the values for rivers and lakes whereas EQSs for maximum allowed concentrations typically are higher.

Only three of the chemicals were detected, bisphenol A, butylphthalate and PFOS (perfluoroctansulfonsyre). Bisphenol A exhibits hormone-like properties and is used in the manufacture of epoxy resins, some types of plastic and in the lining of food cans. Bisphenol A was detected only in the discharge water from the treatment plant, but it was not detectable half way downstream the canal which suggest degradation, sorption or high dilution of the compound in the canal. The national EQS for bisphenol A is 0,1 for inland waters (Miljøministeriet, 2010) which was not exceeded in the treatment plant discharge. Di(2-ethylhexyl) phthalate (DEHP) is the most common phthalate that is used as plasticizers. We did not detect DEHP in any sample, but we did detect another phthalate plasticizer dibutylphthalate in one sample from the canal, but at a concentration of 0,10 µg/L which is below the inland waters EQS of 2,3 µg/L (Miljøministeriet, 2010) .

PFOS is a representative of a large group of surface active perfluorinated compounds that are used in firefighting foam and in textile impregnation products. PFOS is persistent, bioaccumulative and toxic to mammals including humans (OECD 2012). The PFOS concentrations were low, but the compound was detected in all four samples which raises some concern. The EQS for PFOS is 0,00013 µg/L (Madsen 2012) indicating that the acceptable level was exceeded by 60 fold in the treatment plant discharge and by 40-60 fold in the canal water half way to the pumping station. This means that extensive degradation or dilution would be needed to meet environmentally acceptable concentrations.

Octylphenol and 4-n-nonylphenol are examples of alkylphenols that are used as precusors for example in the synthesis of detergents. None of them were detected. Hexabromocyclododecane (HBCD or HBCDD) and brominated diphenyl ethers (BDE) are brominated flame retardants whereas triphenylphosphat (TPP) is an organo-phosphate flame retardant which is also used in lubricants. None of the flame retardants were detected, but the quantification limit of HBCD and BDE were above their EQS.

Table 4.4. Content of industrial focus chemicals in discharge water from Marielyst waste water treatment plant (analysed by Eurofins).

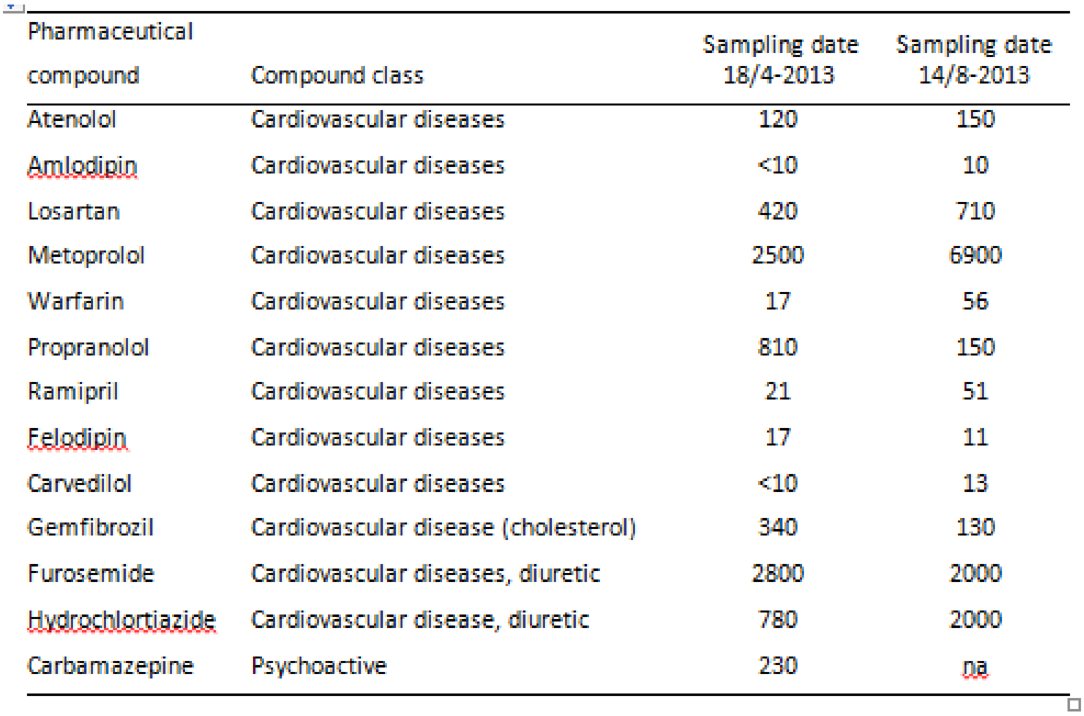


µg/ L	WWTP outlet 24/04-2013	WWTP outlet 14/08-2013	Down stream 24/04-2013	Downstream 14/08-2013
Bisphenol A	0,02	0,02	<0,001	<0,001
HBCD	<0,01	<0,01	<0,01	<0,01
SUM 6 BDE	<0,01	<0,01	<0,01	<0,01
DEHP	<0,1	<0,1	<0,1	<0,1
Di-n-butylphthalat	<0,1	<0,1	0,10	<0,1
Octylphenol	<0,1	<0,1	<0,1	<0,1
4-n-Nonylphenol	<0,01	<0,01	<0,01	<0,01
Triphenylphosphat	<0,02	<0,02	<0,02	<0,02
PFOS	0,006	0,006	0,004	0,006

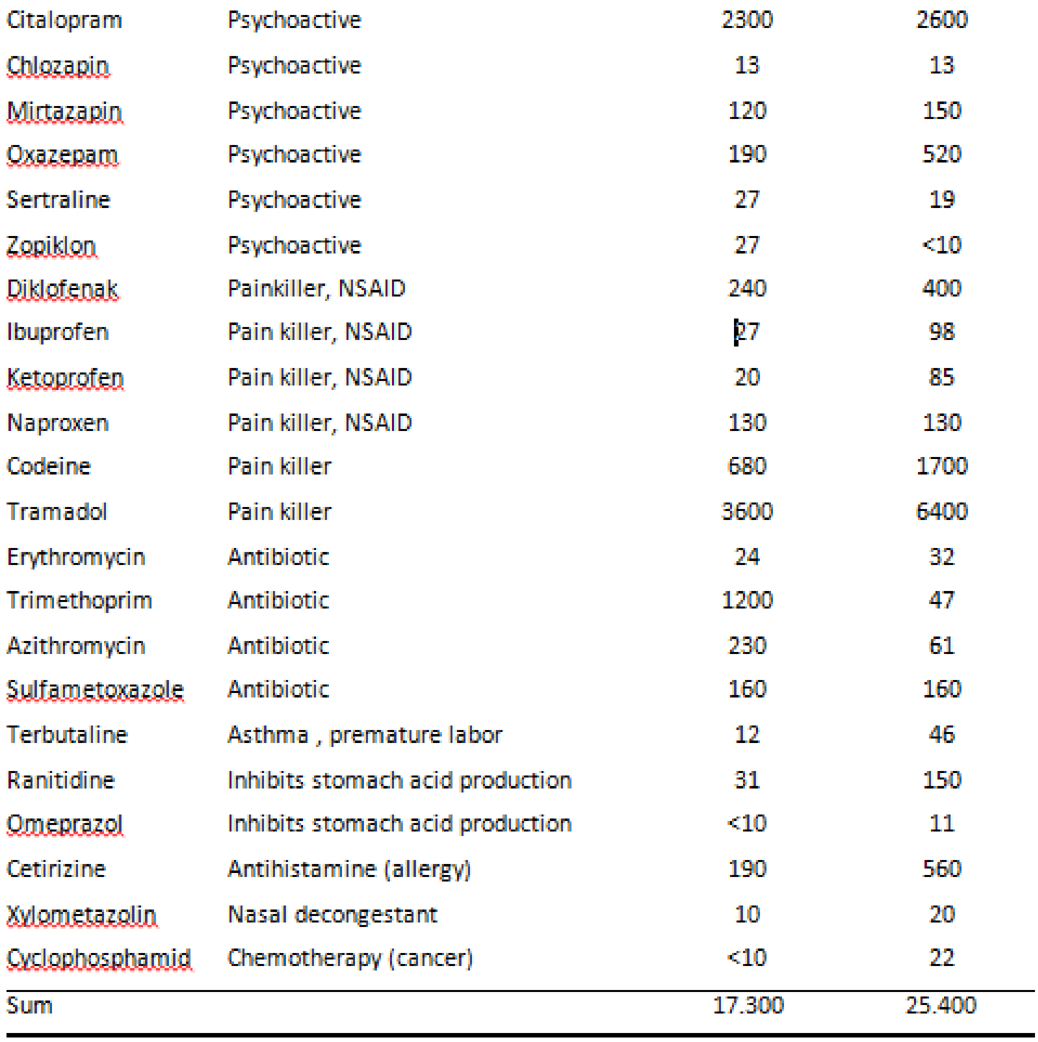
4.2.4 Pharmaceuticals in effluent from WWTP and drainage canal

We screened water from the outlet of the Marielyst WWTP (W4C-1) for the presence of pharmaceutical compounds since pharmaceuticals in high concentrations have been reported to be present in Danish wastewater after waste water treatment (Madsen 2012). Samples taken directly from the WWTP discharge pipe were analysed for the following 93 pharmaceutical compounds: Amilorid, Amiodaron, Amlodipin, Atenolol, Atorvastatin, Azithromycin, Bendroflumetiazid, Bromhexin, Bromokriptin, Budesonid, Cefuroxim, Cetirizine, Ciprofloxacin, Citalopram, Cyklofosfamid, Desloratadin, Dextropropoxifen, Diazepam, Diklofenak, Enalapril , Enrofloxacin, Erytromycin, Etinylöstradiol, Febantel, Felodipin, Fentanyl, Flunitrazepam, Fluoxetin, Fluvastatin, Fluvoxamin, Furosemid, Gemfibrozil, Glibenklamid, Hydroklortiazid, Hydrokortison, Ibuprofen, Ifosfamid, Ipratropium, Isosorbidmononitrat, Karbamazepin, Karvedilol, Ketokonazol, Ketoprofen, Klozapin, Kodein, Lansoprazol, Loratadin, Losartan, Metoprolol, Metronidazol, Mianserin, Mirtazapin, Mometasonfuroat, Naproxen, Nelfinavir, Nitenpyram, Noretisteron, Norfloxacin, Norgestrel, Ofloxacin, Omeprazol, Oxazepam, Oximetazolin, Oxitetracyklin, Paracetamol, Paroxetin , Prazikvantel, Prednisolon, Propranolol, Pyrantel, Raloxifen, Ramipril, Ranitidin, Risperidon, Salbutamol (=Albuterol), Salmeterol, Sertralin, Simvastatin, Sulfametoxazol, Tamoxifen, Terbutalin, Tetracyklin, Tioridazin, Tramadol, Trimetoprim, Tylosin, Warfarin, Xylometazolin, Zolpidem, Zopiklon, Oestradiol, Oestriol, Oestron.

Table 4.5. Pharmaceutical compounds (µg/l) detected in discharge water from Marielyst waste water treatment plant (analysed by Eurofins).



Pharmaceutical compound	Compound class	Sampling date 18/4-2013	Sampling date 14/8-2013
Atenolol	Cardiovascular diseases	120	150
Amlodipin	Cardiovascular diseases	<10	10
Losartan	Cardiovascular diseases	420	710
Metoprolol	Cardiovascular diseases	2500	6900
Warfarin	Cardiovascular diseases	17	56
Propranolol	Cardiovascular diseases	810	150
Ramipril	Cardiovascular diseases	21	51
Felodipin	Cardiovascular diseases	17	11
Carvedilol	Cardiovascular diseases	<10	13
Gemfibrozil	Cardiovascular disease (cholesterol)	340	130
Furosemide	Cardiovascular diseases, diuretic	2800	2000
Hydrochlortiazide	Cardiovascular disease, diuretic	780	2000
Carbamazepine	Psychoactive	230	na



Citalopram	Psychoactive	2300	2600
Chlozapin	Psychoactive	13	13
Mirtazapin	Psychoactive	120	150
Oxazepam	Psychoactive	190	520
Sertraline	Psychoactive	27	19
Zopiklon	Psychoactive	27	<10
Diklofenak	Painkiller, NSAID	240	400
Ibuprofen	Pain killer, NSAID	27	98
Ketoprofen	Pain killer, NSAID	20	85
Naproxen	Pain killer, NSAID	130	130
Codeine	Pain killer	680	1700
Tramadol	Pain killer	3600	6400
Erythromycin	Antibiotic	24	32
Trimethoprim	Antibiotic	1200	47
Azithromycin	Antibiotic	230	61
Sulfametoxazole	Antibiotic	160	160
Terbutaline	Asthma , premature labor	12	46
Ranitidine	Inhibits stomach acid production	31	150
Omeprazol	Inhibits stomach acid production	<10	11
Cetirizine	Antihistamine (allergy)	190	560
Xylometazolin	Nasal decongestant	10	20
Cyclophosphamid	Chemotherapy (cancer)	<10	22
Sum		17.300	25.400

35 out of the 93 compounds were detected above their detection limits. The concentration varied orders of magnitude from close to the detection limit (10 ng/L) to more than 1000 ng/L. The compounds found in highest concentration were associated with cardiovascular disease (furosemide, metropolol, hydrochlortiazide), depression (citalopram), pain relief (codeine, tramadol) and infections (trimethoprim).

EQS values for some of the pharmaceutical focus compounds were reviewed by Madsen et al (2011): dichlofenac 10 ng/L, propranolol 5 ng/L, amiodaron 9 ng/L, ciprofloxacin 5 ng/L, azithromycin 9,4 ng/L, sulfamethoxazol 26,8 ng/L and citalopram 510 ng/L. Some of these compounds were in our study found in concentrations that exceeded the EQS by a factor of up to 40 times (dichlofenac), 162x for propranolol, 24x for azithromycin, 6x for sulfamethoxazol and 5x for citalopram. The focus compounds ciprofloxacin and amiodaron were not detected.

Conclusions

The analysed industrial priority chemicals generally would be of little concern for artificial groundwater injection. One exception was PFOS, which has a very small EQS that was exceeded. PFOS and other perfluorinated chemicals are furthermore resistant to degradation in the environment, which suggests that the surface water in Marrebæk Kanal should either be diluted or treated before injection.

The level of pesticides was generally low, except for MCPA. MCPA is degradable under aerobic condition in most environments and therefore would probably pose a minor risk for aerobic groundwater injection. MCPA, however, might be persistent in many anoxic environments suggesting that aerobic treatment of surface water might be advisable before injection into anoxic aquifers.

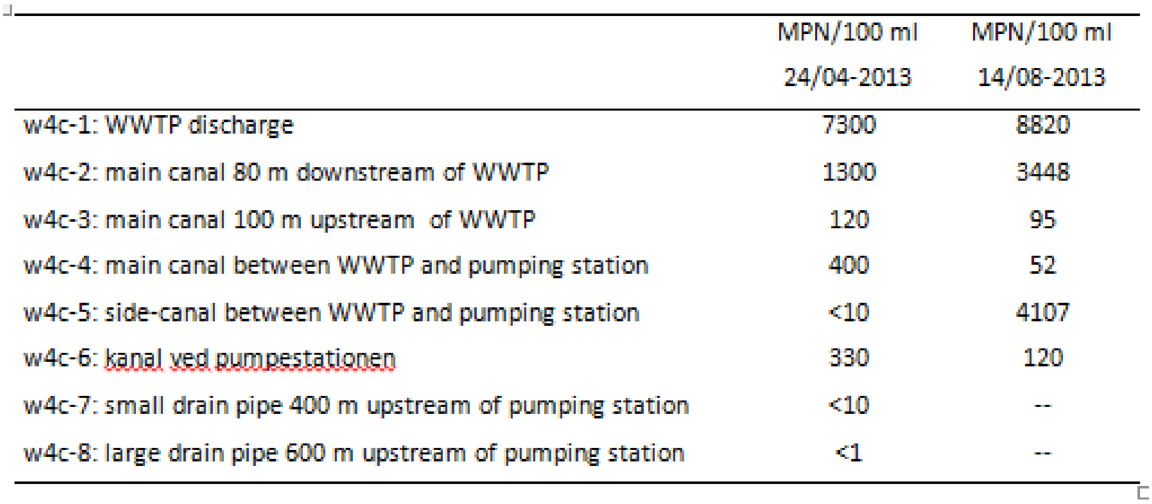
The high load of pharmaceutical compounds in the WWTP discharge (total concentrations of 17,3 µg/L and 25,4 µg/L) is highly problematic. The WWTP is optimized for cleaning the waste water, and still the pharmaceutical compounds are present in the discharge, indicating a low degradability of many of these compounds. Furthermore, much of the water in the drainage canal would during the dry summer months originate from the WWTP resulting in little dilution of the pharmaceutical compounds. Also, these compounds are designed to have an effect in humans. We might be able to estimate the effect of single compounds, but we have little knowledge on possible cocktail effects, that is, the combined effect of the 35 different pharmaceuticals.

4.2.5 Pathogens

E. coli.

Water samples were analysed for the levels of E. coli by the IDEXX Quanti-Tray most probable number (MPN) method. The analyses were carried out by Amphi-Bac Aps. Strains of E. coli are major inhabitant of the gastrointestinal tract in warm-blooded animals; total E coli MPN is thus an indicator of faecal contamination. E coli were detected in highest concentrations in the WWTP discharge followed by lower concentrations 80 meters downstream of the WWTP where the discharge had been mixed with surface water in the canal. In the spring samples, concentrations were further reduced downstream of the WWTP and E. coli were not detectable in water from tile drains or water from the small side-canal. The result was somewhat different for the summer sampling. There was no water running in the tile drains and analyses of these were therefore impossible. The side-canal, however, showed high concentrations (3448 per 100 mL) of E. coli. Aerial photos of the side-canal did not indicate any sources of domestic wastewater. Another source could have been liquid pig manure from the fields. The IDEXX Quanti-Tray was therefore analysed for the presence of the STII gene, which is a specific indicator of E. coli strains from pigs (Khatib 2003). The results were negative indicating that the source was not pigs, but might instead have been cattle or birds. Samples from the main canal upstream of the WWTP surprisingly also showed presence of E. coli which probably originated from domestic waste water leaching into the canal from the houses neighboring the upstream part of the canal. This might either be from leaking sewerage systems or from percolation pipes from septic tanks. For comparison, the EQS defining good quality of inland waters is 1000 E. coli per 100 mL (EU directive, 2006) whereas E. coli is not allowed at all in drinking water.

Table 4.6. Concentration of E. coli in water samples (analyzed by Amphi-Bac APs). MPN: most probable number.



	MPN/100 ml 24/04-2013	MPN/100 ml 14/08-2013
w4c-1: WWTP discharge	7300	8820
w4c-2: main canal 80 m downstream of WWTP	1300	3448
w4c-3: main canal 100 m upstream of WWTP	120	95
w4c-4: main canal between WWTP and pumping station	400	52
w4c-5: side-canal between WWTP and pumping station	<10	4107
w4c-6: kanal ved pumpestationen	330	120
w4c-7: small drain pipe 400 m upstream of pumping station	<10	--
w4c-8: large drain pipe 600 m upstream of pumping station	<1	--

The microbial EQS defining good quality of inland waters is 1000 E. coli per 100 mL (EU directive, 2006). The EQS was exceeded in two samples from the main canal close to the WWTP, but the load was reduced downstream. This suggests that injection of water from the canal would be less problematic with respect to faecal contamination as long as the water would have a retention time in the aquifer that is long enough for faecal microorganisms to be removed. It should be noted, however, that E. coli are not allowed at all in drinking water.

5. Assessment of processes and risks when injecting aerobic water into anaerobic chalk aquifer

The injection of water types (groundwater, surface water or rain water) different from the water types occurring in the aquifer at the injection wells will potentially have negative effects on the water quality at the well and result in water types breaching drinking water standards and/or create technical problems (clogging of screens and pumps of the water supply wells). Preferably the injected water type should be identical or nearly identical to the water type at the well. On the other hand biogeochemical reactions in the aquifer could be a benefit to the aquatic environment if aerobic water with nitrate and/or other contaminants are injected into the aquifer as especially nitrate will be removed efficiently from the injected waters in the anaerobic aquifer by reactions with reduced minerals such as pyrite.

5.1 Inorganic chemistry

A preliminary assessment of the consequences of injection of oxygen and nitrate containing (aerobic) groundwater was therefore conducted as part of the Water4Coasts studies assuming average concentrations of oxygen and nitrate in drainage canal waters and typical contents of pyrite and organic matter in the Chalk aquifer.

As the Chalk aquifer of Southern Falster is impacted by glaciotectonics (the movement of glaciers during the last ice age) as other Chalk deposits in the area e.g. Møns Klint about 50 km northeast of Marielyst clearly demonstrates, significantly affects the area, and as geological logs, borehole flow logs and Geoprobe hydraulic profiling tests also indicate, the hydraulics of the Chalk aquifer is highly varying and complex. Some flow logs indicate dual porosity systems with dominating fracture flow while other flow logs and HPT hydraulic profiles at other locations indicate single porosity behaviour in the region.

It was therefore decided to assess how pyrite in the Chalk would behave and affect water quality in both dual porosity fracture flow and single porosity systems. It should be noted that the behaviour of these two porosity “end-members” is quite different, and that the Chalk aquifer most probably would behave as a mixture of these two systems. Hence it is expected that the properties vary significantly both laterally and vertically i.e. that dual porosity behaviour with fracture flow would be dominant in some areas and at some levels (30 – 80 m below surface?), while single porosity behaviour would be dominant at other locations and depths (< 30 and > 80 m below surface?). At all sites both porosity types may affect the hydraulics significantly depending on the depths. Only very detailed investigations will be able to decide, which of the porosity types dominate at a specific location and depth, and what is the situation at one well most probably will not describe the situation at the next.

In the following sections it is demonstrated how injection of aerobic water types into the anaerobic Chalk aquifer will affect the evolution of the concentrations of some key inorganic hydrochemical parameters dissolved in groundwater.

The first model, “Advective flow” described in section 6.1.1 on the following page is for Darcy flow with pyrite homogeneous distributed in the sediment. The second “Stagnant zone” model described in section 6.1.2 is for a heterogeneous flow system like dual porosity Chalk with hydraulic active fractures. The models are designed to be conceptual to illustrate the characteristic properties and differences between the systems.

Both models are for a breakthrough in a borehole with the filter at 20 m depth.
In both models there is Pyrite in the sediment to reduce the incoming oxygen and nitrate of the injected aerobic water type e.g. representing drainage water of the North Canal in the investigated area.

5.1.1 Simulating pyrite oxidation in single porosity media with advective flow

Figure 5.1 below illustrate the changes over time in oxygen, nitrate, sulphate, hydrogen (pH), alkalinity (HCO3-) and calcium concentrations.

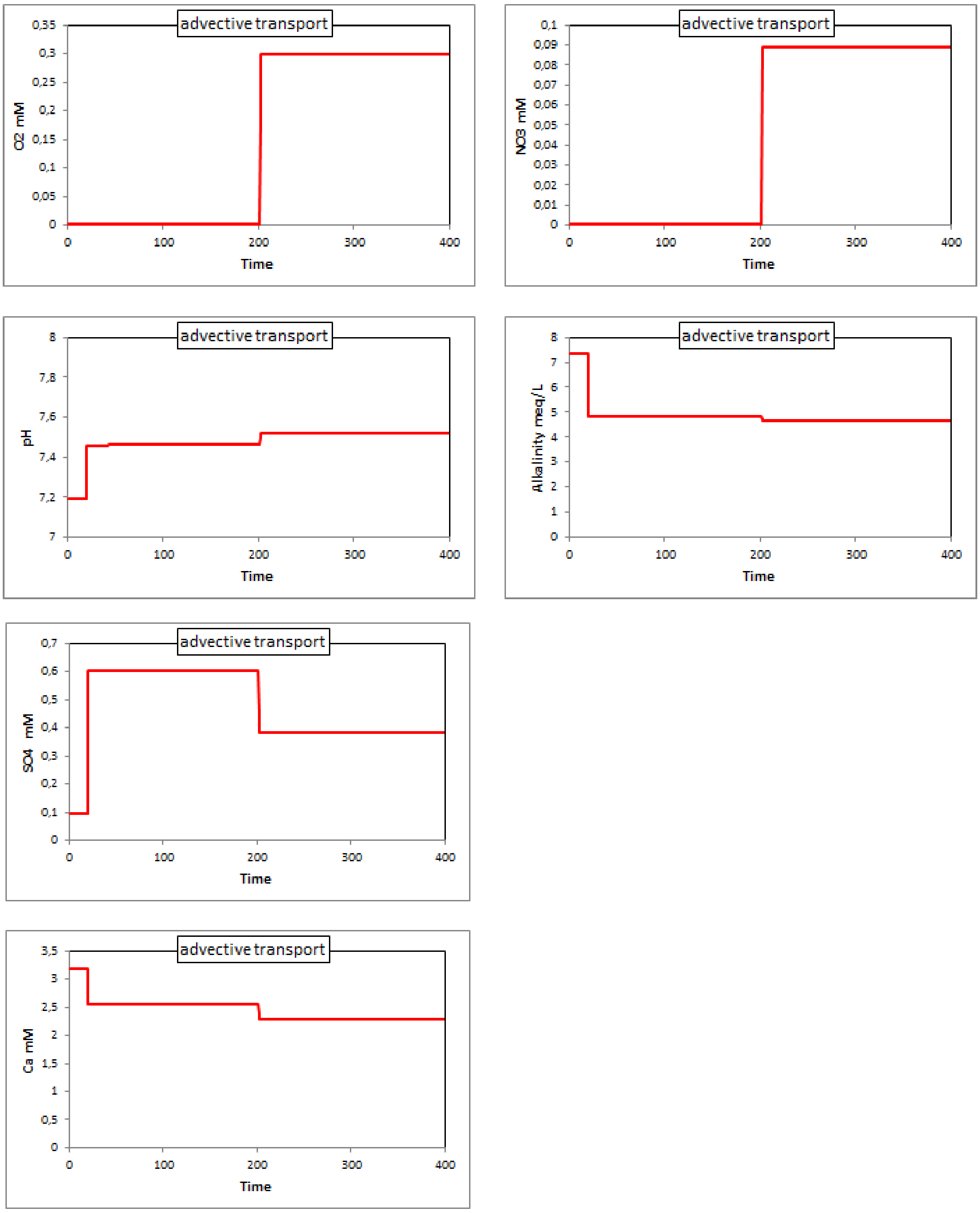


Figure 5.1. Evolution of O2, NO3, pH, Alkalinity, sulphate and calcium concentrations over time when injecting aerobic (oxygen and nitrate containing) groundwater into anaerobic pyrite containing single porosity aquifer.

Both depth and time are arbitrary because we have currently little information on the pyrite content of the sediment. In this example we have made the amount of pyrite present in the sediment small to illustrate what happens when the system becomes flushed.

The SO4 graph has three plateaus. The first is the original groundwater content. Next is channel water with sulfate added from pyrite oxidation and the final one reflects sulphate in channel water. The consumption of pyrite along the flow path is marked by the O2 and NO3 breakthrough curves. All Fe2+ released from pyrite is precipitated as goethite. However, the resulting Fe2+ content in the groundwater depends on the stability chosen for the Fe-oxide. If a less stable Fe-oxide is chosen, sulphide oxidation becomes energetically more favourable and less Fe2+ is oxidized (Increasing SI goethite from 0 to 2 increases Fe2+ to 0.05 mM).

In the channel; O2 = 0.3 mM and NO3 0.09 mM. Accordingly O2 is 2.6 times as important as pyrite oxidant compared to nitrate

The system is buffered by equilibrium with calcite. With respect to the carbonate system, the original groundwater has a lower pH and higher Ca and alkalinity than the channel water. It is caused by a higher P_co2 when the groundwater infiltrates through the soil. Less CO2 will be added when the channel water with the lower Ca, alkalinity and P_co2 is injected directly into the aquifer. This can be expected to be a general feature when injecting surface water into aquifers. The acid production from pyrite oxidation will be buffered by calcite dissolution, temporarily raising the Ca and alkalinity concentrations.

5.1.2 Simulating pyrite oxidation in dual porosity media with fracture flow

This situation corresponds to heterogeneous flow systems like fracture flow through dual porosity Chalk aquifers or alternating sand and clay layers. The reductant, in this case pyrite, will typically be located in the limestone matrix or clay layers where there is no advective flow and the only solute transport is by diffusion. PHREEQC can model this as exchange between a mobile zone and a stagnant, immobile, zone. For this example we have chosen the geometry of alternating sand and clay layers as described by Appelo and Postma (2005, p 508), and the results are shown in Figure 5.2.

In the stagnant model the oxidant (O2 or NO3) has to diffuse from the mobile zone (fracture) into the immobile zone (matrix) where the pyrite is located, with which it can react. The amount of pyrite in the immobile zone is set to be infinite as will be approximately the case in most natural systems at human time scales. Again the system is buffered by calcite and goethite may precipitate. The amount of oxidant (O2 or NO3) that becomes reduced from the water on its way to the screen at 20 m depth will depend on the flow velocity of the water. The faster the flow the shorter the residence time to diffuse into the immobile zone and less oxidant is reduced as well as less pyrite oxidized as is reflected by the sulfate concentration,

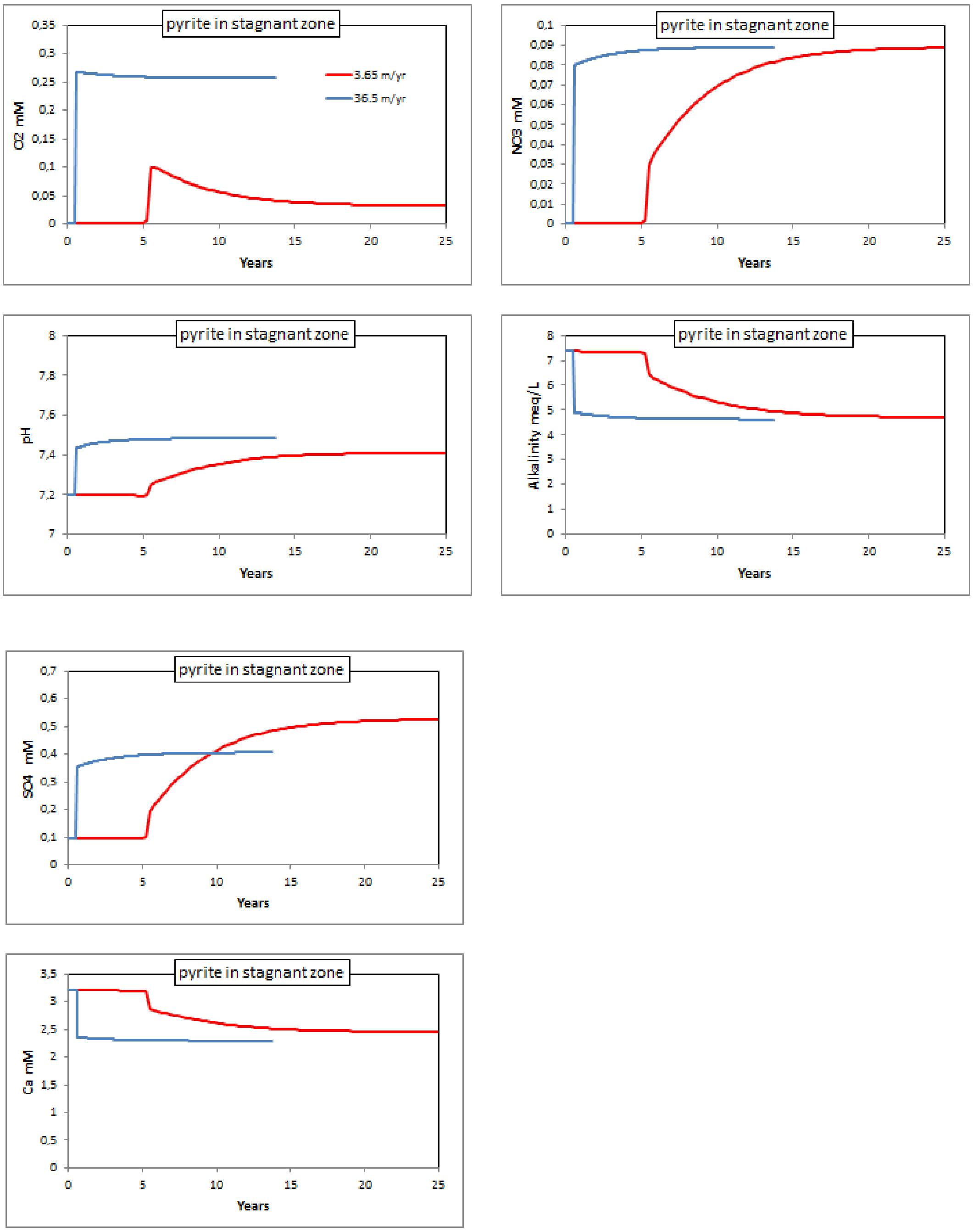


Figure 5.2. Evolution of O2, NO3, pH, Alkalinity, sulphate and calcium concentrations over time when injecting aerobic (oxygen and nitrate containing) groundwater into an anaerobic pyrite containing dual porosity aquifer.

According to Fick's law the flux of oxidant diffusing into the matrix will depend on the concentration gradient. Since the concentrations of O2 and NO3 always will be zero in the immobile zone in the presence of pyrite (in an equilibrium model) the fluxes of O2 and NO3 are directly proportional with the concentrations. In this case the O2 concentration is much higher than the NO3 concentration and therefore much more O2 is consumed. If the NO3 concentration was much higher, the reverse could be the case. In reality it is a complex interplay between diffusive and advective transport and thermodynamics that controls the relative consumption of O2 and NO3. This is quite different from the advective case where thermodynamics are controlling and basically both are consumed at the same time.

As mentioned previously the Chalk aquifer on Southern Falster may be behave as a mixture of both systems with single porosity and advective flow being dominant locally in some areas while dual porosity may be dominating or significant in others. Only detailed investigation of the hydraulics of the Chalk aquifer by well-designed pumping and tracer tests will be able to identify how the hydraulics of the Chalk aquifer works at a given location. Future studies are expected to reveal this and to illustrate how efficient pyrite oxidation would be for nitrate removal in the aquifer and how precipitation of iron oxides may affect the efficiency of water withdrawal from the Chalk aquifer at wells with injection of aerobic water types.

5.2 Organic chemistry

The efficiency of anaerobic aquifers for removal of organic contaminants varies considerably depending on the type of contaminant, but many organic contaminants do not degrade or degrade only very slowly (are recalcitrant) under anaerobic conditions. There is a wide range of possible organic contaminants, which potentially could be found in the drainage canals besides the contaminants found in the North Canal and in the effluent from the waste water treatment plant, at the two sampling campaigns in the project, which may behave very differently, and it was not possible to assess the occurrence and behaviour of these within the scope of the project.

It should be noted that more than 35 pharmaceuticals were found in the discharge from the waste water treatment plant, and that many of these are very resistant to degradation in the environment. Although the effluent from the waste water treatment plant is diluted significantly in the drainage canal, that no pharmaceuticals were found above detection limits in the canal, and that some of the pharmaceuticals would be degraded in the aquifer, there may be a risk that the sum of the concentrations of the pharmaceutical would be a problem for the water works and water supply of the area if injected into the aquifer (Lopez-Serna et al., 2013). Hence, injection of water from the drainage canals into the Chalk aquifer cannot be recommended without an extensive treatment of these waters that efficiently remove the contaminants in combination with an extensive quality control on the injected water.

5.3 Pathogens

Like pharmaceuticals, pesticides and other organic contaminants pathogens is another relevant concern, when considering the injection of surface waters into fractured Chalk aquifers. E.coli was found in high numbers at one location during the project sampling (see section 4.2.5) clearly indicating that it cannot be recommended to inject surface waters into the aquifer without extensive treatment that will also remove any potential pathogens in the drainage waters.

Pathogens are generally removed quite efficiently in single porosity aquifers, but they may be transported fast over rather long distances in fractured aquifer systems (e.g. Masciopinto et a., 2008). Hence, efficient treatment is needed before injection of drainage water into the fractured Chalk aquifer on Falster.

6. Water pre-treatment options before injection, efficiency and costs

Due to the detection of fecal bacteria and organic micro-pollutants in the drainage water different treatment methods will need to be implemented prior to injection into the groundwater aquifer. The broad spectra of contaminants, including potentially pathogenic microorganisms, industrial and household chemicals, pharmaceuticals and pesticide residues detected in the drainage waters may require a treatment train composed of different successive techniques. The most relevant approaches will be discussed in the following section in the light of their efficiency and costs.

6.1 Water quality requirements

The European Drinking Water Directive requires that drinking water, and water used in households and in food products, should uphold a specified quality level. The purity requirements for example include threshold limits for single pesticide residues at 0.1 µg L-1, and a limit for the sum of all residues at 0.5 µg L-1. The threshold for industrial and household chemicals are generally specified for each compound individually, where for example the threshold limit for nonyl-phenols are 20 µg L-1 and for acetone it is 2 mg L-1. In contrast to this, there are currently no threshold limits for pharmaceutical compounds. The occurrence of fecal bacteria, expressed a coliform bacteria, must not exceed zero in a volume of 100 ml water.

6.2 Removal of fecal bacteria

Several methods for disinfection of drinking water exist and the most commonly used are ultraviolet light (UV) irradiation and chemical disinfection using for example free chlorine, ozone or monochloramine.

6.2.1 UV and chlorination

Irradiation with UV and chemical disinfection by e.g. free chlorine is effective at killing a broad range of microorganisms in natural waters. Some specific types of microorganisms may however elude inactivation in such treatments, where for example fractions of different spore-forming bacteria appear resistant (Rose and Rice 2014).

Common for both irradiation and chemical disinfection is the possibility for creation of degradation products from the organic micro-pollutants present in the drainage water. This could potentially broaden the range of organic contaminants making none of these options ideal for disinfection as a standalone technique in the current situation. A scenario where these processes are included in a multi-barrier treatment train could however be a possibility.

6.3 Removal of organic micro-pollutants

Industrial and household chemicals, pharmaceuticals and pesticide residues are more or less comparable organic compounds and their individual removal efficiency in a given treatment strategy will depend on their physical and chemical properties. This means that a chosen treatment approach in theory should be able to cover them all.

It has previously been found that conventional approaches such as chemical oxidation by free chlorine only is capable of removing approximately 50% of the investigated pharmaceuticals (WHO 2011). More promising, however, are advanced water treatment processes including for example activated carbon or membranes (e.g. reverse osmosis or micro- and nano-filtration), where removal efficiencies of above 99% have been reported for pharmaceuticals (WHO, 2011; Watkinson et al., 2007). Similar efficiencies can be expected for organic contaminants from the groups of industrial and household chemicals and pesticides.

6.3.1. Sorption on activated carbon

Granulated activated carbon (GAC) or powdered activated carbon (PAC) are in some cases used in drinking water production for removal of pesticides, for examples – but it has also been implemented for removing organic compounds that negatively affects taste and odour of the drinking water. Activated carbon treatment is especially efficient against hydrophobic compounds and it has previously been shown, that for example the pharmaceuticals diclofenac and carbamazepine (Table 4.5) are removed efficiently by GAC in waterworks (Ternes et al. 2002). In another study with simulated drinking water treatment using PAC, the removal of for example the painkiller ibuprofen (Table 4.5) and a broad range of other pharmaceuticals and personal care products were less efficient (Westerhoff et al. 2005). A similar drawback of activated carbon filtration is the reduced efficiency against polar substances such as MTBE and X-ray contrast agents (Lipp et al. 2010).

Even though activated carbon could be an efficient approach for removing many organic contaminants it appears more relevant for purification of contaminated groundwater, where the particulate and organic matter contents typically is low. One might anticipate that treatment of water from the present study would lead to a frequent saturation of the activated carbon with natural organic matter from the drainage water. This would block the adsorption sites and restrict and eventually stop the removal of organic contaminants (Lipp et al. 2010). Operation of such a system under these conditions could pose a significant economic burden due to the need for periodically removing and regenerating the activated carbon filter.

6.3.2. Membrane filtration

Membrane filtration is based on retaining molecules due to size exclusion, electrostatic repulsion and/or hydrophobic adsorption (Yoon et al. 2006). Although conventional filtration can be efficient at removing a range of different organic molecules such methods can embed impurities in the membranes and accumulate a cake that must be back-flushed periodically to restore productivity (Stover 2014). Advanced membrane processes involving for example nanofiltration or reverse osmosis technology has been shown to efficiently remove a broad spectrum of pesticide, pharmaceuticals and personal care products from contaminated water (Yoon et al. 2006; Lipp et al. 2010; Bodzek et al. 2011).

Reverse osmosis can remove > 99% of large organic molecules, such as most pharmaceutical compounds and pesticides (Lipp et al. 2010; WHO 2011; Bodzek et al. 2011) for example. To prevent clogging of the filters reverse osmosis uses a crossflow to keep the membrane surface clear (Stover 2014). This produces a concentrate containing higher levels of the contaminants and discharge of this fraction need to be addressed (Lipp et al. 2010). Besides the organic pollutants, reverse osmosis has also been used to remove inorganic compounds as nitrate, fluoride ions, boron, arsenic, chromium and different heavy metals (Bodzek et al. 2011). Additionally, microorganisms including e.g. bacteria, protozoa and viruses are also removed during the filtration (Bodzek et al. 2011).

6.4 Suggested treatment strategy

The drainage water attended for injection into the aquifer is affected by fecal bacteria and a range of different organic micro-pollutants – both the ones detected within the Water4Coasts project (Tables 4.3 – 4,6), and without a doubt also a broad range of new emerging compounds not included in our analytical survey. This is obviously a challenge when selecting an efficient treatment strategy.

Composing a multi-barrier approach for water purification with successive techniques such as activated carbon filtration followed by chlorination or UV disinfection could be a strategy. As mentioned above however, activated carbon filters will likely be saturated with natural organic carbon from the drainage water and a frequent and expensive removal and regeneration of the filters need to be implemented.

Technological improvement with advanced membrane systems has however reduced the cost by e.g. reverse osmosis by a factor of four or more (Stover 2014). Ongoing research and development will likely reduce the price even further. Reverse osmosis technology will target all the detected compounds and bacteria and such a versatile technology appears to be the most relevant choice for treatment of the drainage water. Additionally, such a strategy will likely also cover new organic pollutants detected in future monitoring programs.

Initial reverse osmosis purification could be connected to a secondary activated carbon filter, with the aim of removing micro-pollutants having a low molecular weight, as these might pass through the reverse osmosis step (Lipp et al. 2010). A reverse osmosis strategy leaves a concentrate behind from the crossflow of membranes, and this fraction could be transported to the nearby waste water treatment plants. The flow in the suggested treatment strategy is illustrated in figure 6.2.

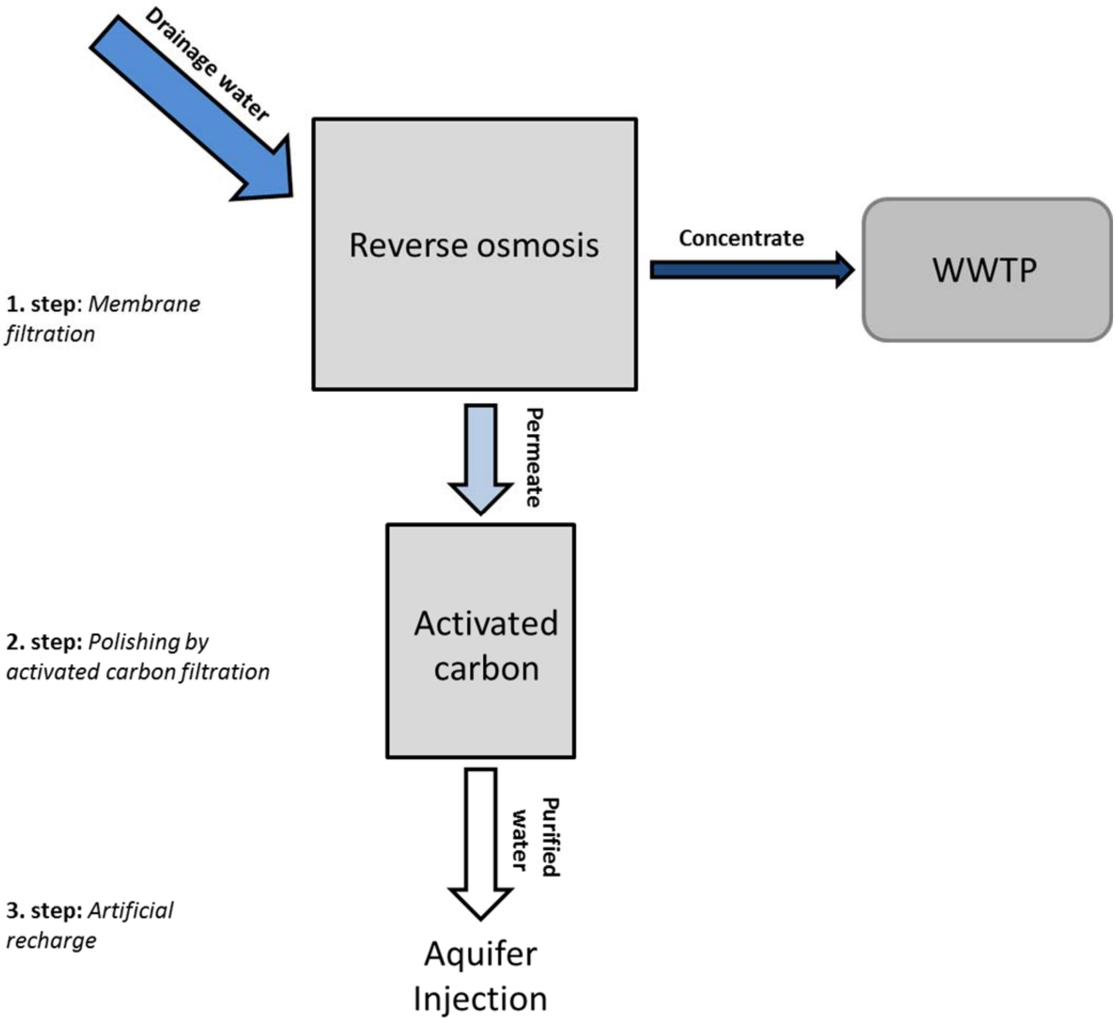


Figure 6.2. A possible treatment strategy for the drainage water prior to injection into the groundwater aquifer. 1. Step: membrane filtration with reverse osmosis; 2. Step: removal of low molecular weight organic compounds from the permeate by activated carbon sorption; 3. Step: artificial recharge of the aquifer. Concentrate produced from the reverse osmosis will separately be treated in a nearby wastewater treatment plant (WWTP).

7. Discussion and conclusion

Managed aquifer recharge and water banking (storage of water for later use) are techniques of increasing importance (Megdal and Dillon, 2015; Zhao and Wang, 2015), which have been increasingly studied and applied for protection, storage and recovery of water resources, globally, during the past decade (Figure 7.1), and there's a strong need to gain experience with the efficiency, positive and negative effects of the different MAR designs in different climatological and geological settings as well as to develop sound policies and risk management frameworks (Nandha et al, 2015).

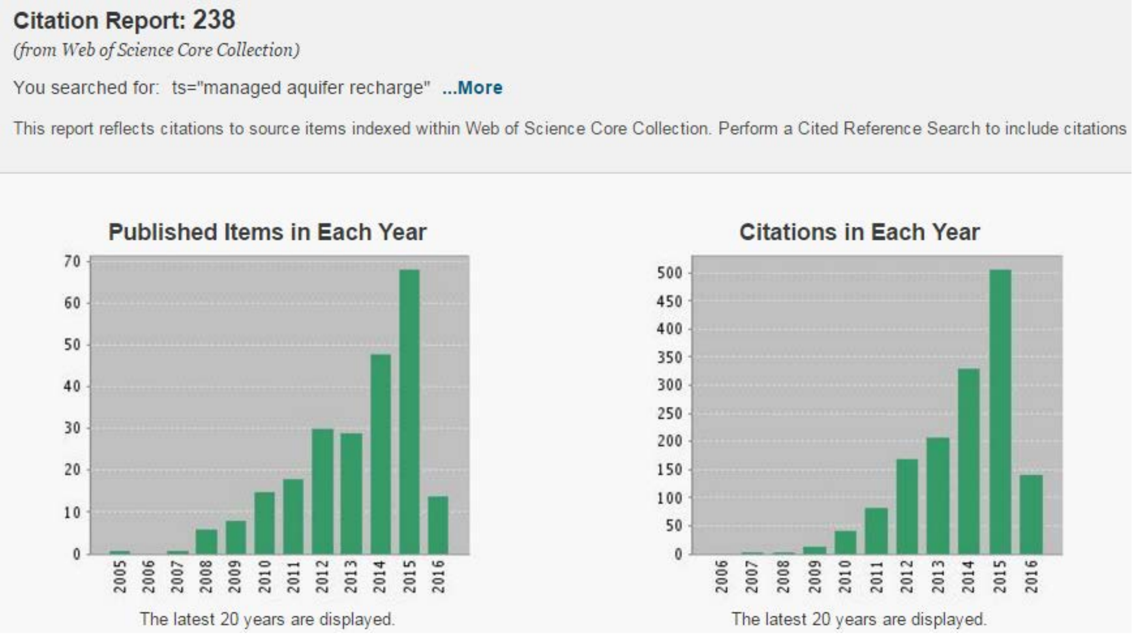


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Figure 7.1. Plot from the Citation report from Web of Science (Thomson Reuters) for a search on the keyword "managed aquifer recharge" in the Web of Science Core Collection.

The application and experience with MAR is still limited in Denmark, but the technique potentially have several beneficial effects that may be applied for the protection of both water resources, ecosystems and the built environment especially in densely populated coastal areas with large groundwater abstraction and drawdown that increase salt water intrusion to coastal aquifers. Hence, there's a need for developing experience and policies for MAR in Denmark, and this report together with the related reports on modelling and monitoring (Rasmussen et al., 2015; Hinsby et al. 2015) provide initial background information of relevance for the further assessment of the application of MAR in Denmark.

The application of MAR is still in its infancy, and the development and application of sound principles for MAR is strongly needed for sustainable water resources management in many areas of the world with excess groundwater abstraction. The application of MAR introduces risks to the quality of the groundwater resources unless proper policies and risk management frameworks for MAR are developed (Nandha et al., 2015) in collaboration between research organisations and water authorities.

This report describes initial assessment of some water quality aspects of MAR that need to be addressed before injection of aerobic groundwater or surface water into the investigated dual-porosity Chalk aquifer. The assessment clearly show that efficient treatment and water quality control is required both of waters injected to and recovered from the aquifer in order to ensure that the MAR procedures do not jeopardize the quality of the groundwater resources abstracted for drinking or irrigation water or for sustaining good ecological status of groundwater dependent terrestrial or associated aquatic ecosystems.

Substances of concern include both inorganic trace elements such as arsenic and nickel, micro-organic contaminants such as pharmaceuticals, industrial chemicals and pesticides and it includes the possible occurrence of pathogens in surface waters. Hence, efficient pretreatment before injection of such water is required in order to ensure that no harm is done to the groundwater quality at and around the injection wells, and in addition efficient quality control of recovered waters are also required in order to demonstrate that the injection has not induced geochemical reactions and e.g. release of harmful trace elements etc.
Concerns associated with application of MAR in the Marielyst area of southern Falster and in general, are mainly related to drinking water quality i.e. human health and the efficiency of the drinking water abstraction wells (clogging risks)

Whether extensive pretreatment and quality control is economically feasible depends on what other options may be available at the investigated site, and this have to be compared and evaluated in cost-benefit analyses. Potential other options and the costs of the treatment compared to these strongly depend on local conditions, and hence they have to be evaluated from case to case. MAR in combination with pretreatment in constructed wetlands may be an interesting option for some areas (Hamadeh et al, 2014).

Managed aquifer recharge may not be the first choice for sustainable water management at a given site, but at some sites it may be the only option, and without any doubt it will be of increasing importance globally for sustainable water resources management in the future considering projected population growth and climate change impacts.

8. Recommendations

This report (and Hinsby et al., 2016) briefly describes the fast development of studies on the application of MAR during the past decade reflecting the need for the development of new techniques for sustainable management and conjunctive use of water resources, globally. However, it also indicates that there are many water quality and technical issues that have to be resolved and efficiently tackled in both policies and technical guidances in order to ensure good practices for MAR under different hydrogeological conditions.

The authors recommend and encourage that regional and national authorities and research institutions as well as the European Commission collaborate on the development of policies, risk management frameworks and technical knowhow and guidances related to proper development of MAR practices. Water resources are under severe pressure due to increasing abstraction, population growth, climate change and sea level rise and there is an increasing need for development of sustainable water resources management and conjunctive use of groundwater and surface water, globally. Managed aquifer recharge may be the most promising technique for sustainable water resources management in coastal regions and other regions with e.g. rapidly declining water tables and salt water intrusion, and new tools and innovative approaches using different designs of MAR such as the techniques described by Zuurbier et al. (2014, 2015) should be supported and encouraged.

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