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Published in:
Water Research

Link to article, DOI:
[10.1016/j.watres.2019.02.026](https://doi.org/10.1016/j.watres.2019.02.026)

Publication date:
2019

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Gejl, R. N., Rygaard, M., Henriksen, H. J., Rasmussen, J., & Bjerg, P. L. (2019). Understanding the impacts of groundwater abstraction through long-term trends in water quality. *Water Research*, 156, 241-251.
<https://doi.org/10.1016/j.watres.2019.02.026>

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1 Understanding the impacts of groundwater abstraction through long-term 2 trends in water quality

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6

7 Keywords:

8 - Sustainable groundwater abstraction

9 - Groundwater impact assessment

10 - Confined aquifer

11 - Groundwater quality

12 - Aquifer deterioration

13 - Groundwater footprint

14

15 Abstract

16 It is vital to understand long-term trends in water quality parameters when assessing the sustainability of
17 groundwater abstraction. Withdrawal-to-availability analysis is still used widely in groundwater
18 management considering quantities and utilization rates based on in- and outflows. In this study, we took a
19 step further than the water balance approach and carried out a detailed investigation of trends in long-
20 term time series of groundwater quality, in order to analyze the sustainability of groundwater abstraction.
21 We assessed trends, links, and patterns in abstraction, potentiometric surface, and water quality
22 parameters for 28 well fields around Copenhagen, Denmark. Groundwater monitoring data from 1900 until
23 2014 were investigated for each well field. During this period, the well fields experienced a 2 to 14 m
24 decrease in the nearby potentiometric surface compared to the first—or pre-pumping—potentiometric

25 surface recordings. Sulfate concentrations increased in 24 out of 27 well fields after the maximum
26 abstraction period, compared to the earliest water quality measurements. The results indicate that in the
27 1980s, when water consumption (abstraction) and drawdown were at their highest, water abstraction
28 caused a steady increase in sulfate and calcium, which we consider unsustainable. In contradiction, the
29 abstraction in 24 well fields show almost steady sulfate levels in the aquifer after decreased water
30 consumption since 1995. Only four well fields showed more than a 20 mg/L increase in sulfate
31 concentration, which indicates that the recent abstraction does not interfere with sulfate levels in the
32 aquifer. Our method and results show how long-term water quality trends can support the management of
33 aquifer exploitation and evaluate sustainability on the well field scale.

34 1. Introduction

35 Groundwater is an important resource around the world (Gleeson et al., 2012; Margat and van der Gun,
36 2013), and some countries are entirely dependent on it for their water supply, for example Denmark. In
37 spite of an increasing focus on the assessment of groundwater resources (Gejl et al., 2018; Gleeson et al.,
38 2012), there is still potential for better representation of aquifer deterioration in terms of both
39 groundwater levels and water quality. Such a quantification could ensure the efficient use of this vital
40 resource and the management of future water availability (Li and Qian, 2018). Existing assessments of
41 sustainable groundwater abstraction are usually based on a snapshot of the water cycle or by looking back
42 over a few decades, which in many cases is too short a period for detecting long-term changes (Loftis,
43 1996). Long-term trends in aquifer drawdown have been investigated, but only by considering quantities in
44 the water balance (Luczaj et al., 2017). Aquifers range from cave systems (Bauer-Gottwein et al., 2011), to
45 fractured rock and limestone (Mosthaf et al., 2018) and unconsolidated, sedimentary deposits (Anderson et
46 al., 2015). Each of these underground systems will respond differently to abstraction, and it is complex to
47 provide predictions on the potential deterioration of the available groundwater resource due to water
48 abstraction. Investigating the links between groundwater abstraction and its levels can help understand

49 future aquifer responses to climatic and anthropogenic stresses and indicate a sustainable abstraction
50 approach (Whittemore et al., 2016). We suggest that understanding long-term trends in quality can provide
51 additional information for detailed investigations into aquifer sustainability and the management of
52 groundwater resources.

53 Building upon the generic sustainability concept (Barnaby, 1987), groundwater abstraction can be
54 considered sustainable when there is sufficient water for human and environmental needs, including for
55 future generations. Furthermore, water abstraction is sustainable when there are no unacceptable impacts
56 on levels, water quality, or environmental flow requirements (Henriksen and Refsgaard, 2013). However,
57 besides rule of thumb values, there are no general accepted definitions of thresholds for acceptable
58 utilization rates for different hydrogeological settings. Indicators take their starting point in water use
59 (Boulay et al., 2017; Pfister et al., 2009), water scarcity (Smakhtin et al., 2004), groundwater footprint
60 (Gleeson et al., 2012), or sustainable groundwater abstraction (Henriksen et al., 2008). These markers are
61 well documented, easily communicated, and in general applicable to worldwide studies. Moreover, they
62 are useful for screening purposes, given that they are based on precautionary principles; however, they are
63 at the midpoint level for identifying environmental mechanisms (Bare et al., 2000) and do not deal with
64 actual impacts or deterioration of the water resource itself. Some evaluations consider surface and
65 groundwater as one resource, resulting in misleading effects for the latter's withdrawal (Gejl et al., 2018).
66 Furthermore, the above-mentioned indicators are scoped mainly towards global or regional issues and they
67 give little assistance to local challenges. We previously proposed a generic indicator aimed specifically at
68 the local impacts of groundwater abstraction, which was applied to groundwater supply systems in
69 Denmark (Gejl et al., 2018), but this indicator is also limited by the use of generic and globally utilized
70 definitions of the water balance. In the following, we investigate the long-term effects of water abstraction
71 on aquifer deterioration, by studying the relationships between abstraction, groundwater level and
72 groundwater quality based on groundwater monitoring data for 28 well fields providing water to
73 Copenhagen, Denmark, which have been influenced by abstraction for decades.

74 We focused on confined aquifers as a typical and important example for worldwide groundwater use.
75 Abstracting water from a confined aquifer will reduce the potentiometric surface (hydrostatic pressure) and
76 induce a change in local vertical gradients that can accelerate groundwater recharge. In turn, these
77 changed gradients will influence the velocities and directions of water flow in the groundwater system. The
78 abstraction-induced decrease of the potentiometric surface can affect water quality in two ways: 1) It can
79 change water quality, as a result of drawing water from one or several sources; and 2) it can influence
80 groundwater processes, again with the same result. Our hypothesis is that an overexploited groundwater
81 system, over time, will tend to undergo deteriorating water quality depending on the geology, the
82 groundwater system, and the well specifications. A continuous change for the worse in water quality
83 parameters indicates unsustainable abstraction, in which case there is a risk that the water quality with
84 time will become unsuitable for drinking water supply.

85 We wanted to investigate what defines sustainable groundwater abstraction in terms of potentiometric
86 surface and groundwater quality, thereby augmenting the volume-based sustainability assessment. Trends
87 in water quality parameters have been used for many years to assess groundwater withdrawal and provide
88 indications of issues such as pyrite oxidation (Andersen et al., 2001), saltwater intrusion (Bryan et al., 2016),
89 and nitrate contamination (Schullehner et al., 2018). Many studies have looked into the details of chemical
90 responses and specific processes governing local water quality (e.g. Jessen et al., 2016; Larsen and Postma,
91 1997), whereas our aim was to investigate overall trends across many well fields. From changes in water
92 quality, we can propose limits to groundwater abstraction that would serve as one criterion among others
93 to assess a sustainable abstraction. The study aimed to:

- 94 • Investigate how abstraction affects the potentiometric surface in the aquifers
- 95 • Identify which groundwater processes and parameters were affected by abstraction in the studied
- 96 well fields

- Evaluate long-term patterns in potentiometric surface and water quality parameters across multiple well fields
- Explore if groundwater quality parameters can serve as indicators for sustainable groundwater abstraction

2. Aquifer systems and water quality

2.1 Water abstraction and hydraulic gradients

Aquifers can be classified as either confined or unconfined. When low permeability layers separate aquifers, these are termed “confined,” and otherwise “unconfined” (Appelo and Postma, 2005; Freeze and Cherry, 1979). Confined aquifers with a potentiometric surface higher than the confining layer are especially relevant for water supply, due to their protection from surface contaminants (Trowsdale and Lerner, 2003), and constitute the aquifers we study in this paper.

Before abstraction (pre-pumping conditions), the potentiometric surfaces in different aquifers at different depths are in balance, and there will typically be a downward flow due to the difference in head (Figure 1.a). Inducing abstraction from a deep aquifer will change its potentiometric surface, and to a lesser degree the potentiometric surface in the upper aquifer, thereby increasing the hydraulic gradient (Figure 1.b). Hence, we can use this change in the deep aquifer’s potentiometric surface as a proxy for the vertical gradient. The change in hydraulic gradient influences the flow direction, and so water may be drawn down, up, or in from the sides. “New” water drawn into the aquifer can have another chemical composition or influence processes that affect groundwater quality.

2.2 Water quality parameters affected by water abstraction

A changed water influx or shift in redox conditions can change a number of water quality parameters, depending on the geology, hydrogeology, and biogeochemical processes in and around the aquifer. In our case, it is relevant to focus on the following water quality parameters: chloride, sulfate, calcium,

120 magnesium, and sodium. Nitrogen in various forms is used as fertilizer and can cause nitrate
 121 contamination, which is a concern for many water supplies (Hansen et al., 2012, 2011; He and Wu, 2018)
 122 and arsenic is a challenge for water supply around the world (Nordstrom, 2002). Nitrate and arsenic is not
 123 the main focus of this study, because the concentrations were low or without a clear pattern for the well
 124 fields (see assessment in section 3). Furthermore, the measurement period for arsenic was too short to
 125 detect long-term changes, however, for both arsenic and nitrate the presence and involvement in
 126 biogeochemical processes have been assessed (see next section).

127
 128 *Figure 1: A conceptual figure of potential changes in a typical Danish confined aquifer resulting from abstraction. a)*
 129 *Before abstraction (pre-pumping conditions) and b) during abstraction. h_{deep} and h_{upper} refer to the potentiometric surface*
 130 *in the deep and the upper aquifer, respectively. Q is groundwater flow, and the length of the arrow indicates the gradient*
 131 *difference. Modified from Vangkilde-Pedersen et al. (2011).*

132 2.3 Processes affecting water quality

133 Changing from reduced to oxidized conditions will affect water quality. In Denmark, the oxidation of pyrite
 134 is a primary concern, as it produces sulfate, iron precipitates, acid, and sometimes releases nickel and
 135 arsenic (Appelo and Postma, 2005; Postma et al., 2007). Pyrite is abundant in certain sand deposits (Jensen
 136 et al., 2003) and the limestone (Jakobsen et al., 2017; Knudsen, 1999) and a reduced potentiometric
 137 surface or transportation of dissolved oxidizers, such as oxygen or nitrate, to the saturated zone may lead
 138 to pyrite oxidation. The acid produced as a result may dissolve calcium carbonate from calcareous or chalk
 139 aquifers, which can correlate with the sulfate concentration (Vangkilde-Pedersen et al., 2011).

140 The background concentration of sulfate in groundwater in Denmark ranges from 10 to 30 mg/L, depending
141 on the atmospheric concentration of sulfur in precipitation (Hansen et al., 2009), but it may be lower in
142 reduced conditions (Miao et al., 2013). Pyrite oxidation is often caused by oxygen and/or nitrate, which is
143 controlled and determined by different processes (Sl. A)). Where nitrate is generated from fertilizers and
144 the concentration will depend on the application, oxygen can come in 1) gaseous form in leaking aquifers or
145 from improper wells (Baba and Ayyildiz, 2006) or in 2) dissolved form with the groundwater recharge,
146 however the latter is often proportionally small compared to the first.

147 There are several other important aspects and processes affecting groundwater quality, such as saltwater
148 intrusion and other dissolution/precipitation processes than the one related to pyrite oxidation, but these
149 are of minor importance in terms of the results in this study and are not discussed further. There were also
150 indications of ion exchange and reverse ion exchange processes at the well fields, but there were no clear
151 patterns or links to abstraction as discussed later.

152 3. Methods: Abstraction, potentiometric surface, and water quality

153 The Danish capital city, Copenhagen, currently receives water from 51 well fields located up to 40 km from
154 the city (Figure 2). The typical hydrological conditions on Zealand consist of layers of sand and clay and the
155 chalk, from which the majority of the drinking water is abstracted (Figure 2.c). The Greater Copenhagen
156 Utility (HOFOR) has supplied water to Copenhagen since 1859 and is now providing 50 million m³ water per
157 year for 1 million inhabitants. HOFOR provided our study with groundwater level datasets starting in 1900,
158 with several measurements of the potentiometric surface per year, and close to annual samples of a range
159 of groundwater quality parameters since 1940.

Figure

2: a) HOFOR's well fields at Zeeland, Denmark. The well fields included in this study are marked with gray squares, and all of those managed by HOFOR are marked with white circles. b) A close-up of Hørup as an example of a typical well field and c) a geologic profile of some of the wells at Hørup well field. Well fields in HOFOR typically consist of multiple wells 'on a string'. P is the pump collecting water from all of the wells before pumping it to the waterworks (WW). Water quality samples are collected downstream of all wells before any treatment at the waterworks.

To find the link between abstraction and the potentiometric surface, we assessed the combined abstraction for each well field and the local drawdown in a monitoring well close to each site (Figure 2b).

All water quality samples used for our analysis were collected from the water mix downstream of all wells and before any treatment (Figure 2b). Historically, groundwater abstraction was monitored at waterworks and not at the individual well field, which means that for most well fields we only had data starting after

171 the actual abstraction started. In the majority of cases, we do not know the size of water abstraction that
172 led to the initial decrease in the potentiometric surface and a change in water quality.

173 HOFOR has 51 well fields that are active or have been active recently, and we made a selection for further
174 study based on the following criteria:

- 175 • Continuous data; well fields with a maximum 10-year gap in data and abstraction.
- 176 • Long time series; well fields that started abstracting water before 1970 and have been active for
177 more than 30 years.
- 178 • No major changes within the well field, e.g. moving the well field, so that changes in water quality
179 is due to the change of location. This was based on expert judgement by HOFOR.
- 180 • Individual data; abstraction and water quality data for each well field.

181 The criteria led to the selection of 28 out of 51 well fields for further analysis (Table 1). All well fields and
182 the reason for their inclusion/exclusion are listed in supporting information B (SI.). We obtained data on
183 water abstraction, potentiometric surface, and water quality for the well fields. Many of the sites lacked
184 early data on abstraction, so we found approximate years for its initiation, through historic waterworks
185 reports. Potentiometric surface measurements was obtained from monitoring wells chosen by their
186 proximity to the well field and expected minimum influence from other well fields (the ID numbers of the
187 monitoring wells can be found in SI. C). The distance between the monitoring well and well field was taken
188 from the monitoring well to the center of the well field, which itself was found by polygon centroids in QGIS
189 from the well field area given by HOFOR.

190 The final dataset consisted of 3,389 samples of water quality analyses for 28 well fields dating from 1940 to
191 2015, resulting in 20,330 datum of water quality parameters. There were 1,458 yearly abstraction
192 observations for the 28 well fields and more than 10,000 water level measurements dating from 1900 to
193 2017. The data were analyzed in different ways, in order to understand links between abstraction,

194 potentiometric surface, and water quality. Firstly, we compared water quality for the first five water quality
195 samples (referred to as the “first period”) with the five-year period of maximum known abstraction
196 (referred to as the “maximum abstraction period”) and the period of the last five water quality samples
197 (referred to as the “last period”). The first period is our best representation of pre-pumping water quality in
198 the aquifer before it is impacted by groundwater abstraction, however, for some of the well fields the first
199 period actually represent an aquifer already impacted by pumping. The parameters were presented as
200 absolute changes, to overcome misleading results from comparing increased concentrations from small
201 numbers or zero values. Secondly, the data were plotted as time series, to show trends and changes in
202 potentiometric surface and water quality. Thirdly, correlations between observed parameters were found
203 with a two-sample t-test (the statistical significance is evaluated for $\alpha = 0.05$). Besides the comparison of
204 different periods, we have used the initial (first) measurement of potentiometric surface to evaluate the
205 drawdown, since the potentiometric surface is rapidly responding to abstraction.

206 *Table 1: List of selected well fields. No. and depth of wells refers to active wells in 2018. Max. abs. recorded refers to the*
207 *maximum known average groundwater abstraction for five consecutive years. dh for max. abs. is the difference between*

- 208 *the initial potentiometric surface and average potentiometric surface during the maximum abstraction period. Dist. to obs.*
- 209 *well is the distance from the center of the well field to the observation well. Abs. is an abbreviation for abstraction.*

<i>Well field</i>	<i>Max. abs. recorded (million m³)</i>	<i>dh for max. abs. (m)</i>	<i>No. of active wells</i>	<i>Depth of wells (m)</i>	<i>Dist. to obs. well (m)</i>	<i>Start of monitoring potentiometric surface</i>	<i>Approx. start of abs.</i>	<i>Start of water quality sampling</i>	<i>Start of abs. data</i>
<i>Almsgård</i>	1.0	-3.5	5	24-31	17	1956	1964	1964	1964
<i>Assermølle</i>	1.5	-12.9	4	33-50	336	1920	1938	1941	1962
<i>Attemose</i>	5.1	-8.8	30	35-44	1620	1918	~1955	1959	1962
<i>Bjellekær</i>	1.8	-4.2	7	65-115	137	1922	~1920	1940	1962
<i>Bogøgård</i>	2.4	-10.1	9	52-65	334	1920	~1920	1940	1962
<i>Brokilde</i>	3.2	-8.2	15	49-63	478	1929	1934	1940	1962
<i>Egholm</i>	2.4	-5.5	6	70-110	417	1938	1940	1940	1962
<i>Gevninge</i>	3.4	-5.7	10	31-75	1653	1934	1938	1940	1950
<i>Havdrup</i>	3.1	-12.3	15	45-100	383	1946	~1950	1951	1952
<i>Havelse</i>	2.4	-10.2	4	40-45	485	1939	~1955	1957	1962
<i>Hule Mølle</i>	3.7	-7.9	10	35-78	1735	1934	1937	1941	1962
<i>Hørup</i>	3.7	-9.8	9	39-100	305	1943	~1955	1955	1962
<i>Ishøj</i>	0.7	-2.7	3	52-66	1340	1900	1914	1981	1970
<i>Karlsunde</i>	0.5	-2.0	4	63-110	682	1943	?	1951	1962
<i>Katrineberg</i>	1.6	-4.3	9	30-63	627	1913	1922	1941	1962
<i>Kornerup</i>	2.3	-8.4	22	23-75	530	1920	1939	1940	1962
<i>Lavringe</i>	1.2	-13.6	7	62-87	1623	1934	1937	1941	1962
<i>Ledreborg</i>	1.6	-7.2	-	-	263	1934	1938	1941	1962
<i>Marbjerg</i>	1.0	-8.9	4	49-51	339	1930	1934	1940	1962
<i>Ravneshave</i>	3.1	-14.3	14	16-54	383	1944	~1965	1966	1965
<i>Solhøj</i>	6.3	-10.0	8	21-36	95	1903	1908	1940	1962
<i>Strø</i>	3.7	-12.2	14	38-100	681	1939	~1955	1956	1962

<i>Thorsbro</i>	<i>3.5</i>	<i>5.5</i>	<i>19</i>	<i>12-54</i>	<i>67</i>	<i>1909</i>	<i>1908</i>	<i>1941</i>	<i>1981</i>
<i>Tåstrup Valby</i>	<i>1.6</i>	<i>3.7</i>	<i>7</i>	<i>12-30</i>	<i>276</i>	<i>1945</i>	<i>1919</i>	<i>1940</i>	<i>1962</i>
<i>Vallensbæk</i>	<i>0.5</i>	<i>5.1</i>	<i>-</i>	<i>-</i>	<i>406</i>	<i>1943</i>	<i>1948</i>	<i>1951</i>	<i>1962</i>
<i>Vardegård</i>	<i>1.2</i>	<i>6.1</i>	<i>-</i>	<i>-</i>	<i>543</i>	<i>1939</i>	<i>1948</i>	<i>1951</i>	<i>1962</i>
<i>Værebros</i>	<i>3.6</i>	<i>2.9</i>	<i>13</i>	<i>34-75</i>	<i>712</i>	<i>1943</i>	<i>1950</i>	<i>1951</i>	<i>1962</i>
<i>Æbelholt</i>	<i>2.3</i>	<i>-10.4</i>	<i>6</i>	<i>60-120</i>	<i>1273</i>	<i>1915</i>	<i>~1955</i>	<i>1961</i>	<i>1962</i>

210 When the water quality sampling started in the 1940s, the water abstraction for Copenhagen was greater
211 than it is now. Furthermore, for the majority of well fields' (24) water was withdrawn for some time before
212 initiating data on abstraction quantities and water quality, and therefore we cannot observe the
213 development from pre-pumping. We excluded some water quality parameters, because we were interested
214 in water quality parameters that consistently responded to groundwater abstraction (Table 2).

215 *Table 2: Water quality parameters excluded from further analysis*

Water quality parameters	Reason for exclusion from analysis
pH	Little development in pH
Nitrate	No clear connection to abstraction Only 8 out of 28 well fields had a nitrate concentration above 10 mg/L (SI. I) Maximum concentration of 28 mg/L
Hydrogen Carbonate	Generally stable concentrations
Cobalt	Short measurements periods (>1990) No clear connection to abstraction

	Generally little development in concentration
Iron	Small concentration (<6 mg/L)
	Generally little development in concentration
Magnesium	No clear connection to abstraction
Nickel	Short measurements periods (>1990)
	Only four well fields have concentrations >20 µg/L
	No clear connection to abstraction
	Generally little development in concentration
Arsenic	Short measurements periods (>1990)
	Only one well field had a concentration > 5 µg/L for a four year period (Sl. I)
	No clear connection to abstraction

4. Results & Discussion

4.1 Long-term abstraction and water level

We compared average concentrations of water quality parameters and potentiometric surfaces for the two periods: The maximum abstraction period and the first period (Table 2). The comparison was only applicable for 27 well fields, because for one well field (Ishøj) the first period and the maximum abstraction period were the same periods. In 23 out of the 27 well fields, the potentiometric surface decreased between the two periods (Table 2). For 24 well fields, abstraction volume observations started more than 5 years after data collection- and water quality sampling started, which is probably the reason for the

224 increased potentiometric surface at four well fields (Table 2). However, when comparing potentiometric
225 surface for maximum abstraction with the initial potentiometric surface, there was a drawdown for all 28
226 well fields (Table 1). In spite of large variations, the changes in potentiometric surface and abstraction
227 showed a statistically significant correlation (Figure 3).

228 *Table 3: Changes in parameters between the first period and the maximum abstraction period. Changes in water quality*
229 *greater than 0, 5, 20, and 60 mg/L resulted in +, ++, +++, and +++, respectively, for increases and -, --, ---, and ----*
230 *respectively for decreases. For changes in drawdown (dh) greater than 0, 1, 2, and 6 m were assigned +, ++, +++, and*
231 *++++, respectively, for increases and -, --, ---, and ----, respectively, for decreases. n.a. was a well field where the first*
232 *period and the maximum abstraction period were the same period. 0 was no measured difference between the periods.*
233 *No. of years between periods is the difference between the first year in each period.*

<i>Well field</i>	<i>No of years</i>	<i>dh (m)</i>	<i>Chloride</i>	<i>Sulfate</i>	<i>Calcium</i>	<i>Magnesium</i>	<i>Sodium</i>
<i>between periods</i>							
<i>Almsgård</i>	15	++	----	++++	+++	--	----
<i>Assermølle</i>	56	+++	---	++	+++	++	----
<i>Attemose</i>	4	++	+	+	+	+	-
<i>Bjellekær</i>	38	+++	+	+++	++	+	--
<i>Bogøgård</i>	28	++++	---	+++	++	+	---
<i>Brokilde</i>	46	+++	-	+++	++	+	+
<i>Egholm</i>	22	++	--	++++	+++	+	-
<i>Gevninge</i>	39	+++	++++	++++	++	+	++++
<i>Havdrup</i>	6	+++	++	---	-	-	-
<i>Havelse</i>	43	+	-	++	++	++	-
<i>Hule Mølle</i>	28	++	-	+++	++	0	--
<i>Hørup</i>	8	++++	-	+++	+++	+	-
<i>Ishøj</i>	0	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>
<i>Karlsunde</i>	34	-	-	+++	++	+	--
<i>Katrineberg</i>	22	-	+	++	++	++	-
<i>Kornerup</i>	27	+++	++	+++	+++	++	---
<i>Lavringe</i>	30	++	-	++	++	--	+
<i>Ledreborg</i>	37	+	---	++++	+++	--	---
<i>Marbjerg</i>	22	+++	-	++	++	-	-
<i>Ravneshave</i>	16	+++	---	++++	+++	-	--
<i>Solhøj</i>	46	++	++	+++	+++	+	-
<i>Strø</i>	7	+++	+	+++	++	++	-

Thorsbro	46	-	++	++++	+++	+	+
Tåstrup Valby	23	++	+	++	++	+	-
Vallensbæk	28	+	+++	++++	+++	++	-
Vardegård	29	---	+	++	-	+	--
Værebros	11	+	+	++	++	+	--
Æbelholt	6	+++	+	0	-	+	+

Figure 3: Correlation between yearly observations of drawdown from initial potentiometric surface and abstraction for 28 well fields.

The well fields responded differently to abstraction, with decreased potentiometric surfaces from 2 to 14 m from the first observation to the average of the maximum abstraction period (Table 1). The correlation between abstraction and change in the potentiometric surface (Figure. 3) is significant despite large variations, such as a drawdown for the maximum abstraction period of 14 m for abstracting 1.2 mill m³ of water from Lavringe well field and a drawdown of 6 m for a similar withdrawal at Vardegård well field (Table 1). There are a few negative drawdowns, which means that the potentiometric surface is higher compared to the first registered potentiometric surface. These levels of potentiometric surface are relatively recent potentiometric surface observations from Thorsbro well field (Sl. D), most likely because the initial potentiometric surface does not represent pre-pumping conditions.

247 4.2 Abstraction and water quality

248 Sulfate concentrations increased for 25 out of the 27 well fields (except Havdrup and Æbelholt well fields)
249 and by more than 20 mg/L for 16 out of 27 well fields (Table 2). Calcium concentrations increased at 24 out
250 of 27 well fields, with increases at similar sites that experience increased sulfate concentrations, except for
251 Vardegård. This was expected, since both parameters are affected by pyrite oxidation (Appelo and Postma,
252 2005). Chloride concentrations increased at 14 well fields and decreased at 13 showing that an abstraction
253 will mobilize new water—sometimes from the saline transition zone, and sometimes younger, fresher
254 water as also reported in Appelo, (1994). Sodium decreased at 22 out of the 27 well fields, thus supporting
255 the notion that saltwater mobilization is not a widespread problem for these well fields, albeit Gevninge
256 well field experienced substantial increases in sodium and chloride, indicating saltwater mobilization.
257 Magnesium concentration increased at 20 out of 27 well fields.

258 Changes in sulfate concentration varied between the well fields, ranging from -20 to 172 mg/L, with an
259 average of 48 mg/L when comparing the first period with the maximum abstraction period (SI. E). Due to a
260 delayed response in sulfate, these periods do not show its maximum concentration (SI. D). Havdrup well
261 field (as one of two well fields) saw a decreased sulfate concentration, which we speculated was due to an
262 initial freshening of the aquifer and a subsequent delayed sulfate response. Havdrup experienced an
263 increase in sulfate concentration over time (see SI. D). This was not captured in Table 2, because the
264 periods compared are chronologically close, and therefore the sulfate did not respond fully to the change in
265 the hydraulic gradient (Table 2). At Æbelholt well field, there are still reduced conditions, and the sulfate
266 concentration is between 0-17 mg/L throughout the analysis period.

267 The results in Table 2 highlight links between changes in hydraulic gradients and changes in water quality,
268 most noticeably for sulfate. The absolute concentrations for the two periods and the last period are
269 illustrated in SI. E.

270 We performed paired correlations of all parameters for yearly observations and for a 20-year delay in water
271 quality parameters compared to the potentiometric surface (SI. F). The correlations are not used further in
272 this study, since processes and drivers (stressors) other than abstraction might affect them, and this was
273 beyond the scope of this article.

274 4.2 The relationship between groundwater quality and potentiometric surface drawdown

275 Long-term changes in abstraction, potentiometric surface and four water quality parameters for two typical
276 well fields showed links between potentiometric surface and water quality limits (Figure 4). One of the well
277 fields, Hørup, had a typical abstraction pattern with high withdrawals before 1995, and lower thereafter.
278 The potentiometric surface showed a response to the abstraction without too much fluctuation. Since the
279 water quality data started approximately with initiating water abstraction, we expected to observe a
280 development in water quality from the beginning of the process. Marbjerg well field has been active since
281 1934, and therefore we expected to be able to observe late responses in terms of long-term abstraction.
282 Long-term trends for all 28 well fields are detailed in SI. D.

283

284 *Figure 4: Water quality parameters, such as sulfate, chloride, calcium, and sodium, plotted with the potentiometric*
 285 *surface and abstraction for Hørup and Marbjerg well fields. The hatched areas refer to the periods compared herein: grey*
 286 *marks the first period, red marks the maximum abstraction period, and green marks 20 years after the maximum*
 287 *abstraction period.*

288 The potentiometric surface at Hørup well field seemed to respond directly to abstraction; when the water
289 abstraction was high, the potentiometric surface was low, and when the water abstraction decreased, the
290 potentiometric surface stabilized at a higher level. We did not have access to data of water abstraction that
291 lead to the initial decrease in the potentiometric surface around 1956. At the start of water quality
292 sampling in 1955, sulfate concentration was 15 mg/L and it increased until around 1982, when it stabilized,
293 followed by a slight decrease from around 1997. Sulfate concentration ended at approximately 140 mg/L,
294 which is 10 times the initial concentration. Chloride concentration increased steadily over the whole period,
295 from 25 to 50 mg/L in 2014. Marbjerg well field had larger fluctuations in potentiometric surface, and so it
296 might have had another abstraction management or been affected by climate and other factors. The
297 potentiometric surface dropped around 1934 and increased from 1941-1944 (probably due to a pause in
298 abstraction, maybe related to the 2. World War). Sulfate concentration initially decreased, either due to a
299 change in water composition or because of processes related to the increase in the potentiometric surface.
300 The final concentration was 71 mg/L, which was twice the concentration of the first period. The
301 potentiometric surface increased from 1990 and the sulfate concentration slightly decreased from 1993.
302 Similarly to Hørup, chloride concentration increased steadily over the whole period, albeit only by 13%.

303 4.3 Potentiometric surface and sulfate

304 From Table 2, we observed indications of a link between drawdown and sulfate concentrations. The
305 correlation between the drawdown for the maximum abstraction period and the sulfate concentration 20
306 years thereafter is statistically significant in spite of variations, which supports the hypothesis that sulfate
307 increases with a decreasing potentiometric surface (Figure 5). Despite the large spread in points the data
308 can be represented by the fitted line (statistical significant for $\alpha=95\%$). Egholm well field was an outlier and
309 we expected two possible reasons for this 1) the initial potentiometric surface did not represent pre-
310 pumping conditions and therefore the measured drawdown was relatively small or 2) that it is a leaky
311 aquifer or only partly protected by an impermeable layer. Since we cannot exclude Egholm well field, it is
312 included in the t-test. Evaluating the residuals (Sl. G), we see that our data are not independent and

313 identically distributed, and therefore not well represented by a linear regression. We expect that the
314 impacts from drawdown on water quality will decrease with increasing drawdown, however for larger
315 drawdowns than represented in our data. Therefore we believe that a linear correlation is the best
316 explanation and we did not find a significant improvement of fit from transforming the data.

317 Since drawdown was measured in a monitoring well at a given distance from the well field (Table 1), we
318 expected that monitoring wells far away from the well field would have a smaller drawdown compared to if
319 the well field was located closer. If the actual drawdown close to the well field result in increased sulfate
320 concentrations, this could be hidden by a relatively small drawdown in a remote monitoring well. However,
321 the distance from center of the well field to the monitoring well does not clearly affect changes in sulfate
322 (Figure 5), and does not improve the statistical significance albeit well fields with distances greater than 800
323 m between the center of the well field to the monitoring well are all below the regression line. The two well
324 fields with the smallest changes in sulfate concentration (and relative large distance between center of well
325 field and monitoring well between 800 to 1600 m) are Attemose and Æbelholt well fields. Attemose well
326 field have a low change in sulfate because there are few years between the periods compared. Æbelholt
327 well field have a steady sulfate concentration throughout the period and continuously reduced conditions
328 with a sulfate concentration of 2 mg/L for the last period for further statistical analysis of the data see SI. G.

Figure 5: Linear Fit of correlation between drawdown and changes in sulfate concentration with 20-years delay for sulfate for 26 well fields including 95% Prediction Interval. Drawdown was compared from the first period and the maximum abstraction period. The change in sulfate concentration was compared between the first period and 20 years after maximum abstraction. The colors of the dots represent the distance between the center of the well field and the monitoring well.

There were large differences in the delay periods of sulfate concentration as a response to abstraction. Studying the development of sulfate concentration over time in SI. D, it is evident that for some well fields the sulfate peaked at the same time as the abstraction peaked (e.g. Ravneshave well fields), whereas other well fields responded slower (e.g. Havelse well field). Several factors influence water quality at individual well fields, and so it is relevant to study further how delay-times affect sulfate concentrations. For 13 out of the 26 well fields, sulfate concentrations were higher for the last period compared with the maximum abstraction period, for seven well fields it was lower, and for six it changed by less than 10%. However, among 0, 5, 10, 15 and 20 years' delay, the best correlation between drawdown and sulfate concentration was found 20 years after the maximum abstraction (Figure 5, SI. H). There linear fit only represents 26 well fields, because for two of the well fields the maximum abstraction is less than 20 years before the last water quality samples.

346 Long-term trends in the water quality parameters excluded from this study can be found in SI. I. These
347 water quality parameters were excluded, because the data did not show developments in concentration,
348 the concentrations were generally low or the data period too short, to detect development or a connection
349 to drawdown (Table 2). We had expected that arsenic and sulfate concentrations would be correlated (e.g.
350 Zhang et al., 2013), however arsenic concentrations were low, with only one well field with concentrations
351 above 5 µg/L, which looks like outliers (Egholm well field). A Danish study finds relatively little arsenic in the
352 groundwater around Copenhagen, however there are larger concentrations in other parts of Zealand
353 (Larsen and Kjøller, 2009). Similarly, a relation between sulfate and nitrate has been reported in literature
354 (Jørgensen et al., 2009; Zhang et al., 2013), however, nitrate concentrations were low at most well fields
355 (only 8 out of 28 well fields had concentrations above 10 mg/L). Since nitrate is an oxidizer in pyrite
356 oxidation the relative high sulfate concentrations are in good coherence with the relatively low nitrate
357 concentrations.

358 4.4 Water quality variations within the well fields

359 Water quality is more complex than appears from samples of combined water taken from a well field, and
360 therefore we cannot expect all well fields to behave uniformly. For example, Bogøgård had a small change
361 in sulfate compared to a large drawdown (Figure 5, Figure 6), thereby indicating that it is not solely
362 abstraction and a changed potentiometric surface that determine groundwater quality—well construction
363 and well screen placing can also affect it (Baba and Ayyildiz, 2006). The correlation between drawdown and
364 sulfate shows variance among the observations (Figure 5), one of the reasons for which could be multiple
365 processes occurring at the same time within the same well field. At the Bogøgård well field, the
366 concentration of water quality parameters differed between the wells, and between two periods, we
367 observed both increases and decreases in different parameters between different wells, for example in
368 sulfate concentration (Table 3). Table 3 reveals that the sulfate concentration increased by 37% in well 1
369 and decreased by 50% in well 2, between the same periods within the well field. Furthermore, sulfate
370 concentrations differ between the wells (79 to 239 mg/L in the second period), indicating that they abstract

371 different types of water. Overall, sulfate concentration for the combined water from the well field
 372 increased by 18%. Measuring the changed water quality in the well field mix can be masked by changes in
 373 individual wells. Hence, we can expect a varied aquifer response to abstraction that depends also on the
 374 distribution of pumping rates between the wells and other factors, and it is important to acknowledge that
 375 the analysis based on combined water from a well field does not explain specific changes or processes for
 376 individual wells.

377
 378 *Figure 6: Sulfate, chloride, calcium, and sodium concentrations plotted with the potentiometric surface and abstraction for*
 379 *Bogøgård well field, which has a relatively low change in sulfate compared to a relatively large drawdown. The hatched*
 380 *areas refer to the periods compared: Grey is the first period, red is the maximum abstraction period and green is 20*

381 years after the maximum abstraction period. The black square represents the first period of water quality samples from
 382 individual wells in Table 3, and the black line represents the second period.

383 Table 4: Water quality samples from individual wells (1-3) at Bogøgård well field for two periods. The first period is 1970-
 384 1979, and the second period is 2012 (these wells closed after 2012).

Wells (DGU no.)	Well 1 (200.3147)		Well 2 (200.3148)		Well 3 (200.3043)		Well field (combined water)	
Period	1970s	2012	1970s	2012	1970s	2012	1970s	2012
Screen depth [m]	43 – 52		38 – 52		43 - 52		38-65	
Chloride (mg/L)	64	43	50	96	40	62	88	91
Hydrogen-carbonate (mg/L)	357	362	363	342	339	324	338	337
Sulfate (mg/L)	95	130	152	79	106	94	73	86
Calcium (mg/L)	121	130	131	110	106	110	105	120
Magnesium (mg/L)	21	19	25	18	28	16	19	20
Sodium (mg/L)	41	34	41	61	27	32	59	57

385 4.5 Defining a sustainable abstraction?

386 Our results support the hypothesis that water abstraction from a confined aquifer induces a decrease in the
 387 potentiometric surface and changed water quality across multiple well fields. This awareness takes us one
 388 step closer to defining a new criterion for sustainable groundwater abstraction and aquifer deterioration,
 389 which should serve as part of the complex task of ensuring sustainable groundwater abstraction, including
 390 sufficient water for environmental uses (International River Foundation, 2007), the use of renewable
 391 energy sources (Flavin and Lenssen, 1994), the efficient use of resources (Giljum et al., 2008), and other
 392 considerations such as toxicity, acidification etc. (Laurent et al., 2012). Since sulfate is the most sensitive
 393 parameter responding to abstraction for the 28 well fields (Table 2), it was the most suitable indicator for
 394 quantifying aquifer deterioration at the investigated well fields. If the conditions/geology are different, e.g.
 395 more risk of saltwater intrusion or mobilization, or pyrite is absent in the ground, another parameter

396 should be chosen. Accepting that groundwater abstraction will affect water quality leads to the following
397 question: When is changed water quality unacceptable?

398 Unacceptable changes can be described by different approaches, which we in the following discussion will
399 refer to as A, B and C. Firstly (A), water quality does not meet drinking water quality standards, e.g. sulfate
400 concentrations above 250 mg/L (The Danish Nature Agency, 2018); secondly (B), trends in one or more
401 parameters will exceed the water quality standard within an unacceptable timeframe; or thirdly (C),
402 persistent increased water quality parameters are unacceptable, no matter the proximity to the threshold
403 values, as a precaution for ecosystem changes and a general sign of human impacts on the aquifer.
404 Additionally, a water utility that has made large investments in constructing pipe systems, waterworks, etc.
405 will be very dependent on stable water quality for decades to come.

406 In terms of approach A, drinking water quality standards are defined to secure healthy water that looks
407 clean and is without color, taste, or odor (The Danish Nature Agency, 2018). For example, sulfate can,
408 depending on the concentration, result in a bitter taste and provoke a laxative effect (Călinescu et al.,
409 2016). Sulfate is only removed by advanced water treatment (Darbi et al., 2003) and is usually not removed
410 at waterworks in Denmark. The sulfate concentrations at the 28 well fields did not exceed drinking water
411 quality standards during the maximum abstraction period; however, two well fields exceeded or came
412 within 5 mg/L of the threshold after the maximum abstraction period (Egholm and Vardegård well fields, SI.
413 D). At Egholm well field, abstraction decreased after 1980, and Vardegård well field was closed in 2010 due
414 to the presence of nickel.

415 Definitions B & C are precautionary approaches to defining unacceptable changes. By studying the time
416 series and defining unsustainable changes in sulfate concentrations as a '*minimum five observations of the*
417 *initial concentration plus 20 mg/L*', then 26 out of 28 well fields experience aquifer deterioration at some
418 point before 1995. If unsustainable changes in sulfate concentration were defined as a '*minimum of 10*
419 *observations of the initial concentration plus 50 mg/L*', 13 well fields experienced aquifer deterioration

420 before 1995. Generally, sulfate increased for a number of years and peaked sometime after high
421 abstractions, after which it stabilized or decreased slowly.

422 *4.5.1 Recent developments at the 28 well fields*

423 Analyzing the sustainability of recent abstractions at the 28 well fields shows stable or slightly decreased
424 sulfate concentrations after 1995 (Figure 7.a). The abstraction peaked in 1982 and the average drawdown
425 was largest in 1978 for the 28 well fields (Figure 7.b). The decreased water abstraction since 1995 appears
426 to have resulted in an increased potentiometric surface and, after some years, stable water quality
427 parameters. Hence, decreased abstraction has alleviated aquifer deterioration in the 28 well fields
428 supplying water to Copenhagen, and so today the abstraction seems to be sustainable in terms of water
429 quality related to potentiometric surface drawdown. Since nitrate is a potential oxidant of pyrite it could be
430 interesting to look further into nitrate leaching and sulfate concentrations (Jessen et al., 2016; Jørgensen et
431 al., 2009).

Figure 7: a) Sulfate concentrations from 1960-2015 for the 28 well fields (represented by different colors). The black line is the average of all sulfate concentrations within each year. The red lines represent +/- std. dev. b) is the total water abstraction since 1962- and the average drawdown at the well fields- at the 28 well fields.

5. Conclusions

Long-term trends in water quality parameters were investigated, using a large dataset of 3,389 water quality samples and more than 10000 potentiometric surface observations for 28 well fields from 1940 to 2015. The analysis enabled us to identify changes in potentiometric surface and water quality over decades and provided valuable information on evaluating sustainable groundwater abstraction:

- Long-term abstraction at 28 well fields resulted in decreased potentiometric surface at all well fields (2 to 14 m), when comparing the initial potentiometric surface observation with the average potentiometric surface for the maximum abstraction period.
- Pyrite oxidation was the main process affecting long term water quality in the studied well fields, as observed in increased sulfate and calcium concentrations.
- The long-term patterns between potentiometric surface and water quality were significant for sulfate and calcium, with increased concentrations for 25 and 24 out of 27 well fields, respectively, when comparing the first period with the maximum abstraction period. There is no clear pattern between the potentiometric surface and the parameters chloride and magnesium, where equal amounts of well fields experience increased or decreased concentrations. However, sodium concentrations decreased for 23 out of 27 well fields.
- If we define sustainable groundwater abstraction as fewer than five observations of the initial sulfate concentration plus 20 mg/L, 26 out of 28 well fields show indications of unsustainable abstraction before 1995. After 1995, the well fields generally show stable concentrations of water quality parameters or slightly decreased concentrations and the groundwater abstraction at 24 out of 28 well fields appear to be sustainable.
- Sulfate concentration had different delay periods from the maximum abstraction period, and the best correlation between increased drawdown and increased sulfate concentration was found for a 20-year delay in sulfate response.

Acknowledgement: We would like to thank Kristian Bitsch and Jörg Schullehner for guidance and discussions of the results and progress. This study is conducted at the Department of Environmental Engineering at Technical University of Denmark in collaboration with Hovedstadsområdet

465 Forsyningsselskab, VandCenter Syd and Aarhus Vand. The work is part of an industrial PhD program, funded
466 by the industrial partners and Innovation Fund Denmark.

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