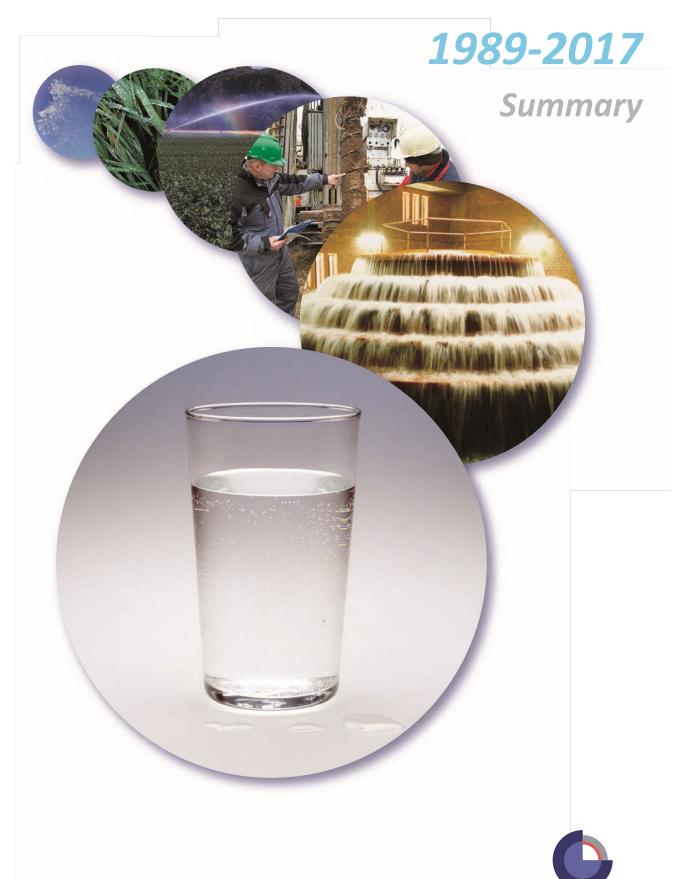
# **GROUNDWATER MONITORING**



GEUS

# 1 Summary

# 1.1 The groundwater resource and its exploitation

#### Introduction

In the past 100 years, the amount of precipitation has followed an increasing trend. Thus, in the latest climate period from 1991 to 2015, precipitation rose by 4.4% compared with the previous climate period from 1961 to 1990. In absolute numbers, the mean amount of precipitation has increased by 33 mm in the past 30 years, which may have produced a higher groundwater level in some parts of Denmark. A higher groundwater level may be expected particularly in areas that are not artificially drained. In drained areas, increased precipitation will mainly increase the drainage water runoff to wetlands. GEUS has previously assessed that, overall, the groundwater level has increased by 1-2 m after 2000, primarily owing to an increase in precipitation (see Thorling et al., 2016), which is generally underpinned by the groundwater table data up to 2017.

The Danish drinking water supply is based on abstraction of groundwater where the island of Christiansø is the only exception. Here, desalinated seawater is also used as drinking water. Approximately 2,600 general waterworks provide the majority of the groundwater supply for drinking water. Additionally, groundwater is abstracted from a number of non-general water supply facilities that each provides water for 1-9 households.

Agricultural irrigation constitutes a heavily fluctuating share of the total amount of abstracted water. In dry years, about one third of all abstracted water is used for irrigation, but this aggregate share varies considerably from one region to the next.

#### Environmental objectives and the purpose of monitoring the resource

The groundwater resource is monitored to ensure regular assessment of the overall water balance with a view to achieving a sustainable exploitation of the available water resource.

#### **Data basis**

The groundwater level is recorded in the National Groundwater Level Monitoring Programme (Det Nationale Pejleprogram), which includes automatic data collection from approx. 160 groundwater level sounding stations, see Figure 1. The statement of surface and groundwater abstraction is based on data extraction from the Jupiter database as per 7 June 2018. The data extraction covers the 1989-2017 period with notifications having been provided by Danish counties until 2007 and then from municipalities.

#### State and trends

The current state and development in the groundwater level was assessed on the basis of long groundwater table data series from a sounding well within five regional areas. For all of the selected series, the lowest water level is seen at the beginning of 2017 compared with the beginning of 2016, which is probably due to a reduction in groundwater formation in the relatively dry period from September 2016 through February 2017. This pattern is characterised by considerable geographical variation, as the overall trend is that wells which had a low water level at the beginning of 2017 are found in Western Jutland, whereas wells which had no significant reduction in the water level at the beginning of 2017 are those found close to the Sea of Kattegat in: East Jutland, on the Island of Samsoe and Northern Funen, and in Southern Zealand and Falster.

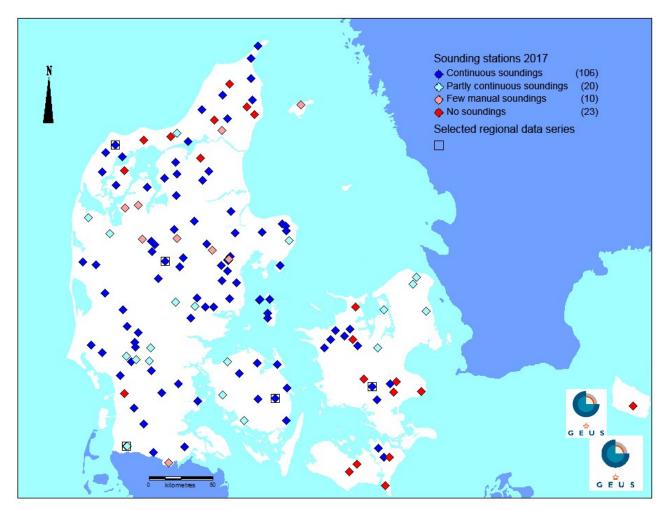


Figure 1. Geographical distribution of the 159 sounding stations that formed part of the National Ground Water Table Monitoring Programme in 2017, including five regional indicator measurement stations with long time series. A detailed presentation of the results for the five regional indicator measurement stations is provided in Annex 1.

Figure 2 shows the abstraction of water by general water works, by professional irrigation, by industry and surface water. The total reported abstraction is presented with a broad blue line. The total annual abstraction (excluding field irrigation) around 1990 was approx. 700 M m³/year. It decreased going forward until 1999 to approx. 530 M m³/year and followed a slightly decreasing trend in the 1999-2017 period from approx. 530 M m³/year to approx. 475 M m³/year, and in 2017 it totalled 473 M m³/year. In the past 15 years, abstraction for field irrigation has varied from approx. 100 to 300 M m³/year, with considerable inter-annual variation, depending on precipitation levels.

For the general water works, the abstraction decreased in the 1989-2000 period from approx. 600 M m<sup>3</sup> to 400 M m<sup>3</sup>/year. Subsequently, consumption decreased at a slower rate, reaching 370 M m<sup>3</sup>/year in 2017. Abstraction of groundwater for field irrigation, horticulture and fish farming (the "Professional Irrigation" category) accounted for approx. 259 M m<sup>3</sup>/year in 2017, which exceeds the median level (210 M m<sup>3</sup>/year) for the entire period (1989-2017).

Water consumption in companies that have independent abstraction facilities followed a slightly decreasing trend from 1989 to 2017.

In Denmark, abstraction of surface water is very limited and was halved in the 1989-2016 period, thus now accounting for approx. 8 M m³/year. Surface water is not included in the drinking water supply.

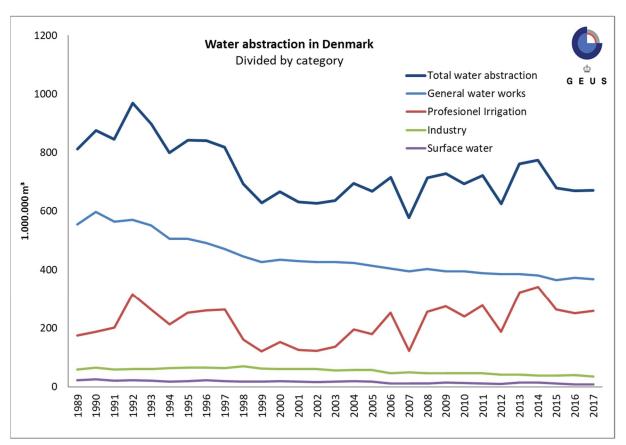


Figure 2. Abstraction of groundwater in the 1989-2017 period by general water works, professional irrigation, industry and surface water. The total reported abstraction is presented with a broad blue line. Please note how total reported abstraction varies with professional irrigation, of which field irrigation constitutes the majority.

#### 1.2 Nitrate

#### Introduction

Nitrate in groundwater should be avoided to preserve drinking water quality and to avoid the risk of affecting the surface water environment and groundwater dependent ecosystems. Specifically, nitrate in drinking water may be harmful, and nitrate in groundwater may contribute to eutrophication of watercourses, lakes and the marine environment through outflow to surface water. The threshold value for nitrate in both groundwater and drinking water is 50 mg/l both nationally and in the EU. Approx. 16% of Denmark is characterised as nitrate-sensitive abstraction areas in the action plans.

#### **Data basis**

Water samples are collected from three types of wells: GRUMO (The Groundwater Monitoring Initiative), LOOP (The Agricultural Catchment Monitoring Programme) and water works wells (The Water Works Well Monitoring Programme). The GRUMO and LOOP wells cover the groundwater part of the national monitoring programme, coined NOVANA. The GRUMO wells are found in groundwater wells with depths down to more than 100 m below surface. The LOOP wells are short, near-surface wells established to monitor nitrate leaching to the upper groundwater located below cropland. Each monitoring well has one or more screens to provide monitoring points at different depths. Data from the active water works wells are contributed from the Waterworks' statutory well monitoring programme. In the 2013-2017 period, groundwater samples from 1,225 GRUMO wells, 98 LOOP wells and 5,949 water works wells were analysed for nitrate.

## State and trend

Figure 3 shows the nitrate content of GRUMO and LOOP monitoring points and active water works wells that were sampled in 2017. Nitrate is calculated as the annual mean value recorded for each monitoring point. In approx. 14% of GRUMO and 20% of the LOOP monitoring points, the nitrate content exceeded 50 mg/l, whereas less than 1% of the water works wells recorded more than 50 mg/l of nitrate. In the GRUMO and LOOP monitoring points, the nitrate concentration reaches 25-50 mg/l in approx. 16% and 31%, respectively, as opposed to only 4.7% in the water works wells. Nitrate-free groundwater (a nitrate concentration  $\leq 1$  mg/l) occurs in approx. 51% of the GRUMO and approx. 27% of the LOOP monitoring points, and in approx. 83% of the water works wells.

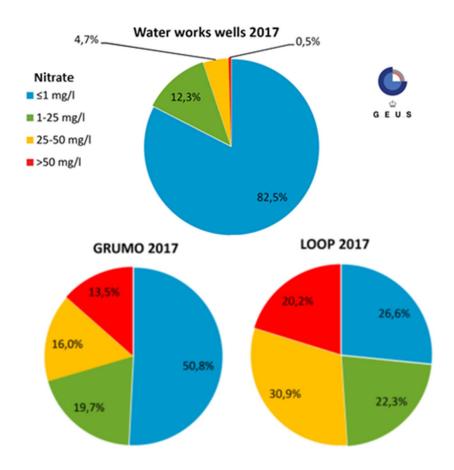


Figure 3. The distribution of the mean nitrate content in 2017 in 1,043 GRUMO, 94 LOOP and 1,681 active water works wells.

Figure 4 presents the geographical distribution of the nitrate content in GRUMO monitoring points in 2017 and shows that nitrate contents exceeding the 50 mg/l threshold value were found evenly in various locations across the country.

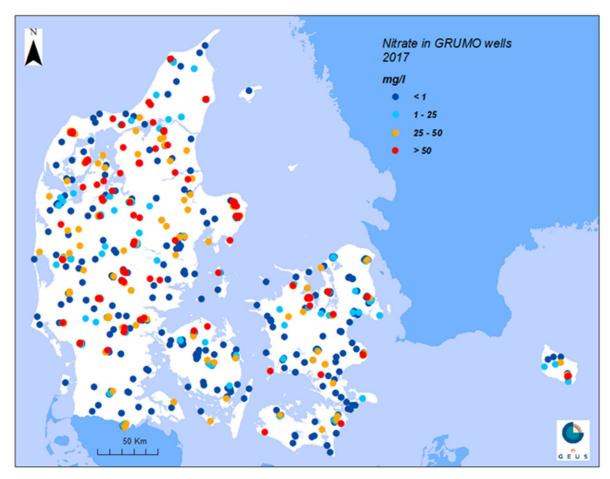


Figure 4. GRUMO. Nitrate content in groundwater in 2017 (1,043 GRUMO monitoring points). The nitrate content is divided into four categories according to concentration. The highest concentrations are depicted on top of lower values.

Figure 5 presents the distribution by depth for nitrate in GRUMO monitoring points sampled in 2017. Depth is divided into 10-metre intervals. Nearest to the terrain (0-10 m below the land surface), nitrate is present (>1 mg/l) in approx. 65% of the monitoring points. The concentration of nitrate in groundwater exceeds 50 mg/l in approx. 17% of the monitoring points and exceeds 25 mg/l in approx. 35% of the monitoring points in the depth interval 0-10 m below the land surface. In general, the nitrate content decreases by depth. From 50 m below the land surface, no mean nitrate content exceeding 50 mg/l has been detected, and the nitrate concentration is generally below 1 mg/ from approx. 80 m below the surface.

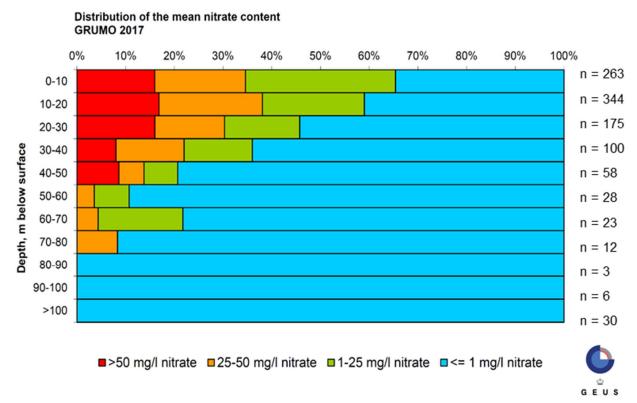


Figure 5. GRUMO. Distribution by depth (to the upper limit of the screen of the monitoring point in m below the land surface) of the mean nitrate content in 2017 in 1,042 GRUMO monitoring points. The red signature presents the percentage share with concentrations exceeding the 50 mg/l threshold value. The number of monitoring points in each depth interval is shown to the right of the figure.

Figure 6 shows the nitrate content in oxic groundwater in GRUMO monitoring points from 1990-2017 by sampling time. The figure is based on the mean annual nitrate content per monitoring point. The nitrate content of oxic groundwater is presented as box diagrams for each sampling year, showing 10%, 25%, 50% (median), 75% and 90% fractiles and average values (mean) and the threshold value.

The figure presents the nitrate content in groundwater at the time of the sampling and does not reflect a real development of the impact from nitrate leaching over time. This is because the groundwater's age varies from a few years to 50 years, as determined through groundwater dating (Hansen et al., 2017).

In all years, the oxic groundwater reflects a considerable spread. Throughout the monitoring period (1990-2017), the median value is somewhat lower than the mean value, indicating that a limited number of very high nitrate values are recorded. The highest median and mean values are seen in the 1996-1998 period.

In the most recent decade, the mean nitrate concentration value in oxic groundwater - depending on the sampling year - has fluctuated around the 50 mg/l threshold value, but with the majority of average annual values falling below the threshold and a trend towards fewer monitoring points recording very high concentrations (a decreasing 90% fractile).

In 2017, the measured mean value in oxic groundwater was 42 mg/l and the median 37 mg/l nitrate, which is the lowest level recorded in the monitoring period.

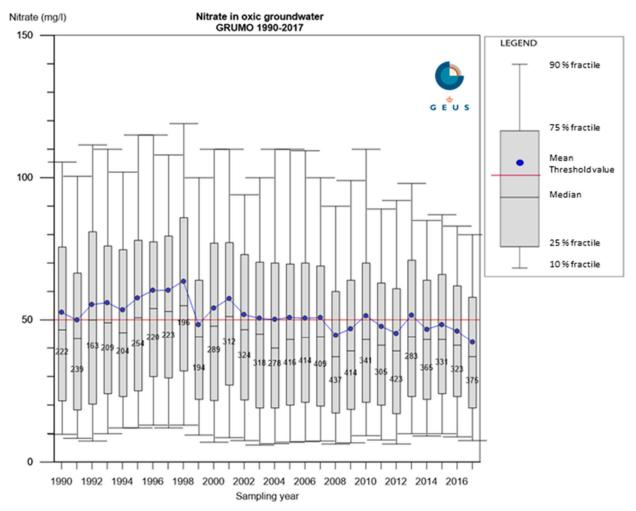


Figure 6. GRUMO. Time series for nitrate in oxic groundwater in GRUMO monitoring points shown as box diagrams for each sampling year in the 1990-2017 period. The figure is based on the mean nitrate content per monitoring point per year. The number of monitoring points is stated for each year.

Figure 7 presents the geographical distribution of the groundwater nitrate content in active water works wells during the five past years (2013-2017), calculated as the mean value from the 2013-2017 period of the annual mean nitrate value in each well.

The highest nitrate concentrations in water works wells were seen mainly in North Jutland, Thy, Himmerland and on the peninsula of Djursland. This is due to a poor natural protection of the aquifers in these areas due to the absence of a protective clayey cover layer and a relative deep-lying nitrate front (the maximal depth extension of nitrate in the aquifers).

Figure 8 Shows the nitrate distribution by depth in active water works wells in the 2013-2017 period. The nitrate concentrations are lower in the water works wells than in the GRUMO monitoring points (Figure 5). Even so, the period 2013-2017 saw nitrate concentrations exceeding 50 mg/l as deep as 90-100 m below land surface in a limited number of active water works wells. Nitrate concentrations decrease gradually with increasing depth. Nitrate concentrations reaching 50 mg/l were also found in the deepest water works wells, which are deeper than 100 m below the land surface.

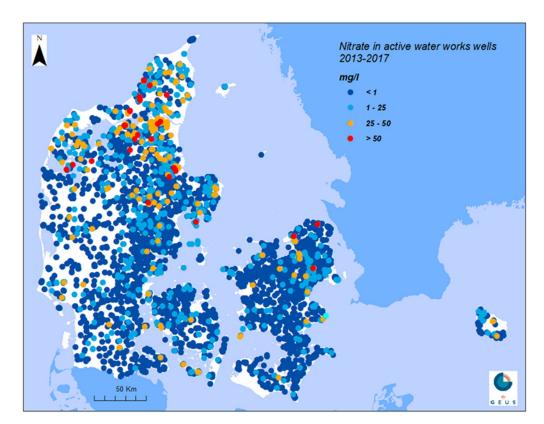


Figure 7. The Water Works Well Monitoring Programme ('Boringskontrollen'). Groundwater nitrate content in active water works wells (5,949), by four concentration categories. Data show mean values per well in the 2013-2017 period. Some wells may have been included that no longer form part of the drinking water supply. The highest concentrations are depicted on top of lower values.

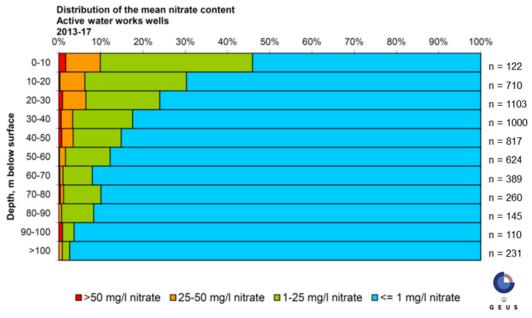


Figure 8. The Water Works Well Monitoring Programme ('Boringskontrollen'). Depth distribution of the mean nitrate content in 2013-2017 relative to top of the well in m below land surface in 5,511 active water works wells. The red signature presents the percentage share with concentrations exceeding the 50 mg/l threshold value. The number of wells in each depth interval is shown to the right of the figure.

The spreading of nitrate at greater depths in the water works wells may occur in locations where pumping cause nitrogenous groundwater to be drawn down to great depths in the aquifers. Additionally, the data basis describing the deep part of the groundwater is larger for the water works wells than for GRUMO monitoring points. The generally lower nitrate content in active water works wells compared with the nitrate content in GRUMO monitoring points is also owed to the fact that the water works avoid abstraction from wells that fail to meet the threshold value of 50 mg/l nitrate (Schullehner and Hansen, 2014).

## 1.3 Pesticides

#### Introduction

Pesticides and their metabolites may occur in groundwater due to professional or private use of pesticides in woods or agriculture, parks, gardens, sports facilities, at fortified areas and infrastructural facilities. Some pesticides are also used, or were previously used, as seed treatment and as biocides in, e.g., paint and wood protection products.

# Environmental objectives and the purpose of the monitoring

For individual pesticides and their metabolites, the threshold value in groundwater and drinking water has been set to  $0.1~\mu g/l$ , whereas the threshold for the sum of individual compounds is  $0.5~\mu g/l$ . The  $0.1~\mu g/l$  threshold value applies to use as a pesticide and a biocide alike. The pesticide content in the groundwater is monitored, among others, to assess if the regulation of pesticide consumption has the desired effects.

#### **Data basis**

This report brings pesticide analyses from the 1990-2017 period from the Groundwater Monitoring Initiative (GRUMO monitoring points) and groundwater samples from active water works wells (the Water Works Well Monitoring Programme), including results from screening studies for desphenylchloridazon (DPC) and methyldesphenylchloridazon (MDPC) and 1,2,4-triazole. To provide a more precise and uptodate status on the occurrence of DPC and MDPC, the results from a recent statement are also presented herein. The statement (GEUS memorandum, 2018) was prepared for the Water Panel's Working Group on Pesticides and Drinking Water Control, which was tasked to collect information on DPC. The statement includes data reported and approved in Jupiter up to and including 23 October 2018.

In 2017, a total of 1,046 GRUMO monitoring points were sampled for pesticide analysis, as the Danish Environmental Protection Agency had in place in 2017 the monitoring of all monitoring points used under the programme in the period. In this context, the Danish Environmental Protection Agency included 126 "resting" monitoring points that have not otherwise been sampled for pesticide analysis in recent programme periods. Additionally, the Danish Environmental Protection Agency has established new monitoring points in the distributed net of monitoring stations to represent all Danish groundwater resources or groups of groundwater resources. The 2017 data set therefore deviates significantly from the data set used in preceding years.

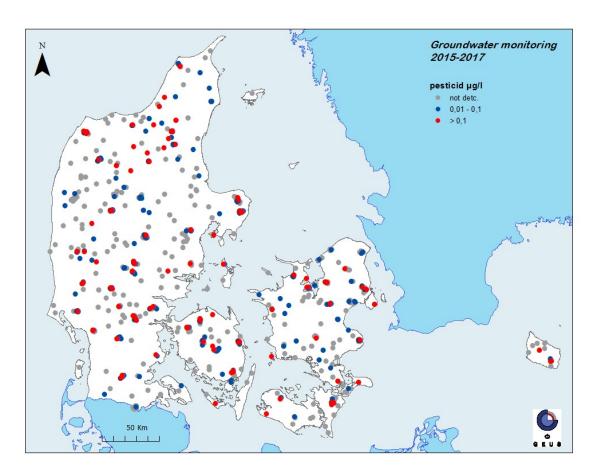
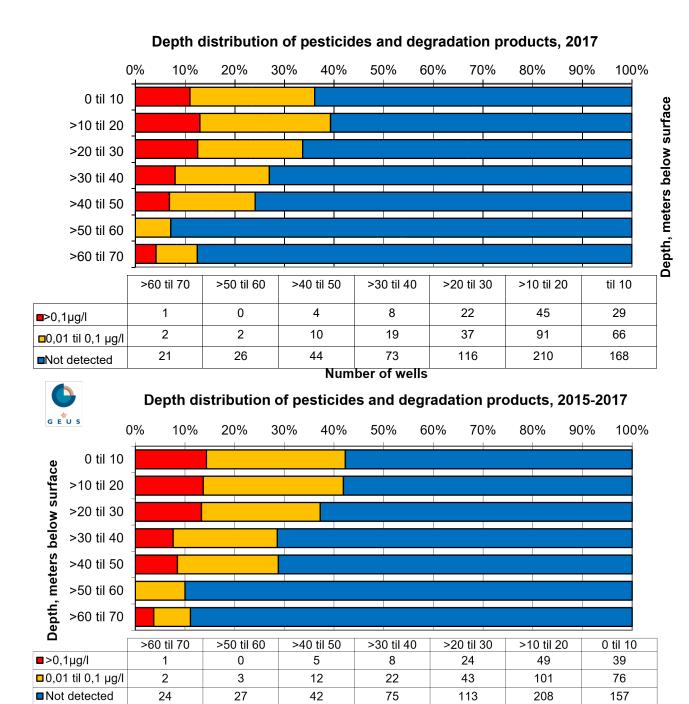


Figure 9. GRUMO. Pesticides and metabolites in GRUMO monitoring points sampled in the 2015-2017 period (1,087 monitoring points). The results are divided into three concentration intervals, where a minimum of one pesticide has been detected at least once at a concentration exceeding the threshold value ( $>0.1 \,\mu g/l$ ), where a minimum of one pesticide has been detected at least once below the threshold value ( $0.01-0.1 \,\mu g/l$ ), or where pesticides have not been detected. The highest concentrations are depicted on top of lower values.

Over the years, a varying number of compounds have formed part of the analysis programme. An overview of the analysis programmes for the groundwater monitoring initiative in previous years is provided in Annex 4. In pesticide statements, each monitoring point only counts towards the total of a single concentration category even though several pesticides may have been detected at different concentrations in any single sample from a monitoring point. If a compound was detected at least once in the relevant period in a concentration >0.1  $\mu$ g/l, the monitoring point is counted as >0.1  $\mu$ g/l. If compounds were detected in lower concentrations, the monitoring point counts towards the concentration interval 0.01-0.1  $\mu$ g/l. Monitoring points in which no compounds have been detected are classified in the group "No compounds detected".

# State and trends in the Groundwater Monitoring Initiative

Figure 9 presents the geographical distribution of groundwater pesticide content in GRUMO monitoring points in the latest 3-year period 2015-2017, during which the majority of monitoring points may be expected to have been sampled at least once. It is evident from Figure 9 that pesticide findings were distributed evenly across the country. Figure 10 shows the distribution of pesticide findings by depth in GRUMO monitoring points, sampled in 2017 and in the three-year-period 2015-2017, respectively. In 2017, pesticides were detected in 24-39% of the sampled monitoring points at each of the used depth intervals down to 50 m below the surface.



#### Number of wells

Figure 10. GRUMO. Distribution by depth of pesticides and metabolites in GRUMO monitoring points analysed in 2017 and in the 2015-2017 period. The monitoring points were divided into three concentration intervals: >0.1  $\mu$ g/l, 0.01-0.1  $\mu$ g/l, and not detected (below the detection limit, typically <0.01  $\mu$ g/l). Depth refers to the distance from the terrain to the upper limit of the monitoring point. Data from screenings are included in the calculations.

The depth distributions for 2017 and 2015-2017 differ from the corresponding figures in previous reports as the fractions with findings now generally decrease by increasing depth. We no longer see a marked peak with higher fractions at depths of 10-40 m below the land surface. This difference is seen most clearly for the 2015-2017 period statement. The difference is likely owed to a combination of the fact that

many new monitoring points have been included in the statement (newly established monitoring points and re-activation of "resting" monitoring points) and results from the screening for DPC, MDPC and 1,2,4triazole in selected monitoring points. It must be expected that the depth distributions will be very different in years to come as only a few monitoring points had been screened for desphenylchloridazon (DPC), methyldesphenylchloridazon (MDPC) and 1,2,4-triazole at the time of the data extraction, and no monitoring points had been tested for the most recently identified (in 2018) problem compound of N,Ndimethylsulfamide (DMS).

#### Allowed and banned compounds detected in the Groundwater Monitoring Initiative.

Pesticides may be divided into three groups: approved, regulated and banned, on the basis of the status of each compound as per 22 June 2018. In this context, regulated pesticides are substances that, pending their approval, have been subjected to restrictions with a view to protecting groundwater. The allowed pesticides include both the approved and the regulated compounds.

With the latest change of the analytical programme, the approved substances are still represented only by glyphosate and its metabolite AMPA. Even so, glyphosat/AMPA are not representative for the many and very different approved compounds. Approved compounds are therefore not stated separately, but rather along with the regulated compounds. Together, the two categories form the group of allowed compounds, i.e., compounds that currently have legal uses. Table 1 presents the distribution of allowed and banned compounds as calculated for the 2015-2017 period. A minimum of one allowed pesticide or metabolite was found at least once in 5.9% of the tested monitoring points, whereas the 0.1 µg/l threshold value had been exceeded at least once in 1.6% of the monitoring points. Banned pesticides and their metabolites were found at least once in 27.3% of the monitoring points, and the threshold value was exceeded in 7.2% of the monitoring points. Banned compounds were thus detected far more frequently than allowed compounds, which may in part be due to the fact that banned compounds constitute the overwhelming majority of the compounds tested for in the analysis programme. Additionally, banned compounds appear in groundwater for many years after their use has been banned. The fractions with findings were considerably lower than in previous statements which is likely owed to the introduction of many new monitoring points (newly-established and re-activated "resting" monitoring points) that have low fractions of findings. Findings of regulated compounds may be due to a previously allowed use that was subsequently banned.

Table 1. GRUMO. Occurrence of allowed and banned pesticides in the 2015-2017 period. Each monitoring point may contain both allowed and banned compounds, and may therefore be represented in both categories. The monitoring points are divided into monitoring points with a minimum of one finding and monitoring points with one or more finding(s) that exceed the threshold value ( $>0.1 \mu g/l$ ). Statements for each of the years in the 2007-2016 period are presented in Annex 7. Data from screenings are included in the calculations.

	Monitoring points Number			Monitoring points Share (%)	
2015-2017	Total	With findings	>0.1 μg/l	With findings	>0.1 μg/l
Allowed compounds	1,086	64	17	5.9	1.6
Banned compounds	1,086	296	78	27.3	7.2

#### Pesticides in water works wells

Figure 11 presents the geographical distribution of groundwater pesticide content in active water works wells in the 2013-2017 period, during which the majority of the active wells may reasonably be expected to have been sampled at least once. It is assessed that the frequency of exceeded threshold levels is over-represented in the northern-most part of Jutland, in a band cutting across South Jutland and Funen and in the Southwestern-most part of the greater Copenhagen area. The map therefore shows a different

extension than the corresponding map that presents GRUMO data. The differences are, in part, due to the fact that over the years, the water works have discontinued wells with high pesticide concentrations due to, e.g., BAM and DEIA, when possible, in part owed to the fact that a considerable share of active water works wells have been tested for DPC and MDPC, which produced many findings.

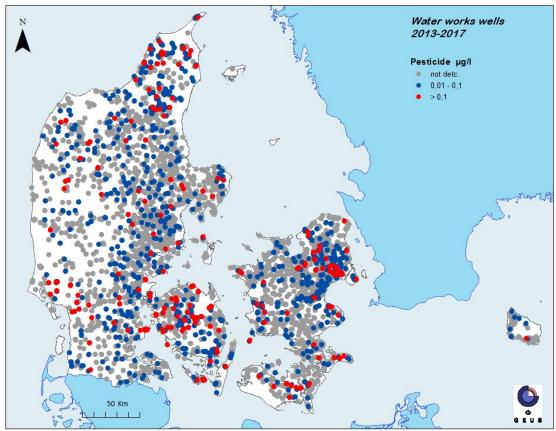
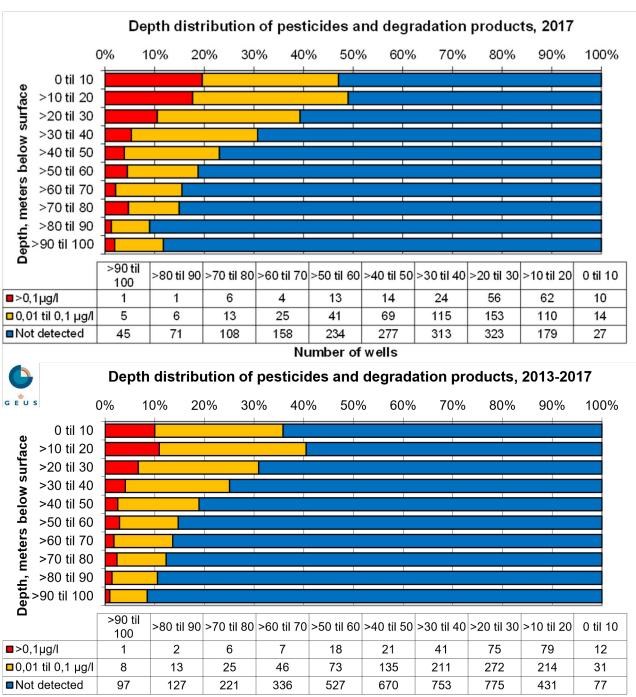


Figure 11. The Water Works Well Monitoring Program ('Boringskontrollen'). Pesticides and their metabolites in groundwater in active water works wells (5,971 wells) in the five-year-period 2013-2017. The results are divided into three concentration intervals, where a minimum of one pesticide has been detected at least once at a concentration exceeding the threshold value (>0.1  $\mu$ g/l), or a minimum of one pesticide has been detected at least once below the threshold value (0.01-0.1  $\mu$ g/l), or pesticides have not been detected. The highest concentrations are depicted on top of lower values.

Figure 12 shows the share of pesticide findings in 2017 and in the 2013-2017 period in water works wells, by depth measured as the distance from the terrain to the top of the screen. The fraction of findings and number of wells that exceed the threshold value abate with increasing depth, but some findings and excess values were observed in wells in which the filter top is located more than 100 m below the surface. In 2017, an increase was seen in the share of wells with findings and wells that exceed the threshold value for the depths 0-50 m below the surface compared with the depth distribution in 2016. This trend is due to DPC and MDPC findings.



#### **Number of wells**

Figure 12. The Water Works Well Monitoring Programme (Boringskontrollen). The depth distribution of pesticides and their metabolites in water works wells. Above we present 2017 data and below a period statement for the 2013-2017 period. The wells are divided into three concentration intervals, where a minimum of one pesticide has been detected at least once at a concentration exceeding the threshold value (>0.1  $\mu$ g/l), or a minimum of one pesticide has been detected at least once below the threshold value (0.01-0.1  $\mu$ g/l), or pesticides have not been detected (below the detection threshold, typically >0.01  $\mu$ g/l). Depth is the distance from the terrain to the upper limit of the filter. All wells in the various concentration classes and depths are included in the table below each sub-figure.

Table 2 shows a statement of the distribution of allowed and banned compounds for the compounds that formed part of the analysis programme in 2017 (See chapter 5 in the main report, Thorling et al, 2019).

A minimum of one of the banned compounds was detected at least once in 21.8% of the tested water works wells, and the  $>0.1~\mu g/l$  threshold value was exceeded at least once in 4.3% of the water works wells. At least one of the allowed compounds was detected at least once in 4.0% of the tested wells, whereas the threshold value was exceeded at least once in 0.5% of the water works wells. It should be noted that wells may contain both allowed and banned compounds. Each well may therefore be represented in both categories. Therefore, the sum of the groups cannot be used as a measure for the overall finding percentage.

Table 2. The Water Works Well Monitoring Programme ('Boringskontrollen'). Period statement for 2013-2017 presenting the occurrence of allowed and banned pesticides in active water works wells. Each well may contain both banned and allowed compounds, and may therefore be represented in both categories. The wells are divided into wells with a minimum of one finding and wells with one or more finding(s) that exceed the threshold value ( $>0.1 \mu g/l$ ).

		Wells Number	Wells Share (%)		
2013-2017	Total	With findings	>0.1 μg/l	With findings	>0.1 μg/l
Allowed compounds	5,863	237	29	4.0	0.5
Banned compounds	5,968	1,299	256	21.8	4.3

Findings of high concentrations of regulated compounds may be due to a less restrictive use before the compound was regulated, but this cannot be quantified, as the age of the groundwater abstracted from the water works wells is not known with precision. Often these samples are from long filters where groundwater of different ages from various depths is mixed in the aquifers. The age of the water frequently exceeds 15 years, and it should therefore be expected that pesticides that are currently banned or regulated may continue to affect the groundwater quality in the future.

#### Screenings and new compounds

**Desphenylchloridazon (DPC) and methyldesphenylchloridazon (MDPC)** are metabolites from the now banned herbicide chloridazon, which was marketed in Denmark in the 1964-1996 period and used mainly for beetroot (sugar beet and fodder beet). In 2017, the Danish Environmental Protection Agency initiated a screening study of the occurrence of these compounds in selected GRUMO monitoring points (Danish Environmental Protection Agency, 2017) following findings in the point source studies of several Danish Regions. As per 27 October 2017, DPC and MDPC were added to the mandatory list of the Water Works Well Monitoring Programme. The number of samples for these compounds is very limited in GRUMO and in the Water Works Well Monitoring Programme datasets for 2017 that form the basis of the present report. This is so in part because many sampling results from the Water Works Well Monitoring Programme were reported and approved only after the present report's standardised data extraction from Jupiter was made, and in part because only a limited share of the GRUMO monitoring points were screened for these compounds.

To provide a more precise and up-to-date status on DPC and MDPC, we present the results from a more recent statement. The statement (GEUS, 2018) was prepared for the Water Panel's Working Group on Pesticides and Drinking Water Control, which was tasked to collect information on DPC (Danish Environmental Protection Agency 2017). The statement includes data reported to and approved in Jupiter as per 23 October 2018. Table 3 shows that until this date, DPC was detected in 34.5% of the sampled GRUMO monitoring points with a content exceeding the threshold value in 19.4% of the sampled GRUMO monitoring points.

Table 3. GRUMO. Occurrence of desphenylchloridazon (DPC) and methyldesphenylchloridazon (MDPC) to the extent that this information was reported to and approved in Jupiter as per 23 October 2018. The monitoring points are divided into three concentration intervals, where the compounds have been detected at least once at a concentration exceeding the threshold value (>0.1  $\mu$ g/l), or have been detected at least once below the threshold value (0.01-0.1  $\mu$ g/l), or have not been detected (below the detection threshold, typically >0.01  $\mu$ g/l).

GRUMO	Number of samples	N	Ionitoring points Number	Monitoring points Share (%)		
	Total	Total	With findings	>0.1 μg/l	With findings	>0.1 µg/l
DPC	439	386	133	75	34.5	19.4
MDPC	427	377	74	25	19.6	6.6

In contrast to other pesticides, the concentration of DPC is more frequently above than below the threshold value when the compound is detected. MDPC was detected in 19.6% of the sampled monitoring points, and the content exceeded the threshold value in 6.6% of the tested monitoring points. As the statements are based on the data that were available in Jupiter when the data were extracted (23 October 2018), the finding percentages may change once all of the GRUMO station net is subsequently tested. The geographical extension of DPC is not limited to areas that have seen intensive production of beets for sugar production, e.g. Funen, South and West Zealand, Lolland and Falster, where the use of chloridazon might have been expected to be high.

**1,2,4-triazole** is a metabolite from a series of triazole fungicides. In January 2017, the Danish Environmental Protection Agency decided to screen for 1,2,4-triazole in selected GRUMO monitoring points because 1,2,4-triazole had been detected frequently and in some cases at concentrations exceeding the threshold value in the Pesticide Leaching Assessment Programme to the Groundwater (PLAP). In the GRUMO screening, 1,2,4-triazole was detected in 32.7% of the tested monitoring points and at concentrations exceeding the threshold value in 1.4% of the monitoring points. In 2014, the Danish Environmental Protection Agency discontinued autumn use of tebuconazole in grain, reduced the allowed dose for 4 triazole fungicides and introduced an upper limit on the total amount that may be used for agricultural purposes in the growth season. Additionally, 1,2,4-triazole may likely have originated from extensive and continued use of triazole fungicides in wood-preserving paint and possibly from use as a nitrification inhibitor in liquid manure and artificial fertilizer.

# 1.4 Inorganic trace elements

#### Introduction

The compounds known as inorganic trace elements include, among others, heavy metals such as cadmium and lead, but also light metals like aluminium and boron, and non-metals such as arsenic. The simple chemical compound of cyanide (CN) also forms part of the group inorganic trace elements. Inorganic trace elements are found naturally in groundwater, typically at concentrations in the  $\mu$ g/l range. Inorganic trace elements have very diverse chemical properties, uses and geological occurrence. A shared characteristic of many of the trace elements is that the measured concentrations may include contributions from both natural processes and human activities.

#### **Data basis**

This year's report describes analysis results collected in the Groundwater Monitoring Initiative (GRUMO) in the 2011-2017 period and in the Water Works Monitoring Programme in the 2013-2017 period. For GRUMO, both the 2017 and the 2011-2016 programme period are reported since the full programme period has not previously been reported. Table 4 shows the analysis parameters that currently form part of the Groundwater Monitoring Initiative for the 2017-2021 period and the parameters that are used in the monitoring of the groundwater quality in the water works wells in the mandatory water works well monitoring programme (The Drinking Water Act). The sampling frequency in both GRUMO and the water works well monitoring programme varies from annual sampling to one sample every five years.

# **Groundwater monitoring**

In 2017, a total of 678 GRUMO monitoring points were analysed for the compounds aluminium, arsenic, beryllium, lead, boron, cadmium, iodine, copper and nickel. In 2017, the threshold value was exceeded in one or more cases for the following five compounds: aluminium, arsenic, lead, boron and nickel. The threshold value was exceeded by 5.6% for aluminium, 9.0% for arsenic, 0.4% for lead, 0.9% for boron and 3.2% for nickel. The excessive values were detected in 130 monitoring points, corresponding to 19% of the sampled monitoring points. In 17 monitoring points (2.5%), the threshold value was exceeded for two compounds (aluminium and arsenic in combination with boron, nickel or lead). The content of cadmium, copper and zinc fell within the threshold value in all tested monitoring points.

Table 4. GRUMO and the Water Works Well Monitoring Programme. 2017-2021 analysis parameters for inorganic trace elements in the groundwater Monitoring Initiative and organic compounds in the Water Works Well Monitoring Programme (the Drinking Water Act).

Inorganic trace elements	Threshold value (µg/l)	GRUMO	Water work wells
Aluminium (Al)	200	Х	Xa
Arsenic (As)	5	Х	Х
Barium (Ba)	-		Х
Beryllium (Be)	-	Х	
Lead (Pb)	5	Х	
Boron (B)	1,000	Х	Х
Cadmium (Cd)	3	Х	
Iodine (I)	-	Х	
Copper (Cu)	2,000	Х	
Cobalt (Co)	5		Х
Nickel (Ni)	20	Х	Х
Strontium (Sr)	-		Xb
Zinc (Zn)	3,000	Х	

a) Is analysed if the groundwater pH value falls below 6.

In the 2011-2016 period, the threshold value was exceeded for six of the compounds tested, i.e.: aluminium, arsenic, lead, boron, cadmium and nickel. The threshold value was exceeded by 8.0% for

b) Is analysed in case of abstraction in areas with white chalk.

aluminium, 7.6% for arsenic, 1.4% for lead, 0.4% for boron, 0.2% for cadmium and 5.6% for nickel. The excessive values were detected in 212 monitoring points, corresponding to 23% of the sampled monitoring points. In 41 monitoring points (4.5%), the threshold value was exceeded for two of the compounds tested (aluminium in combination with lead, cadmium and nickel or arsenic in combination with aluminium, boron and nickel). In 6 monitoring points (0.7%), the threshold value was exceeded for three of the compounds tested (aluminium in combination with lead/cadmium and nickel) and in one monitoring point (0.1%) the threshold value was exceeded for four of the compounds tested (aluminium, arsenic, lead and nickel).

For the 2011-2016 period, the content of copper and zinc was below the threshold value for drinking water in all GRUMO monitoring points.

#### Arsenic

In the main report, Chapter 6, four compounds are described in more detail; arsenic, nickel, copper and zinc. Here, only arsenic is presented, as it is the trace element that most frequently exceeds the threshold value for drinking water.

Arsenic occurs naturally in various minerals, e.g., arsenopyrite (FeAsS) and other sulphides. The mobility of arsenic is limited by its strong bond to clay, ferric oxide/hydroxides and organic substrate. Oxidation/reduction processes very much determine the mobility of arsenic in the soil layers. Generally, anoxic groundwater contains more arsenic than oxic groundwater.

Figure 13 shows that in the 2011-2016 period, arsenic occurs in concentrations below the threshold value for drinking water (5  $\mu$ g/l) in GRUMO monitoring points evenly distributed across Denmark. Water with a higher arsenic content is found in some locations on Zealand, Falster and Lolland, in a NW-SE-going band across Funen, in South and Central Jutland, Himmerland, Thy and Vendsyssel.

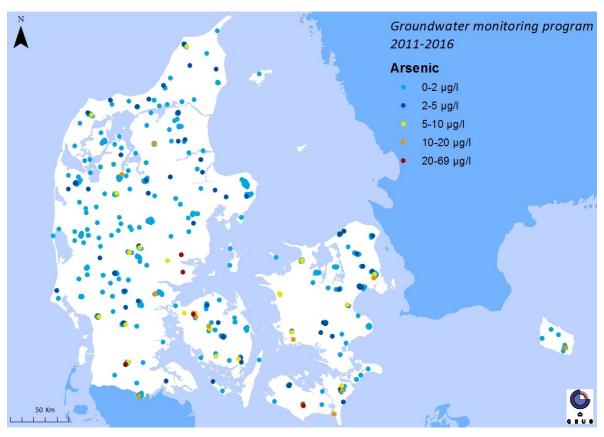


Figure 13. GRUMO. Arsenic concentrations in 911 GRUMO monitoring points in the 2011-2016 period. The highest concentrations are depicted on top of lower values.

#### Water work wells

For 2017, analyses concerning inorganic trace elements were reported from a total of 1,684 water works wells. The majority of the wells were analysed for the mandatory compounds: arsenic, barium, boron, cobalt and nickel (Ministry of the Environment and Food of Denmark, 2018a). Among the 1,684 water works wells, the threshold value was exceeded for one or more compounds in 270 wells, corresponding to 15%. Concurrent excess values for two compounds (nickel with arsenic or cobalt) and three compounds (boron, cobalt and nickel) occur in 5.3% and 2.0% of the wells, respectively.

For the 2013-2017 period, analyses concerning inorganic trace elements were reported from a total of 5,966 water works wells. The majority of the wells were analysed for the mandatory compounds: arsenic, barium, boron, cobalt and nickel (the Drinking Water Act). Furthermore, a large number of wells were analysed for strontium (abstraction from chalk) and aluminium (if pH <6). Among the 5,966 water works wells, the threshold value was exceeded for one or more compounds in 842 wells, corresponding to 14%. The threshold value was exceeded for arsenic (11.9%), nickel (1.7%), cobalt (0.5%), boron (0.3%) and aluminium (0.2%).

Figure 14 presents the geographical distribution of water works wells with an arsenic content that exceeds the threshold value. Excess values of arsenic occur in large parts of Denmark, at a greater density in West Zealand, in the areas along the Bay of Køge, in large parts of Lolland, Mid and West Funen and in the easternmost part of Jutland, from Mols Bjerge down to the town of Kolding. Furthermore, some wells with a high arsenic content are located in the areas of Himmerland and Vendsyssel.

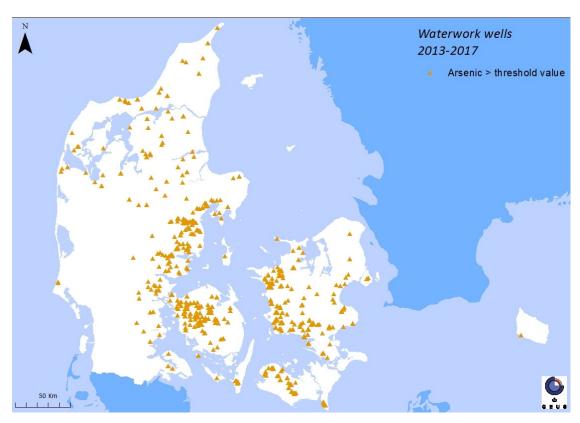


Figure 14. The Water Works Well Monitoring Programme ('Boringskontrollen'). Concentrations of arsenic exceeding the threshold value for drinking water (5  $\mu$ g/l) in 704 waterworks wells in 2013-2017. In most cases, optimised abstraction and treatment of the groundwater will reduce the arsenic content considerably in the water distributed from the water works.

# 1.5 Organic micro-pollutants

#### Introduction

Organic micro-pollutants comprise a very diverse group of compounds with many different detection limits and threshold values. In the report, the use and risk profile of each group of compounds is presented briefly. The compounds have many different uses that may cause the compounds to end up in the water environment. As these organic compounds also have very different chemical properties, their behaviour in the environment varies considerably with respect to degradability, solubility, etc. A common factor describing these compounds is that they are organic compounds that are generally found in low concentrations in groundwater. A special focus is placed on compounds that are used extensively and which have an unwanted environmental impact when the compounds are not fully used as intended. This is so because some of the compounds are toxic for humans or ecosystems or may have hormone-disrupting effects even at low concentrations.

#### **Data basis**

Each programme period under the groundwater monitoring initiative includes monitoring of some selected compounds. This year's report describes analysis results collected in the 2011-2017 period. The main focus is on presenting the overall result for the 2011-2015 programme period, but data on PFAS and dichlorophenols collected in the transitional year 2016 are included in the statement.

In the Water Works Well Monitoring Programme, the choice of analysis parameters depends on which presumed or known risks of groundwater pollution are present within each water work's abstraction catchment areas. The executive order on drinking water (the Drinking Water Act) states that: "Monitoring of other organic micro-pollutants is established in accordance with the sources of pollution that are present in the area in question. If the abstraction catchment area is known to include areas that are or may be contaminated with organic micro-pollutants, these compounds must be monitored unless the compounds are assessed not to comprise a threat to the groundwater".

# State

# The Groundwater Monitoring Initiative

The content of each organic micro-pollution fell below the detection limit (DL) for the overwhelming majority of the monitoring points as the frequency of concentrations  $\geq$ DL was typically less than 1% for each compound in the 2011-2016 period. Nine of the 33 monitored compounds had a finding share exceeding 1: chloroform (9.7 %), PFOA (6.2%), PFOS (5.0%), m+p-xylene (3.4%), PFHxS (2.7%), PFBA (2.6%), toluene (2.2%), PFHpA (1.6%) and 2,4-dichlorophenol (1.1%). Five of the nine compounds belong to the group of perfluorinated compounds, the co-called PFAS.

In the Groundwater Monitoring Initiative, chloroform is clearly the most frequently detected single compound within organic micro-pollutants, both with respect to extension and scope of the values exceeding the threshold value. All monitoring points in which the content of chloroform exceeds the drinking water requirement are located in or near woods/plantations with conifers. It therefore seems likely that the high content of chloroform in these monitoring points may be due to natural formation of the compound in the forest soil.

# Water work wells

In the 2013-2017 period, analyses were performed in the water works wells to detect a total of 142 compounds in a highly varying number of wells (from 1 to 5,849); 109 of the monitored compounds were analysed in a minimum of 10 wells.

Anionic detergent is by far the parameter (sum parameter) within the group of organic micro-pollutants that has the greatest finding percentage (45%). This concentration is far below the allowed 100  $\mu$ g/l in the majority of the tested water works wells. Among 449 wells with findings, 45 wells had concentrations exceeding 10  $\mu$ g/l, i.e., only approx. 10% of the wells with findings had concentrations exceeding 1/10 of the threshold value, and among these only 2 wells (0.2% of the tested wells) recorded values exceeding the threshold value.

The second-most frequently found compound was 1,2-dichloroethylene (cis-DCE), which was recorded in 99 wells (5.8%). Cis-DCE is a metabolite from the two chlorinated solvents trichlorethylene (TCE) and tetrachlorethylene (PCE), which are the compounds found in the third and fourth highest number of wells. Cis-DCE often cumulates when TCE and PCE metabolise and frequently constitutes the main threat against groundwater quality from point source pollution with chlorinated solvents. Cis-DCE matabolises into vinyl chloride, which is the seventh-most frequently found compound. Due to its considerable toxicity, the threshold value for vinyl chloride is lower than that of the remaining compounds in the group of chlorinated aliphatic hydrocarbons. Even though the number of wells with findings of vinyl chloride is lower than the number of wells with findings of its various parent compounds, both the finding percentage (8.1%) and the share of wells which recorded values exceeding the threshold value in the period covered by the statement (1.4%) are higher than those for each of the individual parent compounds.

Both the finding percentage and the share of water works wells with values that exceed the threshold value have increased markedly for vinyl chloride compared with the previous statement period (20102014, Thorling et al., 2015a). The tested number of wells (approx. 500 in both periods, corresponding to nearly 10% of the active Danish water works wells) is so low that it is difficult to conclude if the content of vinyl chloride is increasing in the abstracted water of if the water works are now better at targeting sampling for vinyl chloride given the risk of pollution. It is also possible that water works are more lenient than before, accepting abstraction of water with low concentrations, which will show up as an increase in the number of findings in the mandatory Water Works Well Monitoring Programme.

# Litterature:

Thorling, L., Albers, C.N., Ditlefsen, C., Ernstsen, V., Hansen, B., Johnsen, A.R., og Troldborg, L. 2019: Grundvand. Status og udvikling 1989 – 2017. Teknisk rapport, GEUS 2019. https://www.geus.dk/media/20715/grundvand 19892017.pdf

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GEUS memorandum, 2018. Notat nr.: 05-VA-18-05 af 29. oktober, 2018. Forekomst af desphenylchloridazon og methyldesphenylchloridazon i grundvandet.

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Schullehner, J. & Hansen, B., (2014): Nitrate exposure from drinking water in Denmark over the last 35 years. Environmental Research Letters 9 095001 doi:10.1088/1748-9326/9/9/095001 PLAP: http://pesticidvarsling.dk/om os uk/uk-forside.html