

Iodine in major Danish aquifers

Denitza Dimitrova Voutchkova^{1,2,4} · Vibeke Ernstsen³ · Søren Munch Kristiansen⁴ · Birgitte Hansen²

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Abstract Iodine in groundwater can have direct importance for human dietary iodine intake in areas where drinking water is of groundwater origin, as in Denmark. Knowledge on the sources and processes for the varying iodine concentrations in groundwater is of utmost importance for understanding the variation in iodine intake of the population via drinking water. The aim of this study was to characterize groundwater with elevated iodine concentrations and to investigate the sources and processes controlling natural iodine speciation and concentration at four study sites in Denmark with postglacial sandy, Quaternary sandy, and Cretaceous limestone aquifers. Analyses included iodide (I^-), iodate (IO_3^-), total iodine (TI), major ions, and stable H and O isotopes. Dissolved organic iodine (DOI) was calculated by subtracting I^- and IO_3^- from TI. A diagram of stable $\delta^{18}O$ and δ^2H isotopes in Danish groundwater was compiled in order to interpret the groundwater iodine geochemistry. Groundwater had TI concentrations from 5 to 14,500 $\mu g/L$. Iodine speciation

reflected the prevailing neutral to alkaline and reduced conditions at the investigated sites with domination of I^- and DOI correlated with dissolved organic carbon. We found three different explanations for elevated TI concentrations at the four Danish sites: (1) leaching from soil enriched in iodine due to atmospheric deposition and proximity to the sea, (2) influence from the marine origin of the aquifer sediment due to desorption of iodine from iodine-enriched organic matter or minerals, and (3) influence from residual saline water due to upward advective or/and diffusive transport of iodine.

Keywords Denmark · Hydrogeochemistry · Iodide · Iodine · Groundwater · Spatial heterogeneity

Introduction

Iodine is a trace element, essential for humans and other living organisms. Too low or too high iodine intake, through the food and water, may have negative health outcomes for human, e.g., cretinism, birth defects, goiter, hypo- and hyperthyroidism (Andersson et al. 2007). Most foods (except sea products) are naturally low in iodine. Hence, universal iodizing programs are established in many countries worldwide as a deficiency prevention measure. In general, water has been seen as a minor or even negligible iodine source (Fuge 2005). However, local or regional geographical variation can exist and be important for the iodine intake of the population in areas where drinking water is of groundwater origin, as in Denmark (Pedersen et al. 1999; Laurberg et al. 2006; Voutchkova et al. 2014a, 2015) or as in China (Shen et al. 2011; Lv et al. 2013). Iodine speciation and concentrations in drinking water and groundwater in Denmark have not been

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✉ Denitza Dimitrova Voutchkova
geoddv@nus.edu.sg

- ¹ Present Address: Department of Geography, National University of Singapore, AS2, #04-47, 1 Arts Link, Kent Ridge 117570, Singapore
- ² Geological Survey of Denmark and Greenland (GEUS), Lyseng Allé 1, 8270 Højbjerg, Denmark
- ³ Geological Survey of Denmark and Greenland (GEUS), Øster Voldgade 10, 1350 Copenhagen K, Denmark
- ⁴ Department of Geoscience, Aarhus University, Høegh-Guldbergs Gade 2, 8000 Aarhus C, Denmark

studied extensively. A Danish nationwide survey reported total iodine (TI) concentrations in drinking water to range from below 0.2 to 126 $\mu\text{g/L}$ (mean 14.4 $\mu\text{g/L}$, median 11.9 $\mu\text{g/L}$, $n = 144$) with a spatial pattern possibly reflecting differences in geological layers and hydrogeochemical reactions (Voutchkova et al. 2014b).

Based on a historical data analysis, Voutchkova et al. (2014b) found that iodine concentrations in Danish groundwater were characterized by both small-scale heterogeneity and large-scale spatial trends with lower mean in the western compared to eastern part of the country. Elevated iodine concentrations were dominating in Paleocene and Cretaceous limestone/chalk aquifers, and saline water influence was suggested (Voutchkova et al. 2014b). Further, association between iodine and elements as Li, B, Ba, Br and between elevated iodine and reduced water type was revealed by multivariate analysis of the same Danish historical groundwater data (Voutchkova et al. 2014b).

In this paper, we analyze the results from a detailed hydrogeochemical iodine study at four sites in Denmark representing major aquifers with potentially elevated iodine. The three specific objectives are: (1) to analyze the iodine speciation in Danish groundwater, (2) to assess the spatial variation of iodine concentration on different local scales, and (3) to interpret the iodine findings from a hydrogeochemical perspective.

Background on iodine geochemical cycle

The complexity of the geochemical cycle, the distribution, transport, and transformation of iodine in various environmental media have been discussed in the exhaustive reviews by Whitehead (1984), Fuge and Johnson (1986), Muramatsu and Wedepohl (1998), and recently Fuge and Johnson (2015). Details on the organic iodine geochemistry and the thermodynamic properties of over 40 organic iodine compounds are presented by Richard and Gaona (2011). A meta-analysis on iodine concentration and speciation in different parts of the hydrosphere from different investigations is presented in the Electronic supplementary materials (ESM Table 1). Similar compilation of iodine concentrations in terrestrial waters also is found in Table 2 of Fuge and Johnson's (2015) review.

Seawater is major reservoir of iodine. Iodine is transferred from the marine environment to the atmosphere via volatilization. Subsequently, it is deposited via wet and dry deposition to the terrestrial system. In the hydrogeochemical cycle, total iodine (TI) can be found in the stable inorganic forms of iodide (I^-) and iodate (IO_3^-), as well as in various dissolved organic iodine (DOI) compounds:

$$\text{TI} = \text{I}^- + \text{IO}_3^- + \text{DOI} \quad (1)$$

Whitehead (1984) presented an outline of iodine movement in the environment, covering the atmosphere, hydrosphere, lithosphere, and biosphere. According to his conceptual model, iodine is transferred to the groundwater by: (1) leaching of iodine from the soil and (2) exchange between groundwater and inland surface waters (Whitehead 1984). Other processes can be involved too, e.g., intrusion of seawater, influence of old saline groundwater, or leaching from hydrothermal deposits (Lloyd et al. 1982). Iodine enrichment of the groundwater has been related also to topography, geomorphology, and local hydrogeology (Tang et al. 2013), as well as to the hydrogeochemical conditions and biological activity in the aquifer (Li et al. 2013, 2014).

Weathering of iodine containing minerals might also be a source to iodine in groundwater. The iodine content in Danish soils and sediments has not been investigated nor reported. Natural iodine minerals are rare and forming only a negligible amount of earth's available iodine (Fuge and Johnson 1986). Igneous and metamorphic rocks are generally low in iodine (Fuge and Johnson 1986; Muramatsu and Wedepohl 1998). Opposite to rocks, marine sedimentary deposits are generally enriched in iodine: 3.9 mg/kg (deep sea clays) and ~ 2.5 mg/kg (near-shore limestones) (Muramatsu and Wedepohl 1998). Iodine in recent marine sediment is even higher—from 5 to 200 mg/kg (Fuge and Johnson 1986).

In iodine-rich sedimentary rocks, iodine is adsorbed on grain surfaces or organic matter (Fuge and Johnson 1986). Iodide is strongly polarizable which increases its ability to substitute for hydroxyl ion in various compounds (Whitehead 1984). Most of the studies on iodine geochemistry in the terrestrial environment are focused on soils. However, some of the mechanisms may be relevant also to sediments, which can have importance for iodine in groundwater, as most aquifers in Denmark are from sedimentary origin. The adsorption capacities of I^- and IO_3^- tend to be greater in soils with more organic matter; thus, organic matter plays an important role as a soil-iodine reservoir (Yamaguchi et al. 2010). From the iodine species (see Eq. 1), I^- is the most mobile one due to its lower affinity to soil minerals (Yamaguchi et al. 2010). Three hypotheses on the nature of I^- interaction with the soil matrix were formulated by Zhang et al. (2011): (1) electrostatic adsorption to the mineral surfaces, (2) anion exchange with the positively charged surfaces, or (3) irreversible covalent binding with organic matter.

Mobility of I^- and IO_3^- is concentration dependent: At ambient concentrations, inorganic iodine is immobilized due to covalent bonding with natural organic matter (Zhang et al. 2011). At neutral pH, the retention of iodine is low

because of the negative charges of the sediments (Kennedy et al. 2011). Thus, generation of high-iodine groundwater is promoted by alkaline conditions, which are enhancing the desorption of iodine from clay minerals and iron oxyhydroxides (Li et al. 2013). However, sorption experiment shows that if a bacteriogenic iron oxides (ferrihydrite precipitates and bacterial structures) are present, I^- sorption of about 50% is maintained over the pH range of natural waters (Kennedy et al. 2011). Reducing conditions are also favorable for iodine enrichment in groundwater (Li et al. 2013). Yoshida and Muramatsu (1999) reported that desorption of iodine from flooded soils occurs at reducing conditions. Also, at reducing conditions: IO_3^- and DOI are transformed to the more mobile I^- (Li et al. 2013), I^- is dissociated from organic iodine (and organic matter) (Shimamoto et al. 2011), and reductive dissolution of iron oxyhydroxides occurs (Li et al. 2013). Li et al. (2014) suggested that the major geochemical processes responsible for iodine release into the groundwater are degradation of organic matter and reductive dissolution of iron oxyhydroxides.

Site locations and site description

Four potentially enriched iodine study sites (Fig. 1) with different types of aquifers (Fig. 2) were selected:

- Site a (Skagen)—Postglacial marine sandy aquifer.
- Site b (Randers)—Quaternary sandy meltwater and Cretaceous marine limestone aquifers.
- Site c (Ishøj)—Near-coastal Cretaceous marine limestone aquifer.
- Site d (Stevns-2)—Deep Cretaceous marine limestone aquifer.

Sites *a* and *b* were included in previous epidemiological iodine studies (Pedersen et al. 1999; Andersen et al. 2002, 2008). Sites *a* and *c* were known to be characterized by high-iodine drinking waters (Voutchkova et al. 2014a; b). The wells at Sites *a* and *b* belong to waterworks, Site *c* is part of the Danish national groundwater monitoring program (GRUMO), while Site *d* is a research investigation site. The wells are referred to by their unique identification number (DGU no.) used in the publicly available nationwide geological and hydrological database Jupiter (GEUS, <http://www.geus.dk/DK/data-maps/jupiter/Sider/default.aspx>).

Site *a* comprises of four wells which are part of well field “West” of Skagen waterworks in the northernmost part of Denmark (Fig. 1a; Table 1). The wells are located on a spit system at the peninsula Skagen Odde and are about 1 km from the coastline of Skagerrak Sea. The wells’ screens are in Holocene marine sandy aquifer overlaid by 1–4 m of postglacial eolian sand and thin peat layers or lenses (Fig. 2). Due to the pumping for drinking water

purposes, the groundwater flow lines are most probably variable in time and altered from the natural conditions. The raw groundwater is treated at Skagen Waterworks and supplied to the town of Skagen (about 8000 inhabitants). Based on the climatological standard normals (1961–1990) for the closest station (06041 Skagen Lighthouse), the mean annual precipitation is 613 mm with monthly maximums during October and November (Frich et al. 1997), mean annual temperature is 7.9 °C, July and August (15.8 °C) are the warmest months and February is the coldest one (0.1 °C), and mean relative daily humidity is 89% (Laursen et al. 1999).

Site *b* includes the well sites of four waterworks (Oust Mølle, Bunkedal, Østrup Skov, and Vilstrup) in the vicinity of Randers and the marine inlet Randers Fjord (Fig. 1b). Østrup Skov is the closest one to Randers Fjord, at about 2 km distance, and Oust Mølle is the furthest away. Groundwater samples were obtained from four wells at Oust Mølle, three at Bunkedal, three at Østrup Skov, and four at Vilstrup (Table 1, Fig. 1b). The screens of all wells at Oust Mølle, Østrup Skov, Bunkedal and one well at Vilstrup are situated in Danian (or Selandian) marine limestone (chalk), whereas the screens of the three other wells at Vilstrup are in the glacial meltwater sand aquifer. The limestone aquifers at Oust Mølle, Østrup Skov, Bunkedal are overlaid by Selandian/Paleocene marine clay layer(s) (varying in thickness but up to 40–45 m thickness), while the sandy aquifer at Vilstrup is overlaid by thin glacial meltwater silt layer. Further details about the geology and the screen lengths at each well are presented in Fig. 2. The groundwater from these waterworks supplies Randers (about 60 000 inhabitants). The groundwater flow paths are affected by the strong and variable pumping for the drinking water supply. The climatological standard normals (1961–1990) for the closest stations (precipitation: 22,055 Stevnstrup; temperature: 22,231 Ødum II) show mean annual precipitation 615 mm with the wettest month being November (Frich et al. 1997), mean annual temperature 7.3 °C, July and August are the warmest months (15.1 °C) and January is the coldest (−0.4 °C), and mean relative daily humidity is 83% (Laursen et al. 1999).

Site *c* is at an urbanized area included in the Greater Copenhagen (Ishøj). Groundwater samples were taken from four wells (Table 1; Fig. 1c). The wells are located approximately on a transect from Køge Bay and inland to the west. All screens are located in the Campanian–Maastrichtian chalk aquifer, which is overlaid by glacial clayey till varying in thickness (up to about 15 m). Well no. 207.2827 is located approximately 400 m from the present coastline, where a 4-m-thick postglacial marine sand layer (incl. diatom mud) is present 1.5 m below the surface. Well 207.3004 is located next to a major highway (E20/E47). Taking into account the location of these wells,

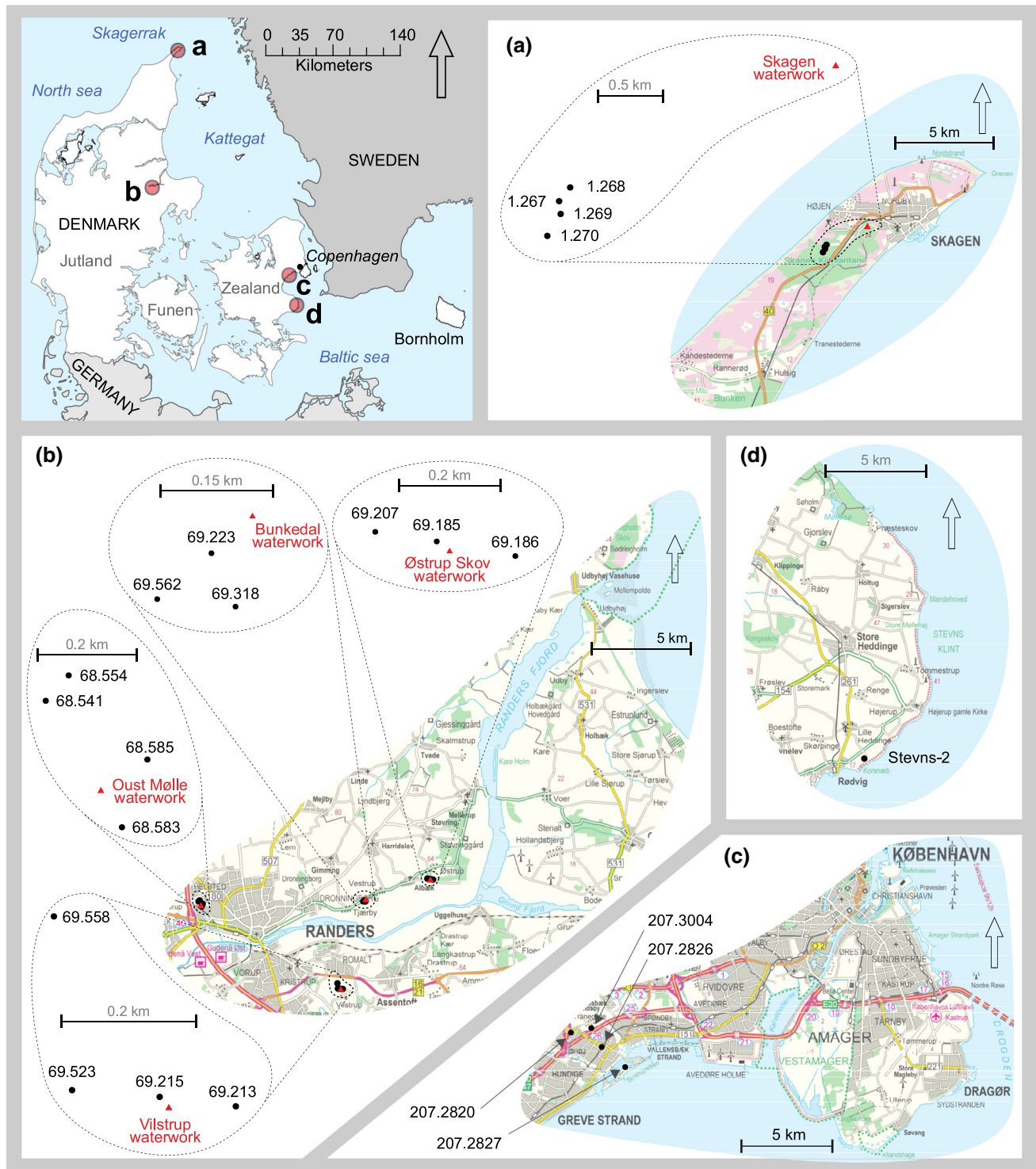


Fig. 1 Map of Denmark and location of the four study sites: **a** Site *a* (Skagen), **b** Site *b* (Randers) with the wells of four sub-sites/waterworks: Østrup Skov, Bunkedal, Oust Mølle, and Vilstrup, **c** Site

c (Ishøj), and **d** Site *d* (Stevns-2); *Note*: the well numbers are unique DGU well IDs from the Danish national monitoring network

it is expected that the groundwater flow is toward the Øresund coast. The recharge zone is probably within the urbanized area; however, it is not attempted to specify exact recharge and discharge zones without

hydrogeological modeling. The climatological standard normals (1961–1990) for the closest station (06180 Kastrup Airport) show mean annual precipitation 525 mm with the wettest month being July (Frich et al. 1997), and mean

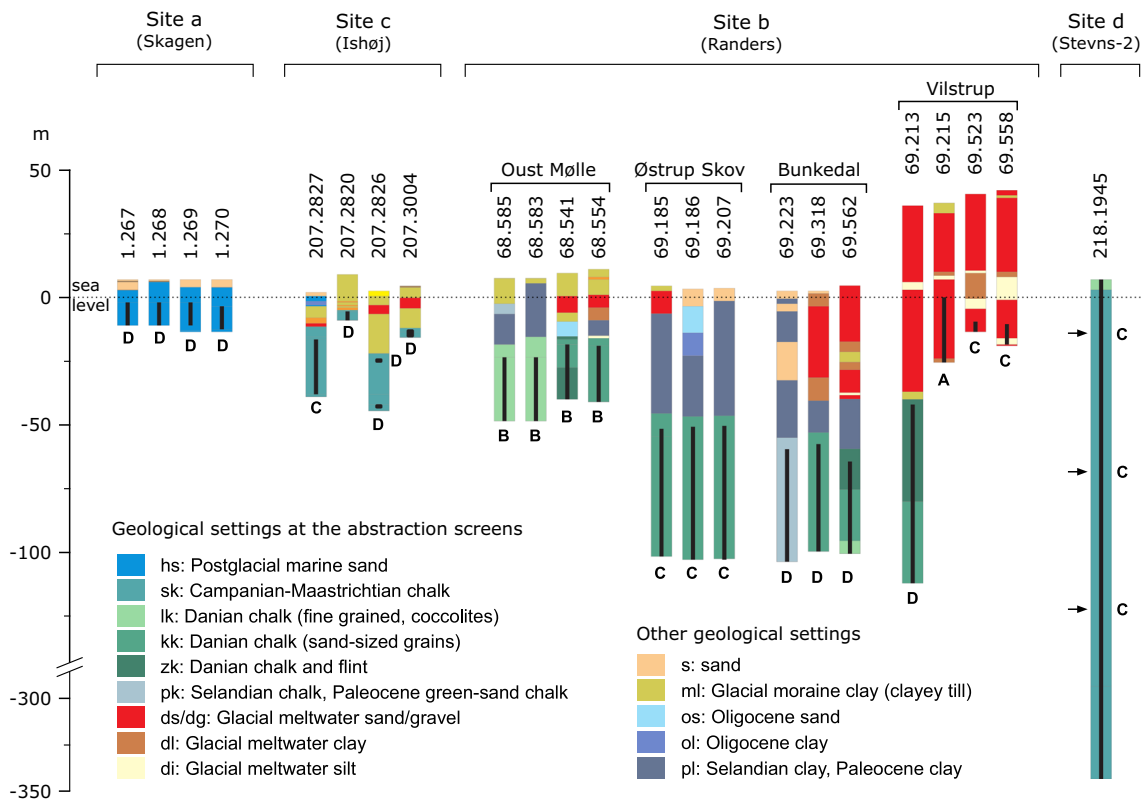


Fig. 2 Geological settings at the wells (Jupiter database, GEUS, <http://www.geus.dk/DK/data-maps/jupiter/Sider/default.aspx>); with abstraction screen location shown with *thick black line* (y-axis meters above/below sea level) and the redox water type is indicated with *bold*

annual temperature 8 °C, July is the warmest month (16.4 °C) and February the coldest (−0.1 °C), and mean relative daily humidity is 79% (Laursen et al. 1999).

Site d is a deep borehole, called Stevns-2, located at an abandoned limestone quarry on the island of Zealand about 200 m from the Baltic sea coast (Table 1, Fig. 1d). The groundwater flow direction is assumed to be toward the Baltic Sea coast; however, it is not attempted to specify exact recharge and discharge zones without hydrogeological modeling. The borehole is drilled to a depth of 350 m, with upper four meters in Danian limestone followed by about 300 m of Maastrichtian chalk (Stemmerik et al. 2006). Two zones consisting of regular closely spaced and up to cm-thick marl layers are found at depths approximately 90–130 and 260–300 m (Bonnesen et al. 2009). Groundwater was sampled at three depths (20, 75, and 130 m.b.t.) to represent salinities ranging from fresh to brackish to saline water. The climatological standard normals (1961–1990) for the closest station (31050 Stevns Lighthouse) show mean annual precipitation 524 mm with the wettest month July (Frich et al. 1997). Provisional normal for temperature and humidity over 1973–1991 for the closest station (31095 Vivede Overdrev) shows mean annual temperature 7.8 °C with July being the warmest

capital letters oxidized water (A), anoxic water with nitrate (B), slightly reduced groundwater with iron and sulfate (C), and strongly reduced groundwater with methane and hydrogen sulfide (D)

month (16.1 °C) and February the coldest (0.0 °C); mean relative daily humidity is 82% (Laursen et al. 1999).

Table 1 provides an overview of the study site characteristics.

Methods and materials

Groundwater sampling

The sampling campaign took place during October 2012. The groundwater samples from all wells listed in Table 1 were taken after pre-pumping. The pre-pumping continued until pH, redox condition, conductivity, dissolved oxygen, and temperature became stable, and representative samples could be obtained. Both filtered at the site (0.45 μm) and unfiltered groundwater samples were stored at about 5 °C until analysis.

Laboratory analysis

Anions (Cl⁻, SO₄²⁻, F⁻, Br⁻, and NO₃⁻) in the water samples were measured using a Metrohm Anion system equipped with a Metrosep A Supp 15–250 IC column and

Table 1 Characteristics (well length, screen length and depth, aquifer type) of the study sites and references to relevant previous studies

Study site	Location	Well number DGU no.	Well length m.b.t.	Screen depth (top) m.b.t.	Screen length (m)	Aquifer type (geology)	Background from previous studies	Drinking water iodine ($\mu\text{g/L}$)	Previous studies	
a	Skagen					Postglacial marine sand	Highest iodine concentrations in drinking water	126–140	[1]	
		1.267	18	9	9					
		1.268	18	9	9					
		1.269	20.5	9	9					
		1.270	20.5	10.5	9					
b	Randers					Danian/Selandian chalk	Low iodine concentration in drinking water	<0.2–2	[2]	
		Oust Mølle	68.585	56	31					25
			68.583	56	31					25
			68.541	49.5	28					21.5
			68.554	52	30					22
		Østrup Skov	69.185	106	56					50
			69.186	106	54					52
			69.207	106	54					52
		Bunkedal	69.223	106	62					44
			69.318	102	60					42
			69.562	105	69					36
		Vilstrup	69.213	148	78					70
			69.215	62.5	37					25.5
	69.523	58	50	8						
	69.558	61	52.5	8						
c	Ishøj					Campanian– Maastrichtian chalk	High iodine content in groundwater	>100	[3]	
			207.2827	41	18.5					21.5
			207.2820-1	18	14.5					3.5
			207.2826-1	47	27					0.5
			207.2826-2	47	45					0.5
	207.3004	19.8	17.6	2						
d	Stevns-2	218.1945	350	0	350	Campanian– Maastrichtian chalk	Influence from old saline water	–	[4]	

Notes drinking water iodine concentrations from previous studies: [1] Pedersen et al. (1999) Andersen et al. (2002, 2008), and Voutchkova et al. (2014a); [2] Andersen et al. (2008); Voutchkova et al. (2014a), [3] Voutchkova et al. (2014b), [4] Bonnesen et al. (2009)

with sequential suppression with a suppressor module (MSM) and a CO_2^- suppressor (MCS 853), and with conductivity detection (Metrohm, Herisau, Switzerland). The eluent was 1 mM NaHCO_3 and 3.2 mM Na_2CO_3 . Cations (Ca^{2+} , Mg^{2+} , Na^+ , and K^+) in water samples were measured using a Metrohm Cation system equipped with a Metrosep C4–250 IC column (Metrohm, Herisau, Switzerland). The eluent was 1,2 mM 2,6-pyridinedicarboxylic acid and solution and 2 mM HNO_3 . Iodide (I^-) in the water samples was measured using an 871 Advanced Bioscan equipped with an Ag flow cell and with

amperometric detection (Metrohm, Herisau, Switzerland). The eluent was 5 mM NaHCO_3 and 3.5 mM Na_2CO_3 . Iodate (IO_3^-) in the water samples was spectrophotometrically determined after sequential suppression as for the anions and postcolumn reaction with KI and measured at a UV absorption maxima (287.8 nm) using a spectromonitor Lambda 1010 UV/VIS detector (Bischoff, Leonberg, Germany). The anion-, cation-, I^- , and IO_3^- systems were all connected to an 838 Advanced IC Sample processor (Metrohm, Herisau, Switzerland). The total concentration of iodine (TI) in the water samples was measured by ICP-

MS (ELAN 6100 DRC, PerkinElmer, Ontario, Canada) equipped with an ELAN software 3.2. The water samples were added 0.7% HNO₃ (water/HNO₃ 11:1) before measurement. DOC, TIC, and TN were measured after 0.45- μ m filtration using a Total Organic Carbon Analyzer equipped with a TN unit (TOC-VCPH, Shimadzu, Tokyo, Japan). HCO₃⁻ was estimated from TIC. Stable isotopes $\delta^{18}\text{O}$ and δD were measured using a L2120i Analyzer for water (H₂O) isotopes (Picarro, Sunnyvale, California, USA). Lower detection limits: 0.9 $\mu\text{g/L}$ for I⁻; 1.4 $\mu\text{g/L}$ for IO₃⁻; 0.2 $\mu\text{g/L}$ for TI; 0.5 mg/L for DOC and TIC; 0.25 mg/L for TN; 0.03 mg/L for F⁻, NO₃⁻, SO₄²⁻, and Na⁺; 0.01 mg/L for Cl⁻; 0.02 mg/L for Br⁻; 0.06 mg/L for Ca²⁺; and 0.04 mg/L for K⁺ and Mg²⁺.

Hydrogeochemical characterization

Two diagrams for hydrogeochemical characterization were used: the Piper diagram (Piper 1944) and the Pratt diagram (Pratt 2003). The Piper diagram is a trilinear diagram, where major ions are plotted in the two base triangles as cation (Ca²⁺, Mg²⁺, Na⁺ + K⁺) and anion (Cl⁻, SO₄²⁻, CO₃²⁻ + HCO₃⁻) milliequivalent percentages and are subsequently projected onto the diamond area. Piper diagram is commonly used for comparing groundwater composition or its evolution through time/space, as well as for groundwater classification based on dominating ions and their relative proportions. The Pratt diagram (Pratt 2003) is another graphical interpretation method for groundwater classification used in Denmark. On the x-axis is plotted Na⁺/(Na⁺ + Ca²⁺), while on the y-axis is plotted (Ca²⁺ + Mg²⁺)/HCO₃⁻, where Na⁺, Ca²⁺, Mg²⁺, HCO₃⁻ are also expressed in milliequivalent per liter. Based on the Pratt diagram, four groundwater types can be distinguished: (1) freshwater type, where Ca²⁺ and HCO₃⁻ are dominating, (2) saline water type with dominating Na⁺ and Cl⁻, (3) mixed water type (there is no dominating or other ions are dominating, e.g., SO₄²⁻, NO₃⁻, and/or Cl⁻), and (4) ion-exchanged water type, where Na⁺ and HCO₃⁻ are the dominating ions.

Na⁺/Cl⁻ and Cl⁻/Br⁻ ratios provide further information on, respectively, the ion exchange state of the groundwater and indication for the groundwater origin. By using molar Na⁺/Cl⁻ ratios, two different conditions can be distinguished (Hansen et al. 2009; Kristiansen et al. 2009): (1) reversed ion exchange (Na⁺/Cl⁻ ratio < 0.75) when saline water infiltrates a freshwater sediment as a result of either seawater intrusion, diffusion from old saline groundwater due to extensive extraction, or infiltration of Na-rich water from the ground surface (e.g., road salt); and (2) ion exchange (Na⁺/Cl⁻ ratio > 1.25) when fresher water infiltrates a sediment of marine origin. An uncertainty interval of ± 0.25 is assumed; thus, the water samples with Na⁺/Cl⁻ ratio between 0.75 and 1.25 are neither representing ion exchange nor reverse ion

exchange (Hansen et al. 2009; Kristiansen et al. 2009). The review on Cl⁻/Br⁻ ratios by Davis et al. (1998) showed that: (1) Cl⁻/Br⁻ between 80 and 160 reflects the local precipitation sources (for Cl⁻ < 5 mg/L); (2) Cl⁻/Br⁻ between 200 and 400 reflects connate water; (3) the seawater influence along the coastline is usually shown by ratios close to 290 (288–292); (4) sewage (or waters characterized by high organic matter) may have ratios between 300 and 600 (sewage is not a likely source in Denmark); and (5) groundwater affected by halite dissolution has ratios in the range 1000 to 10,000. Salt used for road deicing has been recognized also as possible source of saline water infiltrating the aquifers in the vicinity of highways and urbanized areas. Cl⁻/Br⁻ ratio of the most common salt for deicing (vacuum salt) in Denmark is 10,000 (Kristiansen et al. 2009).

The groundwater redox state is assessed based on the measured dissolved O₂, NO₃⁻, Fe²⁺, and SO₄²⁻, by using the algorithm described in (Hansen et al. 2009). Based on the algorithm outlined in Hansen et al. (2009), four redox water types can be defined: (1) oxic water (type A), (2) anoxic, NO₃⁻-containing water (type B), (3) slightly reduced groundwater, containing Fe²⁺ and SO₄²⁻ (type C), and strongly reduced (groundwater potentially containing dissolved CH₄ and H₂S) (type D). This redox state classification of groundwater is widely used by the Geological Survey of Denmark and Greenland (GEUS).

Stable oxygen and hydrogen isotope abundances can provide additional insight into the origin of low-temperature groundwaters (<90 °C) (Geyh 2000). Comprehensive overview on stable oxygen and hydrogen physics is found in (Mook 2000; Appelo and Postma 2010). Most cold (<90 °C) groundwaters are of meteoric origin, which means that their isotopic composition would resemble the precipitation patterns at the recharge zone. The relationship between the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in worldwide precipitation is described by the global meteoric waterline (GMWL) (Craig 1961). The groundwater $\delta^{18}\text{O}$ and $\delta^2\text{H}$ deviation from GMWL indicates isotopic exchange and fractionation due to various processes, e.g., evaporation, temperature, altitude, seasonal and continental effects, as well as exchange with the sediments (Geyh 2000).

Results

Iodine concentration and speciation

Total iodine (TI) concentrations at the four study sites vary from 5 to 14,500 $\mu\text{g/L}$. The highest concentrations are measured at *Site d* (Stevns-2), followed by *Site a* (Skagen) and *Site c* (Ishøj), whereas the groundwater samples with lowest concentrations were at *Site b* (Randers) with TI range 5–19 $\mu\text{g/L}$ (Table 2).

Our results show that TI concentrations in groundwater are variably heterogeneous over the investigated geographical scales. A high degree of variation was found in the concentrations at the wells from a single well field (0.1–0.2 km). These local variations for *Site b* were in the range of 1.9 µg/L (Østrup Skov), 3.8 µg/L (Oust Mølle), 5.8 µg/L (Vilstrup), 8.4 µg/L (Bunkedal), while at *Site a* the TI range was 141 µg/L. When considering the local scale of 5–10 km, TI ranges were 14 µg/L at *Site b* and 175 µg/L at *Site d*. Table 3 provides a summary of TI variability at these different scales in terms of means, standard deviations, and relative standard deviations.

Iodine was present in the form of I^- and DOI (Eq. 1) with site-specific variation in the proportions of these two species (Table 2). IO_3^- was below detection limit (< 1.4 µg/l) at all sites. These findings are consistent with expected inorganic iodine speciation based on a classical chemical equilibrium E_H -pH diagram of iodine (Fig. 3).

Hydrogeochemical characterization

There are two orders of magnitude difference in the electrical conductivity at the investigated wells. A positive relation between TI and electrical conductivity was observed; however, the wells at *Site a* (Skagen) are somewhat more enriched in TI (with respect to the electrical conductivity) than the rest of the sites (ESM Fig. 3). All field and laboratory measurements (including major ions, DOC, TIC, TN, $\delta^{18}O$, δ^2H , and iodine species) are reported in ESM (see ESM xlsx file).

Based on the concentrations of the major anions and cations plotted on the Piper diagram (Fig. 4a), the groundwater at *Sites b* and *c* is classified as $Ca^{2+}-HCO_3^-$ type. There were two exceptions: well 69.213 (*Site b*, Vilstrup), which is $Na^+-HCO_3^-$ type, and well 207.2827 (*Site c*, Ishøj) which is mixed $Ca^{2+}-Mg^{2+}-Cl^-$ type. The sample from well 207.2827 (*Site c*, Ishøj) plots closer to the

Table 2 Iodine concentrations and speciation in groundwater from Sites a–d (see ESM xlsx file for all field and laboratory measurements, incl. concentrations of iodine species)

Site	Location	Well DGU #	Abstr. depth m.b.t.	TI (µg/L)	I^- (%)	IO_3^- -I (%)	DOI (%)
a	Skagen	1.267	9	195	70	0	30
		1.268	9	167	75	0	25
		1.269	9	246	65	0	35
		1.270	10.5	308	57	0	42
b	Randers	68.585	31	7	0	0	100
		68.583	31	8.8	100	0	0
		68.541	28	7	0	0	100
		68.554	30	5	0	0	100
	Østrup Skov	68.185	56	10.2	100	0	0
		68.186	54	11.1	100	0	0
		69.207	54	9.2	100	0	0
		69.223	62	10.6	100	0	0
		69.318	60	19	87	0	13
	Bunkedal	69.562	69	12.8	100	0	0
		69.213	78	14.9	100	0	0
		69.215	37	9.1	100	0	0
		69.523	50	11	100	0	0
Vilstrup	69.558	52.5	12.5	100	0	0	
	207.2827	18.5	198	47	0	53	
	207.2820-1	14.5	32	47	0	53	
	207.2826-1	27	82	45	0	55	
	207.2826-2	45	62	54	0	46	
c	Ishøj	207.3004	17.6	23	80	0	20
		218.1945	20	1120	47	0	53
		218.1945	75	6740	51	0	49
		218.1945	130	14,500	39	0	61
d	Stevns-2	218.1945	20	1120	47	0	53
		218.1945	75	6740	51	0	49
		218.1945	130	14,500	39	0	61

TI total iodine, DOI dissolved organic iodine

Table 3 Ranges of total iodine (TI), $\delta^{18}\text{O}$, $\delta^2\text{H}$ and deuterium excess of groundwater at the study sites (see ESM xlsx file for all field and laboratory measurements)

Site	Location	N	Total Iodine ($\mu\text{g/L}$)					$\delta^{18}\text{O}$ (‰)		$\delta^2\text{H}$ (‰)		Deuterium excess (‰)	
			Min	Max	Mean	SD	RSD (%)	Min	Max	Min	Max	Min	Max
Site a	Skagen	4	167	308	229	62.0	27.1	-8.55	-8.44	-58.82	-58.36	8.67	9.90
Site c	Ishøj	5	23	198	79.4	70.4	88.6	-9.13	-8.69	-62.68	-59.75	9.75	11.31
Site d	Stevns	3	1120	14,500	7453	6718	90.1	-9.35	-5.27	-63.84	-39.19	3.00	10.97
Site b	Randers (all)	14	5	19	10.6	3.5	33.4	-9.17	-8.50	-62.10	-57.27	9.69	11.98
Site b	Oust Mølle	4	5	8.8	7.0	1.6	22.3	-8.81	-8.50	-59.83	-58.14	9.69	11.63
	Østrup Skov	3	9.2	11.1	10.2	0.95	9.3	-9.01	-8.87	-60.29	-59.96	10.81	11.79
	Bunkedal	3	10.6	19	14.1	4.4	30.8	-8.61	-8.50	-57.80	-57.27	10.70	11.57
	Vilstrup	4	9.1	14.9	11.9	2.5	20.6	-9.17	-8.80	-62.10	-58.45	11.28	11.98

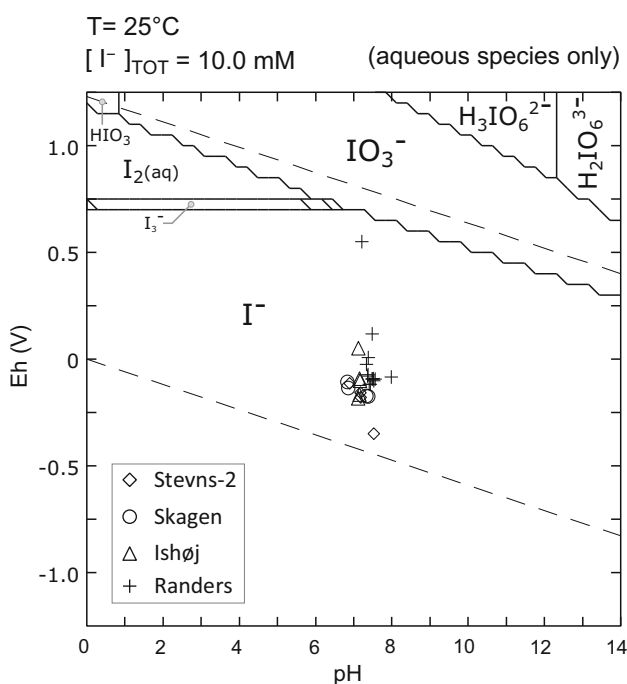


Fig. 3 Pourbaix diagram (also known as E_{H} -pH diagram) for inorganic aqueous iodine species at 25 °C with the groundwater samples from this study. Note: the chemical equilibrium diagram was created with MEDUSA, a software by Ignasi Puigdomenech (<https://sites.google.com/site/chemdiag/>), using the hydrogeochemical log K database HYDRA

samples from *Site a* (Skagen) than to the rest of the *Site c* samples. All samples from *Sites a* and *d* are $\text{Na}^+ - \text{Cl}^-$ type. This is also confirmed by the Pratt diagram (Fig. 4b), where *Site d* plots higher in the saline water zone, and samples from *Site a* plot either in the saline zone or at the border between saline and mixed zones (Fig. 4a). Samples from *Site b* (Randers) plot in the freshwater and in the mixed zones, except for well 69.213 (*Site b*, Vilstrup) which is in the ion-exchanged water zone. The groundwater samples from *Site c*, however, can be found in three

of the four zones: well 207.2820 is in the freshwater zone (together with *Site b*), well 207.2827 is in the mixed zone, but close to the saline border, and the other samples (from wells 207.3004 and 207.2826) are in the ion-exchanged zone. From the Pratt diagram is clear that elevated TI concentrations are found at the more saline zone of the diagram (or close to the border of the saline zone). This is also confirmed based on the Piper classification, from which we see that elevated TI ($> 160 \mu\text{g/L}$) is found in groundwater samples with Cl^- being the dominating anion (Fig. 4a).

Insight into the ion exchange and the groundwater origin is further provided by Na^+/Cl^- and Cl^-/Br^- ratios. Based on Na^+/Cl^- ratios, we see that fresher water infiltrating saline environment (refreshing of the aquifer) is characteristic for well 69.213 (*Site b*, Vilstrup,) (as pointed also on the Pratt diagram) and for the samples from *Site c* with the exception of well 207.2827 (Fig. 4c). Saline water infiltration to a fresher environment is characteristic for *Site d*, well 207.2827 (*Site c*, Ishøj), and some of the wells at *Site b*. Thus, elevated TI concentrations are found in samples indicating reversed ion exchange (*Site d* and well 207.2827 at *Site c*). Taking into account the ± 0.25 uncertainty, *Site a* (Skagen), which is characterized by elevated TI too (TI = 167–308 $\mu\text{g/L}$), represents neither ion exchange nor reversed ion exchange (Fig. 4c). Based on the Cl^-/Br^- ratios, the sample from well 207.3004 (*Site c*, Ishøj), which plotted on the ion-exchanged zone of the Pratt diagram, seems to be affected by road salt (or halite dissolution) with Cl^-/Br^- ratio close to 4000 (Fig. 4d). Few of the samples from *Site b* have Cl^-/Br^- below 200, which is interpreted as reflecting the local precipitation. Based on the results shown in Fig. 4d, it seems that there is no apparent relation between the Cl^-/Br^- ratio and TI.

The redox classification of the groundwater at *Sites a* and *c* (except for well 207.2827), all wells at Bunkedal (*Site b*), and well 69.213 (Vilstrup, *Site b*) shows that

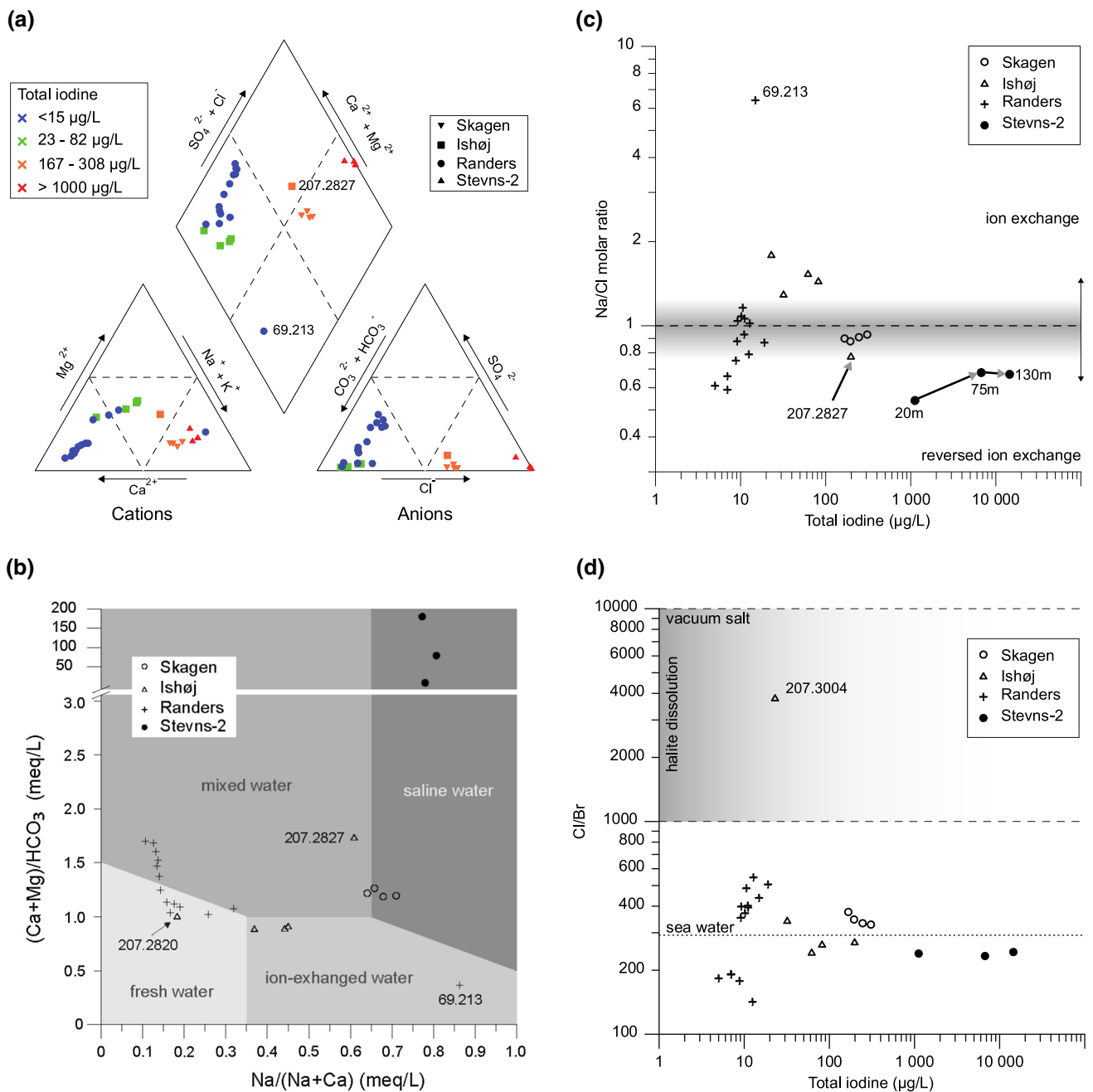


Fig. 4 Groundwater classification based on Piper diagram (a), Pratt diagram (b), Na^+/Cl^- molar ratio (c), and Cl^-/Br^- ratio (mg/L and mg/L) (d) versus total iodine ($\mu\text{g/L}$) from the four study sites

groundwater is strongly reduced (type D), while the groundwater at well 207.2827 (Site c), all wells at Østrup Skov (Site b) and two of the wells at Vilstrup (69.523 and 69.558) (Site b), and Site d can be characterized as slightly reduced (type C). The groundwater at Oust Mølle (Site b) is anoxic nitrate reducing (type B), and well 69.215 (Vilstrup, Site b) is oxic (type A) (the water types are indicated also in Fig. 2). Elevated TI concentrations are found in reduced groundwater, both types C and D.

There is a positive relation between DOC and TI, I^- , and DOI for the sites included in our study (Fig. 5). However, Site a (Skagen) and the samples from 130 m.b.t. at Site d (Stevns-2) are somewhat enriched in DOC ($DOC > 5 \text{ mg/l}$) and do not follow the same trend line as the rest of the samples (Fig. 5). If these samples are excluded, the correlation between DOC and TI is described well by a logarithmic regression line ($DOC = 0.2734 \ln(TI) + 0.6324$, $R^2 = 0.74$). The

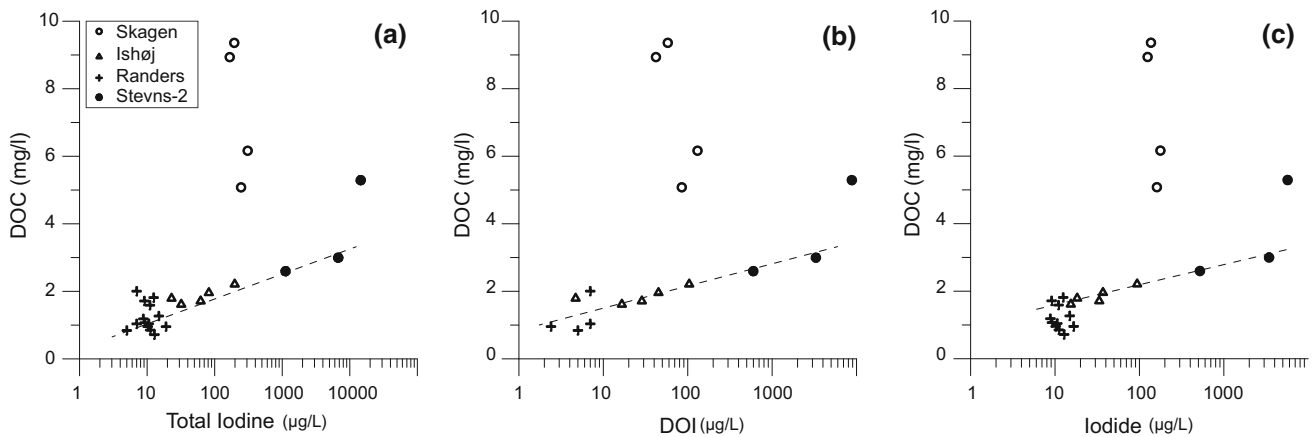


Fig. 5 Dissolved organic carbon (DOC) versus total iodine (a), dissolved organic iodine (DOI) (b), and iodide (c) from the study sites

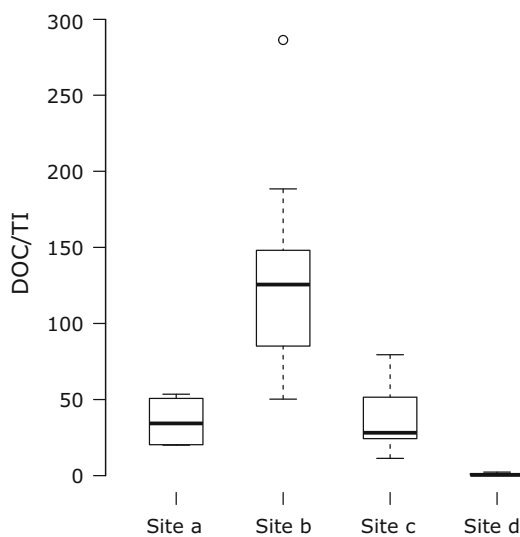


Fig. 6 Boxplots with DOC/TI ratio (mg/L and mg/L) for the four sites

boxplots in Fig. 6 show that based on DOC/TI ratios, *Site a* is somewhat similar to *Site c*, while these two sites are very dissimilar from both *Sites b* and *d*. Median DOC/TI ratios are 34.3 for *Site a*, 125.6 for *Site b*, 28.2 for *Site c*, and 0.5 for *Site d* (Fig. 6).

There is a gradual increase in TI concentrations (I^- and DOI both) with depth at *Site d* (Fig. 5). This trend with depth is also present for most of the other elements too, e.g., Cl^- , Br^- , F^- , Na^+ , K^+ , Ca^{2+} , Mg^{2+} (see ESM Fig. 4). However, for HCO_3^- the trend is reversed—higher TI associates with lower HCO_3^- in depth at *Site d*. Total nitrogen also increases in depth together with the increase in DOI (and I^-). However, NO_3^- was detected only at 75 m depth with 0.1 mg N/L and NH_4^- was below detection limit for all three depths, indicating presence of organic nitrogen (ESM Fig. 5).

Discussion

Iodine speciation and variation

The TI concentrations in groundwater revealed spatial variations both at a 0.1–0.2 km scale and at a 5–10 km scale within the same local geological settings. The relative standard deviations for TI concentrations were < 31% at 0.1–0.2 km scale (based on *Site a* and the sub-sites at *Site b*) and > 33% at 5–10 km scale (based on *Site b* and *Site c*) (Table 2). The TI variability at 0.1–0.2 km scale may be indicative for the small-scale spatial heterogeneity within the local aquifers at both *Site a* and *Site b*. Groundwater TI concentrations reported in scientific literature (see ESM Table 1 and Table 2 from Fuge and Johnson (2015)) vary few orders of magnitude; however, these variations are over larger spatial domains and sometimes due to different geology or geomorphology.

The dominating iodine species in our study (representing mostly reduced aquifers) were I^- and/or DOI, while IO_3^- was not detected (Table 2). As mentioned above, our results are consistent with the chemical equilibrium E_H -pH diagram (Fig. 3). There are only few studies reporting iodine speciation in groundwater samples (see ESM Table 1). For example, Tang et al. (2013) observed that iodine in alkaline and reduced groundwaters from Taiyuan Basin ($n = 950$) was present mainly in the form of I^- , IO_3^- was either absent or negligible, and about 60% of the samples contained also DOI. Results from Datong basin show varying proportions of I^- , IO_3^- , and DOI (Li et al. 2013, 2014). Compared to other compartments of the iodine cycle, groundwater (iodine speciation, transformation, and transport) is receiving relatively low attention. The most recent conceptual model of the global geochemical cycle of iodine by Fuge and Johnson (2015) completely omits groundwater-related processes in the saturated zone.

Stable isotopes $\delta^{18}\text{O}$ and $\delta^2\text{H}$

The stable oxygen and hydrogen isotopic composition of the groundwaters (see ESM xlsx file) were interpreted in order to shed light on possible geochemical processes leading to elevated iodine levels at the four locations. The wells at Skagen, Randers, Ishøj (*Sites a, b, c*) have a relatively constant oxygen and hydrogen isotopic composition ($\delta^{18}\text{O}$: -9.17‰ to -8.44‰ ; $\delta^2\text{H}$: -62.68‰ to -57.27‰), while the samples from Stevns-d (*site d*) are different (Table 3).

These results are consistent with published data from other studies on Danish groundwater (Fig. 7), and the samples plot close to the global meteoric waterline (GMWL) (Craig 1961). Any given locality will be characterized by its own local meteoric line which could differ from the GMWL; however, no local meteoric waterline is established for these locations. Regional variations are due to the origin of vapor mass, secondary evaporation during rainfall, annual temperature variations, among others (Clark and Fritz 1997). Next to the hydrological effects connected to the precipitation and the climatic conditions,

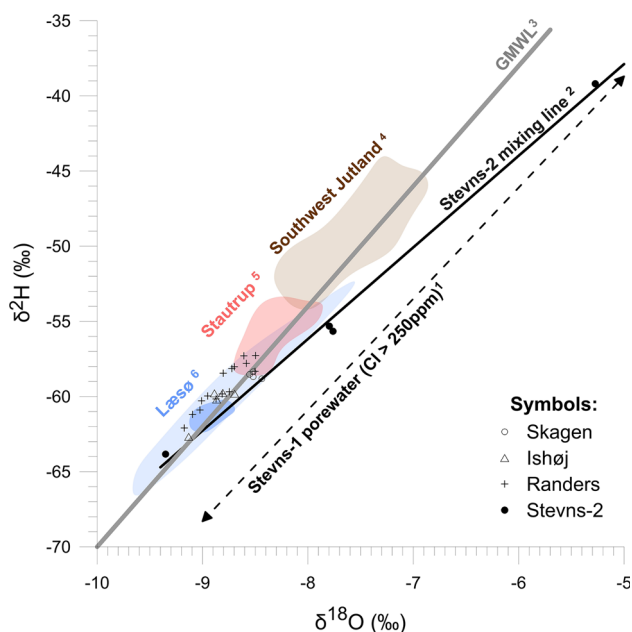


Fig. 7 Stable oxygen and hydrogen isotope distribution in Danish groundwater. *Symbols*—samples collected October 2012 at our four study sites with a fitted line (**black bold trend line**) for deep saline water mixing, based on the measurements at Stevns-2 borehole [2]; *Literature sources*: [1] **black dashed trend line** of pore water samples with $\text{Cl} > 250 \text{ mg/L}$ from Stevns-1, where the *arrows* show the span of the samples from Bonnesen et al. (2009) from the same site; [3] GMWL—Global meteoric waterline (Craig 1961); the *colored areas* are the outlined data clouds from: [4] Jørgensen et al. (1999), [5] Jørgensen and Holm (1995), [6] Jørgensen (2002) dug wells (*light blue*) and drinking water wells (*dark blue*). See ESM Table 2 for further details

the stable isotopic composition of groundwater can vary due to water–rock (soil, sediment) interactions, mixing with different paleo-waters, seawater, or mixing between different groundwaters. The proximity of *Sites a, b, and c* samples to the GMWL can be interpreted as the groundwater at these locations has a close resemblance with the isotopic composition of the precipitation in Denmark. The small variation in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ which is observed for those three study sites is most probably caused by minor natural differences in the local hydrological conditions. This may indicate that elevated iodine levels are due to recent process at *Sites a, b, and c*.

The isotopic composition of *Site d* samples varies substantially with depth and Cl^- concentration too, as shown in Fig. 7. The shallowest sample (20 m.b.t.) has similar isotopic composition as the groundwater samples from the other locations ($\delta^{18}\text{O} = -9.35\text{‰}$ and $\delta^2\text{H} = -63.84\text{‰}$), whereas the deepest one (130 m.b.t.) is well below the GMWL ($\delta^{18}\text{O} = -5.27\text{‰}$ and $\delta^2\text{H} = -39.19 \text{‰}$). This is also in agreement with pore water data from another borehole in the same area (Bonnesen et al. 2009) (Fig. 7). The middle depth (75 m.b.t.) sample's isotopic composition is interpreted as mixing between these two types of groundwater: the present day, shallow (20 m.b.t.), fresher groundwater and the deep residual saline pore water (130 m.b.t.). The mixing line from Stevns-2 samples is with the equation $\delta^2\text{H} = 6.11 \delta^{18}\text{O} - 7.4$ ($r^2 = 0.995$), Fig. 7. Such departure from the GMWL could be caused by evaporative enrichment and exchange with the chalk; partially it could also be representing the climatic differences at the recharge period. Bonnesen et al. (2009) argued that the combination of salinity and lighter isotopic composition cannot be explained simply by evolution of the connate seawater trapped in the pores of the chalk during deposition. Instead, they suggested that transport of saline water from the underlying Mesozoic sediments, as a result of compaction which terminated around 4 million years ago is influencing the formation waters in the chalk (Bonnesen et al. 2009). Additionally, a refreshing of the chalk aquifer has taken place for the last 1–5 million years since the latest uplift (Bonnesen et al. 2009).

Iodine in different types of aquifers

The postglacial marine sandy aquifer at *Site a* (Skagen) is not protected by an aquitard; thus, iodine leaching through the soil (arenosols developed on eolian sand parent material) can be a minor local source, which would be governed by the sorption capacity of the topsoil. Recent seawater intrusion due to the groundwater abstraction practices is not a likely source even though the wells are about 1–2 km from the North Sea, as the groundwater pumping volumes are highly restricted for protection of the local flora. The

observed groundwater TI concentrations (167–308 $\mu\text{g/L}$) are too high to reflect present seawater TI (ESM Table 1). The major iodine source in the groundwater at *Site a* is interpreted to be the marine origin of the sediment. The postglacial marine sand at *Site a* is high in Holocene marine organic matter (mean DOC ± 1 standard deviation is 7.4 ± 1 mg/L); thus, iodine may be released to the groundwater from the decomposing of and desorption from this natural organic matter. The reduced conditions can be favoring groundwater enrichment in iodine due to I^- dissociation from natural organic matter (Shimamoto et al. 2011), conversion of IO_3^- and DOI to the more mobile I^- (Li et al. 2013), and/or dissolution from iron oxyhydroxides (Li et al. 2013, 2014).

The groundwater at *Site b* (Randers) is with the lowest TI concentrations of all the study sites (varies between 5 and 19 $\mu\text{g/L}$). The groundwater sampled at this site represents two different aquifers: the glacial meltwater sandy aquifer and the pre-Quaternary limestone/chalk aquifer. The positive relation of depth and TI (ESM Fig. 3) could be an indication for the importance of the residence times (age) of the groundwater. It can be assumed that the longer the residence time the higher TI, as the groundwater and sediment had interacted over a longer period, which was also proposed by Lloyd et al. (1982) for groundwaters from Cretaceous English Chalk. Accordingly, the primary iodine source in Randers is considered to be the influence from the marine origin of the pre-Quaternary aquifer. Some minor influence of other sources is also possible. At some of the wells, the Na^+/Cl^- ratio suggests saline water infiltration at a fresher environment and the groundwater composition is characteristic for fresh and mixed groundwater (Fig. 4). This could be explained by intrusion of brackish water from Randers Fjord (Cl^- levels are, however, low) or leaching from the agricultural practices in Randers Fjord catchment. The glacial meltwater sand aquifer at the sub-site Vilstrup is characterized by similar TI concentrations as the limestone/chalk aquifer at the rest of the sites in Randers. This is, however, not unusual, as in Quaternary sediments above pre-Quaternary marine calcareous deposits iodine concentrations were found to be generally elevated, according to Fuge (2005). It is possible that there is connection between the two aquifers and the TI concentrations in the late glacial meltwater sandy aquifer reflect the higher TI concentrations from the pre-Quaternary limestone/chalk aquifer.

The TI concentrations in the aquifer at Ishøj (site c) vary substantially (Table 2) even though the groundwater samples are from the same Campanian–Maastrichtian chalk. Initially recent seawater intrusion was suspected as TI concentrations are lower inland than close to the sea (respectively, $32 \rightarrow 23 \rightarrow 62$ (82) $\rightarrow 198$ $\mu\text{g/L}$). However, the Na^+/Cl^- ratio suggests that saline water is

infiltrating a fresher environment at well 207.2827 only, but Cl^- concentrations are still low and the TI concentration (198 $\mu\text{g/L}$) here is about 4 times higher than TI in the seawater (ESM Table 1). Opposite, refreshing of the aquifer is indicated by Na^+/Cl^- ratios for the rest of the wells at this site. Based on that, even though an iodine trend is observed toward the coast, other source than seawater intrusion must be considered. Both old saline water diffusion from the deeper underground or/and leaching from the recent marine sandy parent material are possible (see geology in Fig. 2). Well 207.3004 could be influenced also by anthropogenic road salt based on the Cl^-/Br^- ratio, suggesting that a contact between the topsoil (terrain) and the aquifer at the vicinity of the well should be present although no obvious anthropogenic sources of iodine are expected. Together, the main source of the elevated but variable iodine concentration at the Ishøj site has to be related to the sedimentary differences and/or different geochemical processes within the Campanian–Maastrichtian chalk aquifer.

The TI concentrations at Stevns-2 (1.12–14.5 mg/L) are unprecedentedly high for Danish groundwater, and are comparable to levels generally found in brines, mineral waters, and formation waters as well as for the groundwaters in some Chinese inland basins (ESM Table 1). Stevns-2 is located in Campanian–Maastrichtian chalk similar to the wells at *Site c* (Ishøj), but there is definitive difference in the water composition, the stable isotopes, and the TI levels (see previous sections). This indicates that there is a different water source at Stevns-2 and most probably different hydrogeochemical processes are affecting iodine mobilization at this site. The Na^+/Cl^- ratio suggests that saline water is infiltrating a fresher environment, but the observed TI concentrations are too high to be explained by recent seawater intrusion even though the well is located 200 m from the sea. Our stable isotope results are in agreement with the study of Bonnesen et al. (2009) on the origin of saltwater in the chalk of Northwest Europe, suggesting that diffusive transport, from the underlying sandstone formation (Gassum formation) as a result of compaction, is influencing the chalk aquifer geochemistry. The compaction of marine sediments and the resulting release of saline formation waters to the groundwater are a potential iodine source and should be studied in more detail. The groundwater sampled at Stevns-2 does not satisfy drinking water quality standards due to its high salinity levels; however, the area is classified as valuable for groundwater abstraction and it is not far from a particularly valuable zone (Thomsen et al. 2004); thus, further investigations should establish the extent to which fresh groundwater resources are affected by these underlying high-iodine waters.

Table 4 Summary of study sites hydrogeochemical characteristics, observed iodine concentrations and speciation

Study site	Site a (Skagen)	Site b (Randers ^a)	Site c (Ishøj)	Site d (Stevns-2)
Aquifer type	Postglacial marine sand	Danian/Selandian chalk (OM, ØS, B, V-69.213)	Campanian–Maastrichtian chalk	Campanian–Maastrichtian chalk
Aquitard overlaying the aquifer	None	Glacial meltwater sand (V) Paleocene clay (OM, ØS, B)	Glacial moraine clay	None
Parent material (1 m depth) ^b	Postglacial eolian sand	Glacial meltwater silt (thin layer) (V) Glacial moraine clay (OM) and sand (V) Postglacial marine sand (B) and freshwater sand (ØS)	Glacial moraine clay Postglacial marine sand (207.2827)	Campanian–Maastrichtian chalk
Dominating soil types ^c	Arenosols (100%)	Gleysols (90%) (ØS, B, V) Luvisols (45%) (OM)	Luvisols (75%)	Luvisols (75%)
Water type (Piper diagram)	Na ⁺ –Cl ⁻	Mainly Ca ²⁺ –HCO ₃ ⁻	Mainly Ca ²⁺ –HCO ₃ ⁻	Na ⁺ /Cl ⁻
Water type (Pratt diagram)	Mainly saline water	Mainly fresh and mixed water	Mainly ion-exchanged water	Saline water
Cl ⁻ /Br ⁻ (mg/mg)	328–376	142–546	243–343 (3817 at well 207.3004)	233–243
Na ⁺ /Cl ⁻ (mol/mol)	0.88–0.93	0.59–6.41	0.78–1.80	0.54–0.68
Ion exchange (Na ⁺ /Cl ⁻ based)	Mainly equilibrium	Mainly equilibrium	Mainly ion-exchanged water (when fresher water infiltrates a sediment of marine origin)	Reversed ion-exchanged water (infiltration of saline water to fresher sediment)
Redox state	Strongly reduced (type D)	All redox conditions (types A, B, C and D)	Slightly and strongly reduced (type C and D)	Slightly reduced (type C)
Stable isotopes	Resemble precipitation	Resemble precipitation	Resemble precipitation	Resemble precipitation (20 m.b.t.) Mixing of fresh and saline groundwater (75 m.b.t.) Resemble old saline water (130 m.b.t.)
DOC (mg/L)	5.08–9.36	0.72–2 (positive correlation with TI)	1.65–2.25 (positive correlation with TI)	2.6–5.29 (positive correlation with TI)
Iodine concentration (µg/L)	167–308	5–19	23–198	(1.12–14.5) × 10 ³
Iodine species	I ⁻ and DOI	I ⁻ or DOI	I ⁻ and DOI	I ⁻ and DOI

^a OU—Oust Mølle; ØS—Østrup Skov; B—Bunkedal; V—Vilstrup

^b see ESM Fig. 2

^c Soil Map of Denmark (Breuning-Madsen and Jensen 1996)

Summary and conclusions

Our findings show that high-iodine groundwater concentrations at the selected four Danish study sites are influenced by different factors, which were elaborated on the basis of the hydrogeochemical interpretations summarized in Table 4.

Based on our results, we identified three potential explanations for the observed elevated iodine in Danish groundwater, which are due to different types of marine influences and have varying importance within the four sites:

1. Leaching from potentially enriched in iodine topsoil (suspected to be enriched due to atmospheric deposition and proximity to the sea). This is considered to be of minor importance at our four sites. The aquifers at *Sites b* and *c* are protected by thick clay layers (Fig. 2), and at the other two sites its contribution is probably relatively low (e.g., below few 10s of $\mu\text{g/L}$). Topsoil TI concentration characterization is, however, lacking for Denmark.
2. Desorption from iodine-enriched organic matter or minerals within the marine sediments. This influence is most pronounced in the groundwater from the shallow Holocene marine aquifer (*Site a*), which is characterized by high DOC ($> 5 \text{ mg/L}$) and high TI ($> 167 \mu\text{g/L}$).
3. Influence from deep residual saline water due to advective or/and diffusive transport of iodine. This effect was observed in the deep well at *Site d* where TI ranged between 1.12 and 14.5 mg/L and Cl^- was between 2×10^3 and $28 \times 10^3 \text{ mg/L}$, but may also be an important source at other chalk/limestone aquifers.

Further hydrogeochemical investigations addressing potential temporal variations in iodine concentration and speciation at these four sites, as well as spatiotemporal investigations at other hydrogeological settings, are needed. Understanding iodine behavior and spatiotemporal patterns in groundwater has direct importance for improving estimates of iodine exposure via drinking water.

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