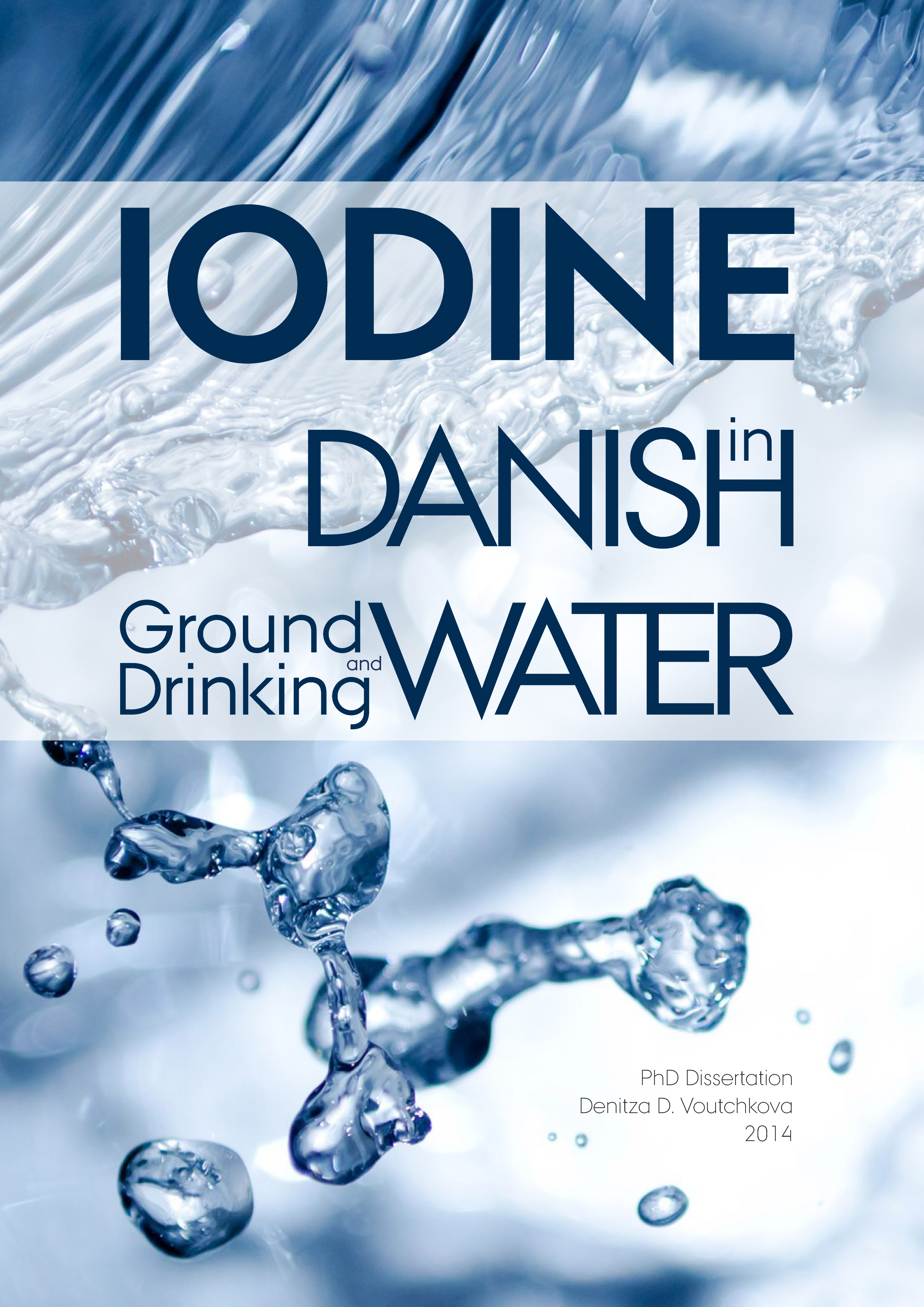

IODINE in DANISH Ground and Drinking WATER

PhD Dissertation

Denitza D. Voutchkova

2014

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CONTENTS

Preface

This thesis is a result of a three-year PhD project which is part of the **GEO**CENTER research project *"Iodine in the hydrological cycle of Denmark: implications for human health"*, jointly financed by the Geological Survey of Denmark and Greenland (GEUS) and Aarhus University (AU).

The study was conducted between August 2011 and July 2014 under the main supervision of Associate Professor Søren M. Kristiansen (AU) and Senior Scientist Birgitte G. Hansen (GEUS). The research was carried out at the Department of Geoscience (AU) and the Department of Groundwater and Quaternary Geology Mapping (GEUS), both situated in Aarhus (Denmark). Additionally, I have spent three months (Autumn 2013) at the School of Geography and Archaeology, NUI Galway (Ireland) working together with Dr. Chaosheng Zhang.

During my enrolment as a PhD fellow and in accordance with *the Danish Ministerial Order on PhD Degree Programme*, next to conducting an independent research under supervision while participating in different active research environments (as mentioned above), I have also completed PhD courses totalling 30 ECTS credits, gained teaching experience, and disseminated the results of my work both nationally and internationally (see *Appendix A*).

The PhD thesis is composed of the enclosed five manuscripts which are in a different stage of completion (throughout the *Summary Chapter*, referred to by roman numerals):

Paper I: **Voutchkova, D.D.**, Kristiansen, S.M., Hansen, B., Ernstsen, V., Sørensen, B.L., Esbensen, K.H. (2014) Iodine concentrations in Danish groundwater: historical data assessment 1933–2011. *Environmental Geochemistry and Health*, p.1-14, DOI 10.1007/s10653-014-9625-4

Paper II: **Voutchkova, D.D.**, Ernstsen, V., Hansen, B., Sørensen, B.L., Zhang, C., Kristiansen, S.M. (2014) Assessment of spatial variation in drinking water iodine and its implications for dietary intake: a new conceptual model for Denmark. *Science of the Total Environment 493* (2014), p.432–444, DOI 10.1016/j.scitotenv.2014.06.008

Paper III: **Voutchkova, D.D.**, Hansen, B., Ernstsen, V., Kristiansen, S.M. Hydrogeochemical characterisation of Danish groundwaters in relation to iodine (to be submitted at *Hydrogeology Journal*)

Paper IV **Voutchkova, D.D.**, Sørensen, L.T., Ernstsen, V., Kristiansen, S.M., Hansen, B. High resolution depth profiles of iodine concentration in groundwater at four multi-screen wells in Denmark: possibilities for future research *(work in progress)*

Technical Note I: **Voutchkova, D.D.**, Hansen, B., Ernstsen, V., Kristiansen, S.M. Design of a drinking water sampling campaign for nationwide assessment of drinking-water importance for dietary iodine intake (to be submitted at *Hydrogeology Journal)*

In accordance with the *Rules and Regulations* of the Graduate School of Science and Technology (GSST, AU), the PhD thesis, composed of the listed above manuscripts, has to resemble a review paper. Thus, the first part of the PhD thesis is a Summary Chapter presenting some background, the PhD objectives, the used data, and study locations, methodologies, and the main results. Next to that, a general conclusion and outline of some topics for further persuasion are given. The five manuscripts follow the Summary Chapter and some additional materials are provided in Appendices, e.g., a list of published conference abstracts and the electronic supplementary data accompanying the manuscripts,.

I would like to note that, while the frame of the **GEO**CENTER project includes the whole hydrological cycle of iodine, my work was limited to a small part of it, namely the iodine concentration and speciation in Danish groundwater and drinking water. The decision of narrowing the focus was taken in the planning phase of my PhD project and reflects the imposed by the three-year PhD programme time limitations. Even though the presented here work is based on the enclosed, thoroughly reviewed, and revised manuscripts, the PhD thesis itself has not been subjected to a review, thus it is possible that there are some linguistic inaccuracies and/or small mistakes. Nevertheless, I hope you will find my PhD thesis interesting!

Denitza D. Voutchkova
(Деница Д. Вучкова)

Aarhus, July 2014

Acknowledgements

Roll on, Roll on, Roller Coaster
We're one day older and one step closer
Roll on, there's mountains to climb
Roll on, we're on borrowed time

Kid Rock, "Roll On"

During the last few months, while I was trying to finalise this work, there were many occasions I would reflect on the past. Mostly, late in the night when everything was quiet and peaceful. Or early in the morning, while listening to the first songs of the birds and greeting the Scandinavian summer sunrises. If I had to choose a single song to be the soundtrack for the past three+ years, it would be *Roll on* by Kid Rock. Being a PhD fellow at Aarhus University was like a roller coaster – ups and downs, excitement, fear, fun, stress… Being able to write this acknowledgements part makes me feel especially happy, because it means that we've (all project participants and I) overcome the numerous challenges. Still, there are mountains to climb, as Kid Rock sings. Many questions are waiting to be answered and many doubts are still present. Nevertheless, the Voltaire's *"Doubt is not a pleasant condition, but certainty is absurd."* make me think it is ok to have doubts.

First and foremost, I would like to thank my main supervisors Søren M. Christiansen (AU) and Birgitte Hansen (GEUS). Without their positive attitude, I would have sunk in my personal pool of negativism. It has been a real pleasure to interact with them throughout the past three years, filled with many (and not only) scientific discussions. I wish to think that I have learned from them not only on work related subjects but also about the Danish ways… the culture, society, ethics etc.

Second, I had the chance to work together with Vibeke Ernstsen (GEUS) and even though our offices were in different cities, I feel that we had a good communication and mutual understanding. I enjoyed the times I was visiting her in GEUS, Copenhagen and I believe that without her we wouldn't have been able to achieve the project goals in the existing time frame.

Next to Søren, Birgitte, and Vibeke, acknowledgements are also due to Kim Esbensen (GEUS) for being part of the **GEO**CENTER project. The PhD position I was employed at wouldn't have existed without their group effort to write the project proposal and get it funded. Kim Esbensen was also the person who introduced me to the universe of multivariate data analysis and for this I am especially thankful. When it comes to data, I am grateful also to Brian Sørensen because he shared his extensive knowledge on Jupiter database and downloaded (prepared) the huge datasets I have been working on (both iodine and arsenic).

I wouldn't like to miss the opportunity to thank also to Lasse Gudmundsson, Christina Lynge, Pernille Stockmarr, Jørgen Kystol, Lærke Thorling, Keld R. Rasmussen, Bent Odgaard and all other nice people from GEUS and AU, who have helped me in one or other occasion throughout the three years. Also, I would like to thank Dr. Chaosheng Zhang for making my three-month stay at NUI Galway pleasant and fruitful.

Special thanks are due to all happy inhabitants of the Quality Street (AU) for creating a nice working environment and for being entertained by my linguistic (and otherwise) clumsiness. I have spent many hours talking about work or plain weird things with my office-mates Margrethe, LP, Jane B., and Rasmus, and with all the rest of the PhD crowd at the Department of Geoscience (AU).

Funding for this PhD project has been provided by **GEO**CENTER Denmark, with the participation of Aarhus University and the Geological Survey of Denmark and Greenland. During my PhD studies I got a student travel award by the *International Medical Geology Association* (IMGA) to attend the MEDGEO2013 (USA). Also, I was awarded on behalf of the *International Registry of Pathology* (IRP) with the IMGA Gardner Research Grant (US$2000) for my application essay entitled *"Geographical distribution of drinking water iodine in Denmark as important factor for recognizing population groups with low iodine intake"*. I would like to thank the Danish state for funding my Master studies at Aalborg University and the Republic of Bulgaria for providing me with many years of almost free education through elementary, high-school, and the University of Architecture, Civil Engineering, and Geodesy (UACEG, Bulgaria). UACEG not only gave me the title master in civil engineering, but also shaped who I am today over the long and hard six years.

On a more personal note, I would like to express my gratitude to Niels Claes for the support, patience, and love… for the stimulating scientific discussions, for taking care of the important things, while I was trying to finalise this work. The first year of my PhD, while he was at ETH Zurich, was the hardest time I have experienced and I am thankful he came back to Denmark to share his life with me.

Next to Niels, my parents and relatives have been very supportive all the way through. Even though they are more than 2000 km away, I had the feeling that they were constantly with me. I can't miss the opportunity to thank my father for sharing the wisdom *"everything is possible"* and to my mother for being a great moral and professional example. We've spent many Skype hours during the last three years discussing what a good science practice is and how things should be done in a perfect world. And while my father can be kept responsible for my willingness to jump into new topics and to experiment, it is entirely my mother's fault that I am so demanding both to myself, but also to everyone surrounding me.

Thank you all,

Denitza D. Voutchkova
(Деница Д. Вучкова)

Aarhus, July 2014

Abstract

Iodine plays an essential role in the metabolism and the early development of humans. Both, insufficient and excessive iodine intakes can cause health problems. Worldwide, the focus falls mainly on the iodine deficiency (ID) and the usual prevention measure is implementation of universal iodizing program (USI) – iodizing the table salt or/and fortifying some foods (e.g. bread). Denmark is classified as country with mild ID status, thus a mandatory USI was implemented in 2001.

One of the natural dietary sources of iodine is water. On average, for Denmark, beverages (mainly water) provide about 14% of the dietary iodine (before the USI – 25%). Spatial variation of iodine concentrations in drinking water (DW) was reported in 1999. DW in Denmark is of groundwater (GW) origin, thus the variation was suspected to be governed by the geology. However, no special attention has been paid to DW and GW iodine concentrations and speciation and comprehensive hydrogeochemical or geostatistical studies are lacking.

Therefore, three main objectives were formulated in this PhD project: 1) to map iodine concentration and speciation in DW and GW in Denmark, 2) to study the spatial patterns and to elucidate the factors governing them, and 3) to evaluate the importance of the spatial variation of DW iodine to the populations' nutrition (health). Two types of data were used for fulfilling the project objectives: 1) from two sampling campaigns (DW: 2013, GW&DW: 2012) designed as part of this project, and 2) historical data (two GW datasets: 1933-2011 and 2011-2014) extracted from the public nationwide geological and hydrological database, Jupiter. The samples from both sampling campaigns were analysed for iodide, iodate, total iodine (TI) and the major constituents. However, iodine speciation data was not present in the historical datasets.

Overall, the results from the different GW investigations showed that the factors governing iodine concentration in GW are site and depth specific. Also, it is probable that different geochemical processes are dominating at different iodine levels. There is a need for further geochemical studies focused on the small scale local variations in order to identify the sources, processes, and mechanisms governing iodine enrichment in GW. That way, the large scale trends of iodine in GW and in DW, will be better understood. The next three paragraphs provide an in-depth overview of the main findings from the different GW and DW investigations which were part of this project.

The nationwide DW sampling campaign covered 144 waterworks, representing approximately 45% of the total annual GW abstraction. TI concentrations in treated DW were found in the range <0.2-126 μg/L (mean: 14.4 μg/L, median 11.9 μg/L) with complex spatial pattern both with respect to the concentration and speciation. Both the geology and the GW treatment are responsible for this complexity. Local Moran's I analysis, employed to study the clustering patterns, resulted in a new conceptual model for iodine in Danish DW. The new conceptual model incorporates the observed variation on the continental part of Denmark (Jutland), separating it in five areas with different iodine content in DW. Whereas, the previous widely recognised model lumps whole Jutland in one area with overall low DW iodine content. However, Jutland is the part of Denmark exhibiting the largest difference in the DW iodine levels. As part of this study the drinking water contribution to the dietary iodine intake was estimated to vary from 0% to above 100% (adults) or 50% (adolescents) from the recommended by WHO daily intake. Therefore, it has been suggested that monitoring of the iodine status of the population in only one city on Jutland may not offer a sufficiently accurate picture. Instead, local variations of DW iodine should be mapped and incorporated in future adjustment of the monitoring and/or the USI programs.

The two historical datasets provided information on GW iodine with samples covering the entire country. GW iodine was in the range <0.4-1220 µg/L (mean: 13.8 µg/L, median 5.4 µ/L, n=2562) based on 1933-2011 dataset; and <0.3-240 µg/L (mean: 8.3 µg/L, median 4.4 µ/L, n=589 only last sample per location) based on the 2011-2014 dataset. The first dataset (1933-2011) revealed that GW iodine is characterised by far from homogeneous spatial distribution with both small scale variation and large scale trends. High iodine and low iodine samples were clustering together. The middle part of Jutland (Central Denmark) was the administrative area with the lowest average TI concentration (7.6 µg/L), while the administrative Capital Region was with the highest (26.8 µg/L). Elevated iodine concentrations were observed predominantly in GW from depths below 40 m.b.t. The highest 75th, 90th, 95th percentiles were for GW samples representing Paleocene to Cretaceous limestone/chalk. Multivariate analysis (PCA) of center log-ratio (clr) transformed data revealed association between iodine, Li, B, Ba, Br. Additionally, high iodine was associated with reduced and alkaline GW ($Ca\text{-}HCO_3$ was the dominating GW type). The second dataset, based on data from 2011-2014 confirmed the small scale spatial variability–high and low TI concentrations were found to cluster together too. A depth-age-concentration analysis showed that TI concentrations >27 µg/L were found in samples from GW older than 25 years (except for one sample).

The small scale variation of iodine in GW was studied based on the GW&DW 2012 sampling campaign at four study areas and data from four multi-screen wells (2nd historical dataset). TI concentrations varied locally both at 0.1-0.2 km scale and 5-10 km scale within the same aquifer. At the four sites TI concentrations were in the range 5-14500 µg/L. The dominating iodine species in the predominantly reduced GW were iodide and dissolved organic iodine. The elevated iodine concentrations seem related to the marine origin of the aquifers, as the GW with elevated iodine concentrations were from postglacial marine sand or pre-Quaternary marine chalk. Diffusion of old saline water was suspected to be the main source of iodine at the well with the highest TI concentration. Additionally, a relation between iodine and DOC was observed which points to the importance of the organic matter. Possible governing processes at the four investigated sites are organic matter degradation and/or reductive dissolution of oxyhydroxides (iodide is strongly polarizable and substitutes for hydroxyl ion in various compounds). The depth profiles of four multi-screen wells located in different parts of Denmark (10 cm long screens, n=10-23, in glacial melt-water aquifers) showed that TI is highly variable (2.2-7.1 µg/L, 1-4.2 µg/L, 2-48 µg/L, 2.2-25 µg/L). Both, small (±1-2 µg/L) and large (±10-20 µg/L) differences in the TI concentrations were observed at different depths at the same well(s). The local heterogeneity of the aquifers (in depth), changes in the redox conditions, pH, organic matter and metal hydroxides content, as well as, complex hydrogeological conditions may explain these observations.

Based on the results from this three-year PhD project, it is recommended to continue investigating iodine variation in DW and GW on different temporal and spatial scales in order to enable data-based informed decision-making for future adjustments of USI and/or the monitoring programme following up on the iodine status of the Danish population.

Dansk resumé

Jod har ikke været studeret ret meget i dansk grund- og drikkevand, på trods af, at det har en essentiel rolle i menneskers stofskifte, og at drikkevand er en vigtig kilde til jod i befolkningens kost. Både for lavt og for højt indtag af jod kan skabe sundhedsproblemer igennem hele livet. På verdensplan er fokus primært på at forebygge jodmangel, og mange lande har indført jodberigelse af fødevarer som bordsalt og brød. Danmark er klassificeret som et land med generel mild jodunderskud i kosten, og obligatoriske jodberigelse af bordsalt og brød blev derfor indført i 2001. I Danmark får vi i dag gennemsnit ca. 14 % af jodindtaget fra drikkevarer, primært via drikkevandet, og med store lokale variationer. Dette tal var før 2001 ca. 25 %. Drikkevandet i Danmark er udelukkende grundvand og de rummelige variationer skyldes derfor geologiske forskellige.

For at belyse jods naturlige variationer i grund- og drikkevand startede Geocenter Danmark dette ph.d. projekt med 3 formål: 1) kortlægge jod koncentrationer og kemisk speciering (hhv. jodid, jodat og organisk bundet jod) i dansk grund og drikkevand, 2) beskrive de lokale variationer og forstår de geologiske og kemiske faktorer som styrer dem, og 3) at vurdere betydningen af de naturlige, lokale variationer for befolkningens jodindtag.

To typer data anvendes til at beskrive dette, 1) vandprøver som blev indsamlet fra udvalgte vandværker og boringer over hele landet i løbet af projektet, og 2) alle eksisterende data med jod fandtes i den offentlige database Jupiter.

Generelt viste undersøgelserne, at grundvandets indhold af jod, og dets speciering, er meget betinget af lokale forhold i geologien og geokemien. Et af studierne viste fx, at total jodindhold i grundvandet varierer lokalt både på en 0,1-0,2 km og 5-10 km skala selv indenfor det samme grundvandsmagasin. Højere jodkoncentrationer i grundvandet er især fundet dybere end 40 m. under terræn, mens de højeste koncentrationer (75, 90, 95 % percentiler) findes i grundvand fra Paleocæne samt ældre kalk- og kridtgrundvandsmagasiner. Yderligere fandt vi, at høje jodindhold var korreleret med reduceret grundvand og Ca-HCO_3 grundvandstypen. En alders-dybde analyse viste, at total jod i grundvandet over >27 µg/L næsten udelukkende findes i grundvand som er ældre end 25 år. De dominerende kemiske species i dansk grundvand var jodid og opløst organisk jod. Hvor der findes svagt forhøjede jodindhold skyldes det især, at grundvandet er i kontakt med gamle marine aflejringer, som post-glacial saltvandssand og kridt/kalk. Disse har dog sjældent salt grundvand i sig i dag. Et semi-log forhold mellem total jod og opløst organisk stof viste, at desorption/opløsning af organisk stof fra gamle marine aflejringer er vigtig for mængden af opløst jod i grundvandet. Reduktion og opløsning af jernhydroxider kan dog også spille ind ved at frigive jod til grundvandet. Hvor der er meget høje jodindhold i grundvandet (>3-400 µg/L), tyder resultaterne på, at det skyldes diffusion af opløst jod fra dybtliggende, gammelt salt grundvand. De observerede store forskelle i jodkoncentrationerne i dansk grundvand skyldes sandsynligvis derfor en kompleks geokemisk kombination af redox forhold, pH-værdi, organisk stof og jernhydroxid hydroxider i grundvandsmagasinet; men er også styret af grundvandets strømning.

En landsdækkende indsamling af drikkevandsprøver fra 144 vandværker, som I alt repræsenterer 45 % af den indvundne mængde drikkevand, viste at total jod indholdet varierer mellem <0,2 til 126 µg/L (gennemsnit: 14,4 µg/L, median 11,9 µ/L) med komplekse rummelige mønstre for både totalt indhold og speciering, som både er relateret til geologien og vandbehandlingen på vandværket. Især Jylland har store regionale og lokale forskelle. På baggrund af ovenstående er der udarbejdet et forslag til en bedre rummelig opdeling af landet i delområder hvor befolkningen i gennemsnit indtager ca. lige meget jod via drikkevandet. Vores undersøgelser indikerer også, at Danmarks befolknings indtag af jod via drikkevandet varierer fra 0 % til over 100 % (voksne) eller 50 % (yngre mennesker) af det af WHO anbefalede daglige indtag.

Translation in Danish:
Søren M. Christiansen

Резюме

Йодът е жизнено необходим за метаболизма и ранното развитие на човека. Негативен ефект върху здравето имат както недостигът, така и излишъкът на йод. В глобален план, обаче, фокусът пада предимно върху йодната недостатъчност, като обичайното средство за профилактика е универсалното йодиране на трапезната сол и другите хранителни продукти, например хляба. Дания е класифицирана като страна с лека йодна недостатъчност. По тази причина през 2001 влезе в действие универсална йодираща програма (УЙП), включваща йодиране на трапезната сол и на солта за производство на хляб и сладкарски изделия. Един от естествените източници на йод е питейната вода. Установено е, че в страната 14% от йода в датската диета е от консумирани напитки (предимно вода). Преди въвеждането на УЙП те са допринасяли средно с 25% за дневната доза йод. През 1999 г. за първи път е докладвано наличието на различие в концентрацията на йод в питейната вода в отделни части на Дания, където основният (и единствен) източник на питейна вода са подпочвените води. Предполага се, че причините се коренят в различния геоложки произход на определени райони. Въпреки това липсват геохимични и геостатистически проучвания с фокус върху йода (относно концентрацията и химичната форма) в датските питейни и подпочвени води.

Поради тази причина целите на тази докторантура са: 1) да се картографират видът и концентрацията на йод в датските подпочвени и питейни води; 2) да се изследват геопространствените тенденции и да се изяснят факторите, които ги обуславят; и 3) да се направи оценка на важността на географскити различия на концентрацията на йод в питейната вода за здравословния статус на датското население.

За постигане на тези цели са използвани два типа данни: 1) от две кампании за вземане на водни проби за лабораторни изследвания (питейна вода – 2013 г., подпочвена и питейна вода – 2012 г.), организирани като част от този проект, и 2) два масива с архивни данни от публичния геоложки и хидрогеоложки регистър, Jupiter (подпочвени води 1933-2011 и 2011-2014). Лабораторните изследвания на водните проби включват анализи за концентрацията на йода и формата му (вкл. двете неорганични форми – йодид и йодат), докато архивните данни предоставят информация само за общата концентарция на йода.

Резултатите от проведените анализи показват, че факторите, които обуславят концентрацията на йод в подпочвените води, са специфични за изследваните географски локации и дълбочини на водовземане. Също така е много вероятно различни процеси да са доминиращи при различни йодни нива. За да се идентифицират източниците, процесите и механизмите, които обуславят високите концентрации на йод в някои попдпочвени води, са необходими допълнителни проучвания в локален мащаб. Това би допринесло и за изясняването на тренда на регионално и национално ниво. В следващите няколко параграфа са резюмирани основните резултати от изследванията, които са съставна част на тази докторска дисертация.

Националната кампания за проучване на питейните води вкючва водни проби от 144 пречиствателни станции, покриващи цялата страна и представляващи около 45% от общонационалния годишен вододобив. Концентрациите на йод в пречистената питейна вода са в интервала <0.2 – 126 µg/L (средно аритметично 14.4 µg/L, медиана 11.9 µg/L), с комплексна вариация в географски план. Факторите, обуславящи тази комплексност, са свързани и с геологията, но и с използваните методи за пречистване на подпочвените води. За геопространствен анализ е използван локалният индекс на Моран (Local Moran's I), въз основа на който е съставен нов концептуален модел за географската вариация на йода в датските питейни води. Този нов модел разделя континенталната част на Дания (Ютландия) на пет отделни района с различни нива на йода в питейната вода, докато предишният утвърден модел обединява цяла Ютландия в един район с относително ниски нива на йода. Нашите данни показват, че Ютландия е една от частите на Дания, която се характеризира с най-голяма вариация на концентрациите, основани на географски принцип – районът с най-ниските и районът с най-високи нива на йод, са разположени в Ютландия. Приносът на питейната водата към препоръчания от СЗО дневен хранителен

прием на йод (възрастни - 150 µg, подрастващи - 120 µg) варира от 0% до >100% (възрастни) и >50% (подрастващи). Съмнително е настоящата мониторингова програма, която следи статуса на датското население въз основа на две кохорти (Олборг – Ютландия и Копенхаген – Зеландия) да предоставя адекватна информация. В тази връзка при бъдещи промени на мониторинговата програма и/или на УЙП би следвало да бъдат взети предвид локалните вариации на йода в питейната вода.

Двата масива с архивни данни, които са с национално покритие, предоставиха информация за вариацията на йода в подпочвените води – от <0.4 до 1220 µg/L (средно аритметично 13.8 µg/L, медиана 5.4 µg/L) за данните от 1933-2011г.; и от <0.3 до 240 µg/L (средно аритметично 8.3 µg/L, медиана 4.4 µg/L) за данните от 2011-2014г. Първият масив (1933-2011) разкри вариации на йода както на локално географско ниво, така и в национален мащаб, и че проби с високи и с ниски концентрации формират заедно географски клъстери. От петте административни региона Централна Ютландия е с най-ниската средна аритметична концентрация (7.6 µg/L), докато Столичният регион е с най-висока (26.8 µg/L). Високи йодни концентрации се наблюдават предимно при подпочвени води, добити от дълбочини >40m, както и при проби от водоносни хоризонти във варовик (горна креда – палеоген). Мултивариантният анализ (PCA) разкри зависимост между йода, лития, бария, бора, и брома. Наред с това високи нива на йод се наблюдават предимно в проби, представляващи редуцирани и алкални подпочвени води (доминиращ Ca-HCO_3 тип). Вторият масив (2011-2014) потвърди наличието на локални различия в нивата на йод в подпочвените води. Анализът на зависимостта между йодните концентрации, дълбочината на водния хоризонт, и възрастта на подпочвените води показа, че йодните концентрации >27 µg/L са характерни само за води по-стари от 25 години.

Вариацията на йод в подпочвените води на локално ниво беше изследвана въз основа на резултатите от кампанията за вземане на водни проби от четири пилотни района (2012г.) Различия в концентрациите на йода бяха регистрирани както на ниво 0.1-0.2 км, така и на 5-10 км за същия геоложки пласт. Концентрациите в пробите от тези райони бяха в интервала 5-14500 µg/L. Йодид и органичен йод са двете доминиращи форми, тъй като подпочвените води са предимно редуцирани. Високите нива на йод са приписани на морския произход на седиментите – подпочвените води с високи концентрации на йод са от водоносни хоризонти във варовик (преди кватернера) и морски пясък (следледников). Възможните процеси, контролиращи тези нива, са: 1) дифузивен транспорт на високоминерализирани подпочвени води, 2) мобилизиране на йода при разграждане на органична материя, 3) редуктивно дейодиране на оксихидроксиди.

Вторият масив (2011-2014) съдържа данни за четири кладенеца с възможност за водовземане от различни дълбочини (дължина на екрана 10 cm, брой 10-23). Резултатите показват, че концентрациите на йод са много променливи в дълбочина. Наблюдават се както малки (±1-2 µg/L) така и големи разлики (±10-20) между различните дълбочини при идентична геология. Промени в pH, съдържанието на органичен материал и метални хидроксиди, редуцирана/окислителни среда, микрохетерогенност на седимента, както и комплексни хидрогеоложки условия са сред възможните фактори, обуславящи тези разлики.

Въз основа на резултатите от този три-годишен докторски труд, се препоръчва да продължат изследванията на вариацията на йод в питейните и подпочвените води в различни темпорални и пространствени димензии. Това би улеснило и информирало компетентните институции при едно бъдещо коригиране на УЙП или на мониторинговата програма, следяща статуса на населението.

Summary chapter

Abbreviations

CFC – chlorofluorocarbon;
clr – centred log-ratio
DOC – dissolved organic carbon
DOI – dissolved organic iodine
DW – drinking water
EI – excessive iodine
GEUS – Geological Survey of Denmark and Greenland
GRUMO – Danish Groundwater Monitoring Program
GW – groundwater
ID – iodine deficiency/deficient
NIPALS – nonlinear iterative projections by alternating least-squares
NS – normal score
PCA – Principle Component Analysis
RNI – recommended nutrient intake (here the nutrient is iodine)
TI – total iodine
UI – urinary iodine
USI – universal iodising programme
WHO – World Health Organisation

Table 1: Epidemiological criteria for assessing of iodine status (nutrition) in a population of school-aged children [1, 6]

Median UI concentration (μg/L)	Iodine intake	Iodine status
<20	Insufficient	Severe ID
20-49		Moderate ID
50-99		Mild ID
100-199	Adequate	Optimal
200-299	More than adequate	Optimal, but may pose a slight risk of more than adequate intake in the overall population
≥300	Excessive	Risk of adverse health consequences

1. Introduction

Iodine plays an essential role in human metabolism and the early development of humans [1]. Insufficient or excessive dietary iodine intake can both cause health problems. Worldwide, the focus falls mainly on the iodine deficiency (ID), as it is *"the single most important preventable cause of brain damage"* [2]. Lower IQ and learning capacities, worse quality of life and lower economic productivity are some of the effects of severe ID [2], however even mild ID could result in learning disabilities, poor growth and diffuse goitre in school children [3].

The iodine status of the population is assessed based on the median urinary iodine (UI) concentration in school-age children or pregnant women (see criteria in Table 1), because UI is considered a reliable marker of the recent dietary iodine intake [1]. Nationally representative surveys on the populations' status (1993-2012) are available for 119 countries worldwide; 33 countries, amongst which is Denmark, lack recent national data, thus sub-national surveys are used [4]. Globally 111 countries have adequate nutrition, 30 countries are iodine deficient (9 with moderate ID; 21 with mild ID, 0 with severe ID), and 10 are classified as countries with excessive iodine (EI) [4]. ID is not confined to developing countries [5]. Zimmermann and Andersson [6] estimated that iodine intake is insufficient in 43.9% (n=30.5million) of 6–12-year-old children and 44.2% (n=393.1 millions) of the general population in the WHO European Region.

Iodine in the human body originates mainly through dietary intake or inhalation of atmospheric iodine. The recommended daily nutrient intake (RNI) for iodine on age principle is given in Table 2. The main strategy for elimination of ID worldwide, recommended officially by WHO and UNICEF in 1993, is the universal salt iodization (USI) [1]. USI programmes consist of iodization of all salt meant for human and animal consumption [1]. The sustainability of USI as a prevention measure depends on continuous monitoring [1], however, it is also crucial that the USI strategy and the strategy for reduction of salt consumption are integrated [7]. In the context of the ongoing debate on how to ensure adequate iodine intake in industrialised countries and the need for coordination of the interventions to reduce populations' sodium intake with the USI programmes [4, 5, 8, 9], it becomes important to focus on regional (local) differences in other products rich in iodine [8] like water, milk, etc.

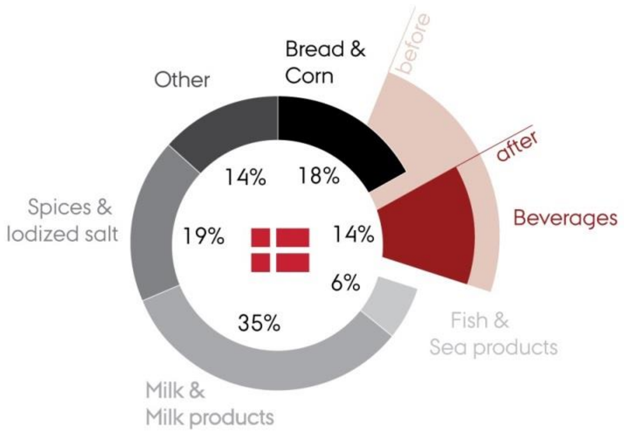
Table 2: Recommended daily nutrient intake (RNI) for iodine [1]

Age group	RNI (µg/day)
0-59 months	90
6-12years	120
12-17 years	150
Adults	150
Pregnancy/lactation	250

Drinking water (DW) is generally considered a minor or even negligible source of dietary iodine intake, providing 10% only [10]. The dietary habits could differ from regions to region; moreover, they may change throughout the years. The present dietary sources of iodine in Denmark, based on the latest survey on the dietary habits of the population, are presented in Figure 1. After the mandatory USI was introduced in 2001 [11], about 14% of the dietary iodine intake was derived from DW and other beverages (w/o juices and milk) [12]. This percentage was 24/25% before 2001 [13, 14]. Unfortunately, these estimates do not provide information on the geographical and seasonal variations of iodine in DW, which in Denmark originates from groundwater (GW). When this PhD project was initiated, the existing data on iodine in Danish DW were limited to four studies [13, 15-17], which cover very few sampling locations (max 55). Further information on the Danish USI, monitoring of the iodine status, the dietary habits, and the geographical distribution of the population are provided in the *Introduction* of **Paper II.** Details on the GW abstraction and DW supply in Denmark can be found in [18] and in **Technical Note I.**

In geographical regions, where DW is of GW origin, iodine concentrations may vary substantially, depending on the geology and probably the water treatment. Thus, thorough understanding of iodine variation in GW is crucial for understanding the differences in the nutrition and the epidemiology in different geographical regions. It is also a key to long-term effectiveness, i.e. sustainability, of iodine deficiency/excess prevention, since it may allow a fine tuning of USI for the specific needs of different sub-population groups (if needed).

Figure 1: Major dietary sources for iodine, based on data from the last study on the dietary habits of Danes [12]

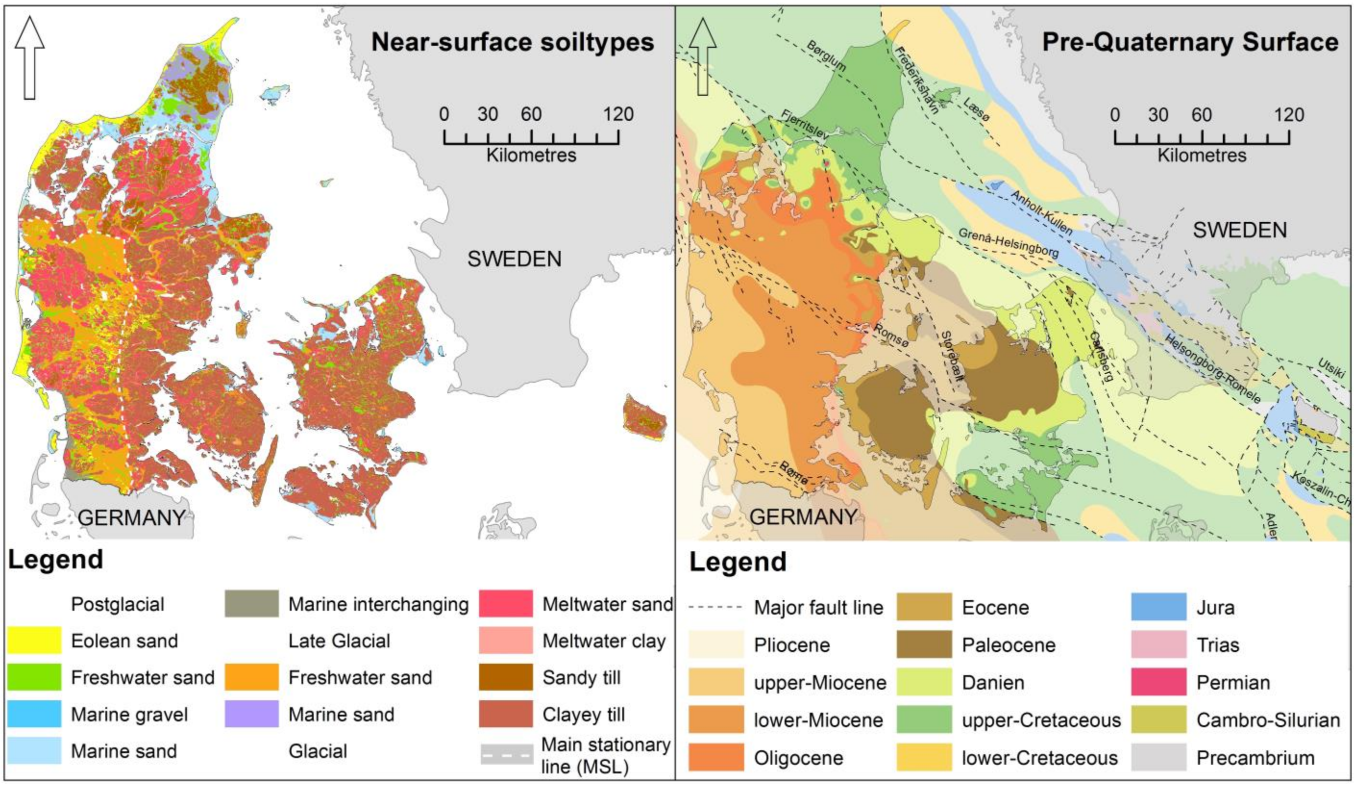


Note: "before" and "after" mark the proportion of iodine derived from beverages before and after 2001 when the salt iodizing became mandatory

In the hydro-geochemical cycle, total iodine (TI) can be found in the stable inorganic forms of iodide (I^-) and iodate (IO_3^-), as well as in various organic iodine compounds (further called dissolved organic iodine, DOI). The organic iodine geochemistry and the thermodynamic properties of over 40 organic iodine compounds are presented by Richard and Gaona [22]. According to the conceptual model of Whitehead [21], iodine is transferred to the GW by: 1) leaching of iodine from the soil solution or/and the solid soil material, and 2) exchange between GW and inland surface waters (both input and output). Other processes can be involved too, e.g. intrusion of sea water, influence of old saline GW, or leaching from hydrothermal deposits [23]. Iodine enrichment of the GW is related also to topography, geomorphology, and local hydrogeology [24], as well as the hydrogeochemical conditions and biological activity in the aquifer [25, 26].

The present Danish landscape is shaped mainly since the last glaciation (Weichselian glaciation). The Main Stationary Line of the Scandinavian Ice Cap (Figure 2 left) forms a boundary west of which a huge outwash plain and remnants from Saalian landscape are situated [27].

Figure 2 Left: Map of the near-surface soil-types (at about 1m depth) [29], the Main Stationary Line of the Scandinavian Ice Cap (20 ka BP) is indicated with white dashed line; Right: Map of the pre-Quaternary surface geology [30]



The pre-Quaternary surface (the boundary between pre-Quaternary sediments/rocks and the Quaternary glacial sediments) has been developed as a result of deposition, tectonic movements and erosion [27]. Most of the aquifers in Denmark are situated in the pre-Quaternary sediments (Figure 2 right), however there are also aquifers in the Quaternary deposits. The primary and secondary aquifers consist mainly of Quaternary or Miocene sand/gravel, Palaeocene to Late Cretaceous chalk/limestone [28]. However, on the island of Bornholm aquifers can be found in Late Cretaceous limestone/sandstone/sand, Jurassic and Early Cretaceous gravel/sand, Middle Cambrian to Silurian shale/limestone, Early Cambrian sandstone/quartzite, and pre-Cambrian gneiss/granite [28].

Igneous and metamorphic rocks are generally low in iodine [19, 20]. 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) [20]. Iodine in recent marine sediment is even higher – from 5 to 200 mg/kg [19].

The general assumption about iodine-rich sedimentary rocks is that iodine is adsorbed on grain surfaces or organic matter [19]. Iodide is strongly polarizable which increases its ability to substitute for hydroxyl ion in various compounds [21]. Most of the existing studies on iodine geochemistry in the terrestrial environment are focused on soils. Even though, some of the mechanisms may be relevant also to sediments, which on other hand has importance for iodine in GW, as most aquifers in Denmark are from sedimentary origin. Further details on the geochemistry and the possible sources, processes, and mechanisms for iodine enrichment of GW are provided in the *Introduction* of **Paper III**. The iodine content, speciation, and geographical variation in Danish soils, sediments, and GW had not been reported prior to the initiation of this PhD project.

2. Objective

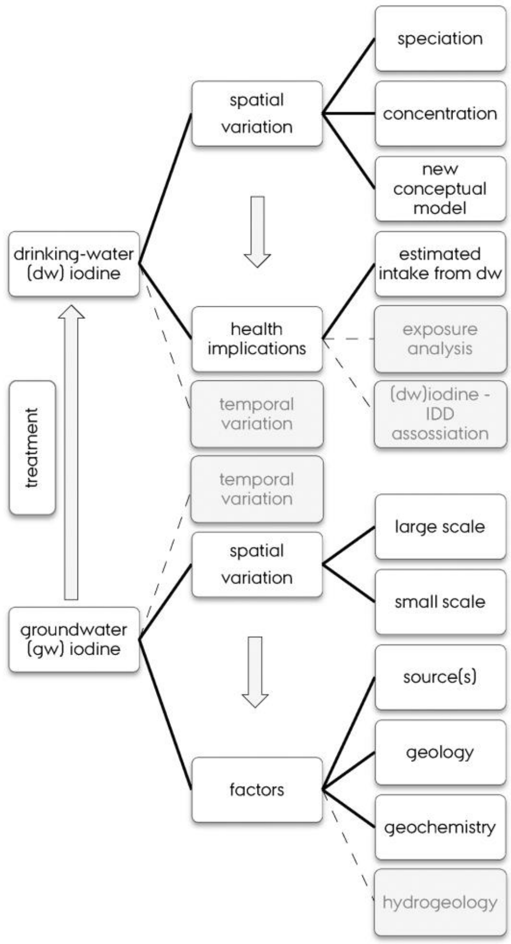
The general objective of this PhD is to study iodine in Danish DW and GW in order to fill in a knowledge gap on spatial variation of iodine concentration and speciation, what factors are governing it, and what are the potential health implications. Figure 3 presents in a schematic way the main PhD subjects and the links between them, as well as the topics which were only briefly addressed or are found to be perspective for future research (with light grey colour). This structure is followed when presenting the main findings as part of this *Summary Capter*, however for simplicity, the main objectives of this PhD can be summarised in the follwing three points:

- **To map iodine concentration and speciation in DW and GW in Denmark.** Rather large part of the PhD has been devoted to the design and implementation of two sampling campaigns in order obtain DW and GW samples for iodine speciation analysis, as such data was lacking for Denmark. Thus, iodine speciation data for Danish DW and GW was reported for first time in **Paper II** (DW) and **Paper III** (GW). Additionally, all available and accessible data on iodine concentration in Danish GW was overviewed and presented in **Paper I and IV**. One of the sampling and data collection campaigns (nationwide, DW) is discussed in detail in **Technical Note I**, where important insight into the rationale behind the design, the coordination, and the success rates (design vs. execution) is provided.

- **To study the spatial patterns of iodine concentration (and speciation) and to elucidate the factors governing them**. Studying the large scale patterns of iodine variation in DW and how they can be explained and generalised is the purpose of the study reported in **Paper II.** Whereas, **Paper I, III, and IV** focus mainly on iodine variation in GW and what is causing it, while exploring the topic on different scales: large scale – **Paper I**, local scale (<1 km and <5 km) – **Paper III**, and a combination of large scale and a single locations (concentration-depth profiles) – **Paper IV**

- **To evaluate the importance of the spatial variation of DW iodine to the populations' nutrition (health).** The human health implications stemming from the observed complex spatial variation of iodine concentrations in Danish DW are yet to be revealed. However, the first step in that direction was done by estimating what is the DW contribution to the dietary iodine intake as % from RNI (Table 2 provides information on RNI). The results from this estimation are reported in **Paper II**.

Figure 3 Scheme visualising the main PhD subjects (in the white rectangles) and the links between them; with light grey colour are marked additional topics, which haven't been discussed in detail and further research is needed



3. Data and Data analysis

Two different types of data were used for fulfilling the PhD project objectives as stated previously: 1) data from two sampling campaigns, designed as part of this project, and 2) historical data, extracted from a public database. The spatial coverage of these different datasets is presented in Figure 4.

3.1. Sampling campaign

A DW sampling campaign, covering spatially the entire country (Figure 4, dataset DW 2013), was executed in the period April-June 2013. Treated DW samples were obtained from 144 waterworks, abstracting annually 175 million m^3 of GW, which accounts for about 45% of the total annual abstraction volumes from public and private water companies (n>2500). The single wells and small waterworks, supplying <10 households, were excluded from this study. The water treatment is predominantly simple, consisting of aeration and sand-filtration. The samples represent treated GW water, ready to be supplied to consumers. The main results from this sampling are reported in **Paper II**.

Additionally, full account on the design of the sampling campaign, e.g. motivation, selection criteria, data collection success rates etc. are provided in **Technical Note I**.

A combined DW and GW sampling campaign at four study sites (Figure 4, DW&GW 2012) took place in October 2012. Filtered and unfiltered GW samples were taken after pre-pumping of the wells until the on-line readings for pH, redox potential, conductivity, dissolved O_2, and temperature became stable. The wells at two of the study sites are production wells belonging to five waterworks. Thus both GW and treated DW samples were obtained. However, only the results from the GW sampling have been reported in **Paper III**. Some of the DW results are used for illustrative purposes in this *Summary Chapter*.

3.2. Historical data

Two GW datasets, covering the periods 1933-2011 and 2011-2014 with samples distributed over the entire country (Figure 4, GW 1933-2011 and GW 2011-2014), were used in the PhD project. The data was extracted from the Danish public nationwide geological and hydrological database,

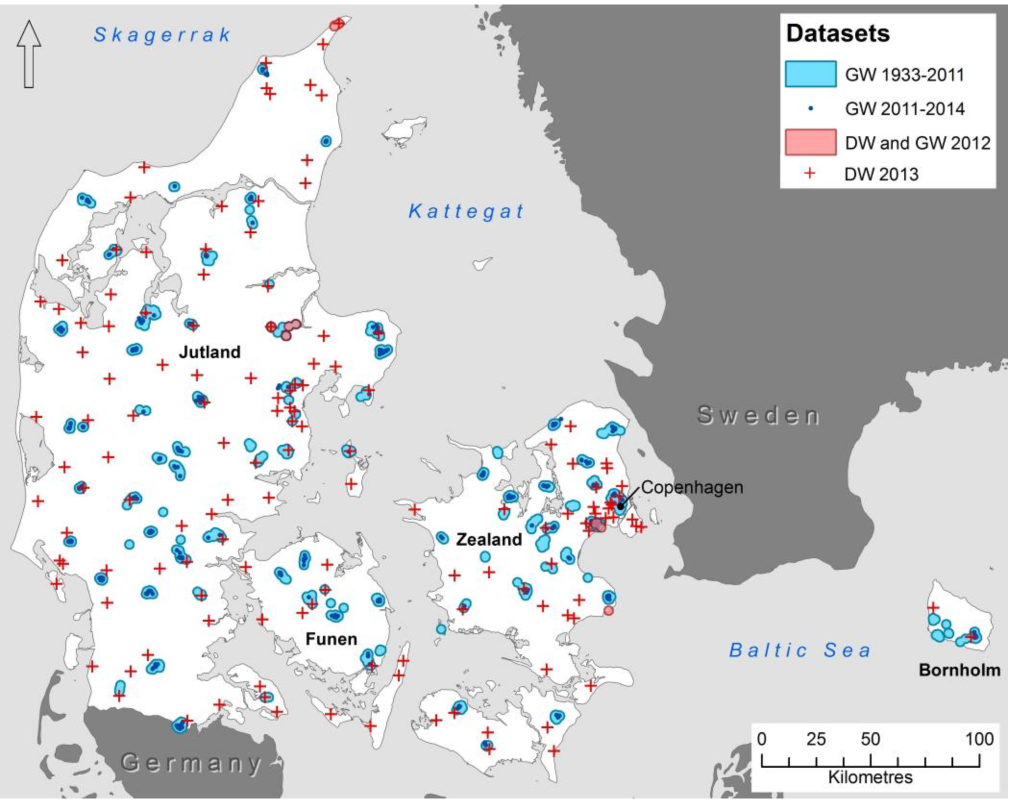


Figure 4 Spatial coverage of the four datasets used in this PhD study;

Abbreviations:
GW – groundwater,
DW – drinking water;

Note: The locations of the samples from GW 1933-2011 and DW&GW 2012 are visualised by 2km buffers instead of the point-locations.

Jupiter [31]. Jupiter database is maintained by the Geological Survey of Denmark and Greenland (GEUS). It contains geological information (for all wells in Denmark: from geotechnical to DW production wells), data on GW levels, and water-chemistry data, obtained as part of monitoring programs, routine quality checks, or scientific projects.

The two datasets cover the period before and after iodine was officially included in the analytical program of the Danish Groundwater Monitoring Programme (GRUMO) in 2011. The purpose of GRUMO is to document quantitatively and qualitatively the GW status and trends, so the effect of the national action plans on the aquatic environment can be evaluated [32]. Jørgensen and Stockmarr [33] provide further details on groundwater monitoring in Denmark and a comparison with other countries.

The first dataset (Figure 4, GW 1933-2011) consists of GW samples analysed for iodine (n=2562) and 26 other constituents, as well as, supplementary information on methods, objectives for sampling, locations, dominating geology at the screen level, etc. **Paper I** provides extensive description on the dataset preparation, quality assessment, and the pre-treatment of this heterogeneous compilation of data.

The second one is the GRUMO 2014 dataset. The GRUMO dataset is updated annually, and, based on it, a report on the GW quality is issued by GEUS each year ([34] is the latest). Two sub-sets of data from the GRUMO 2014 dataset were used for the purposes of this PhD project. The first sub-set includes only last iodine analyse (2011-2014) and last chlorofluorocarbon (CFC) analyse (1997-2013) per location (n=589) (Figure 4 GW 2011-2014). The second sub-set includes depth profiles of iodine concentrations and data on redox sensitive elements and field parameters for four multi-screen wells (n=10-23, total n=70). The preliminary results from the data analyses of these two sub-sets are provided in **Paper IV**.

3.3. Laboratory analyses

The laboratory analyses of the water samples obtained within the two sampling campaigns were handled by the Inorganic Lab at GEUS. The inorganic iodine species, iodide (I^-) and iodate (IO_3^-), and the total iodine (TI), as well as other constituents were included in the analytical program. ICP-MS was used for detecting TI; IC – for detecting the two inorganic species. The organic iodine fraction (dissolved organic iodine, DOI) was estimated by subtraction (DOI = TI – (I^- + IO_3-I)), as in e.g. [35] and [25]. A full account on the laboratory methods for all analytes and used instruments is provided in **Paper II** and **Paper III**.

3.4. Data-analytical methods

The data-analytical techniques varied depending on the purpose of the particular study. A combination of uni- and multivariate analysis was used in **Paper I**. In **Paper II** the initial data exploration was followed by spatial autocorrelation analysis. **Paper III** relied on traditional geochemical tools for GW characterisation, while in **Paper IV** the preliminary results are based on data visualisation and descriptive statistics. The only quantitative data analysis employed in **Technical Note I** was calculating success rates for different data collection activities.

3.4.1. Descriptive statistics

The standard data exploration was based on means, medians, standard deviations and other traditional attributes of the descriptive statistics. Probability plots and box-plots were used to compare groups of samples. Different graphical techniques were also applied for initial data exploration: from mapping concentrations with ArcMap [36] to plotting two (three) variables against each other. Grapher [37] was used for box-plots and other graphs. Descriptive statistics was used in all of the papers.

3.4.2. Multivariate analysis

Multivariate analysis was applied only in **Paper I**. Principal component analysis (PCA) was chosen because it is suitable for simultaneous multivariate data description, data-structure exploration, and discovering grouping of samples or variables which otherwise may be swamped if only uni- and bi-variate analysis is used [38]. The software package Unscrambler 10.1 [39] with nonlinear iterative projections by alternating least-squares (NIPALS) algorithm was used for PCA.

A controversial point in employing PCA (or any multivariate analysis) is the choice of most appropriate data-transformation (pre-treatment). Wide variety of transformations exists and different methods are used in scientific literature to address various issues concerning non-normal data distribution, noise reduction, de-trending, auto-scaling etc. However, transformations addressing the *closure problem of compositional data* (see **Paper I** for details) is not yet widely accepted in the area of applied hydrogeo-chemistry, even though from strictly theoretical viewpoint this must be done (e.g. [40, 41]). In the peer-review process of **Paper I** this issue was pointed out by one of the reviewers, which resulted in prolonged discussion between the co-authors and consequent withdrawal of the paper. The revised and published version incorporates pre-treatment agreed upon with the co-authors, namely center log-ratio (clr) transformation [41, 42]. In practice the clr transformation consists of normalising each variable with the geometric mean of the sample (for each sample in the dataset) and then taking the normal logarithm of the normalised values. The clr transformation was performed with the open source software CoDaPack [43] For more details on the *closure problem*, *compositional data*, and *clr transformation* see **Paper I** and further references herein.

3.4.3. Spatial autocorrelation analysis

Spatial autocorrelation analysis was used in **Paper II** to distinguish between areas with high or low iodine concentrations (spatial clustering) and to recognise spatial outliers. A spatial outlier is a sampling point, where the concentration (here iodine) differs significantly from the concentrations at the neighbouring sampling points. The method chosen in **Paper II** is Local Moran's I, which allows for differentiating between statistically significant *high-high* and *low-low clusters* and *high-low* and *low-high outliers* [44, 45]. The significance level is pseudo-significance, based on randomisation test with permutations [46]. The free software GeoDa [47] was used for Local Moran's I calculation. Prior to the analysis, the data were Normal Score (NS) transformed to address the not-normal distribution. The NS transformation was based on Blom's proportion estimation formula [48] and performed with the statistical software SPSS [49]. Full account on the Local Moran's I, the data-pre-treatment, and the parameterization is provided in **Paper II.**

3.4.4. Standard hydrogeochemical tools

Different approaches for DW and GW description and classification based on the chemical composition were applied. This was done mainly with the objective of recognising potential iodine sources or associations between elevated iodine and other constituents. A Piper diagram was used in **Paper I, II, and III** for water type classification, based on the major ions (Ca^{2+}, Mg^{2+}, Na^{+}+K^{+}, Cl^{-}, SO_4^{2-}, CO_3^{2-}+HCO_3^{-}) (software GW_Chart by Winston [50]). Another similar graphical way for water type characterisation was employed in **Paper III** - the Pratt diagram [51], which takes into account only Na^{+}, Ca^{2+} Mg^{2+}, and HCO_3^{-} concentrations. As hydrogeochemical characterisation of GW is the main focus in **Paper III**, the tools listed next were only used there. The ratios of Na/Cl and Cl/Br provided information on respectively the ion exchange state of the GW [52, 53] and indication of the GW origin [54]. The GW redox state was assessed based on the algorithm described by Hansen*, et al.* [52] taking into account the measured dissolved O_2, NO_3, Fe, and SO_4 by classifying the GW into A) oxic, B) anoxic, containing NO_3, C) slightly reduced – Fe and SO_4 zone, and D) strongly reduced – CH_4 and H_2S zone. The oxygen and hydrogen isotopic composition of GW ($\delta^{18}O$, $\delta^{2}H$, and deuterium excess) provides an idea on the origin of the GW and what processes may have shaped the present GW composition. Detailed theoretical background and examples are provided by Clark and Fritz [55] and IAEA-UNESCO [56].

4. Main results

The main results of the work done throughout the PhD period are summarised in the next sub-sections. The summary follows the structure proposed in Figure 3. Thus, the findings are grouped logically in different topics (DW, GW, DW-GW differences). The chronology or the completeness of the papers are not reflected by this structure, therefore, a brief overview follows. The chronological order in which the papers were prepared is (earlier → later work): **Paper I** → **Paper II** → **Technical note I** and **Paper III** → **Paper IV** (see *Preface* for citation details). With respect to the status of completion: **Paper I and II** are published in peer-review journals, **Paper III** and **Technical Note I** are manuscripts ready to be submitted, while **Paper IV** is work in progress, reporting on preliminary results and outlining future study.

4.1. Drinking-water iodine

The topics related to iodine in Danish DW and the specifics of the DW supply in Denmark are discussed in **Paper II** and **Technical Note I**. An overview of the TI concentrations and speciation from the two DW investigations is presented in Table 3 (DW 2013, and DW samples from DW&GW 2012 dataset).

The study presented in **Paper II** is, so far, the most comprehensive one with respect to iodine in Danish DW. The previous investigations on DW iodine, which are reported by Pedersen*, et al.* [15], Rasmussen*, et al.* [13], and Andersen*, et al.* [17], are lacking information on the selection criteria of the sampling points (max 55) and the iodine speciation. The design of our DW 2013 sampling campaign (**Technical Note I**) allowed us to obtain samples from waterworks (n=144) representing 45% of the total national GW abstraction for DW purposes and at the same time to cover as evenly as possible the entire country (Figure 4). The GW abstraction volumes have been used as a proxy for the size of the waterworks, as there was no available data on the DW supply volumes or supplied population by each waterwork.

4.1.1. Spatial Variation

The data used in **Paper II** represents one point in time, thus the analysis are focused on the spatial variation of iodine only. The short-term temporal variation of iodine concentrations has been evaluated only at one of the waterworks supplying Copenhagen, based on eight samples taken in two week period (**Paper II**); however, the results were not conclusive. **Paper II** provides a visualisation of the TI concentration and speciation (**Paper II**, Fig.4), showing that there is a complex spatial pattern both with respect to the TI concentration but also the speciation.

The TI concentrations (Table 3) were generally in line with the previous investigations by Pedersen*, et al.* [15] and Andersen*, et al.* [17]. However the maximum TI concentration (at Skagen waterwork) of our DW 2012 dataset was 13-14 μg/L lower than the concentration reported in these two previous studies for Skagen. This difference was attributed to one or more of the following factors: change in the GW treatment in 2006, difference in the analytical methods for iodine detection, natural temporal variation (**Paper II**). It is interesting to point out that this concentration is 94 μg/L lower than the result from our other sampling campaign (DW&GW 2012) when DW sample was obtained from the same waterwork (Figure 5). The samples from both campaigns have been analysed in the same lab, using the same methods end equipment.

Table 3 Overview of total iodine (TI) concentrations (min, max, mean, median) and iodine speciation from the four datasets used in the PhD study.

Dataset	Paper	Samples		TI concentration (μg/L)				Iodine speciation
		Type	n	min	max	mean	median	
GW 1933-2011	I	GW	2562	< 0.4	1220	13.8	5.4	x
GW 2011-2014, sub-set 1	IV	GW	589	< 0.3	240	8.3	4.4	x
GW 2011-2014, sub-set 2	IV	GW	70	1	48	x	x	x
DW&GW 2012	III	GW	26	5	14500	x	x	I^-, DOI
DW&GW 2012	III	DW	5	6.5	220	x	x	I^-, IO_3^-, DOI
DW 2013	II, TNI	DW	144	< 0.2	126	14.4	11.9	I^-, IO_3^-, DOI

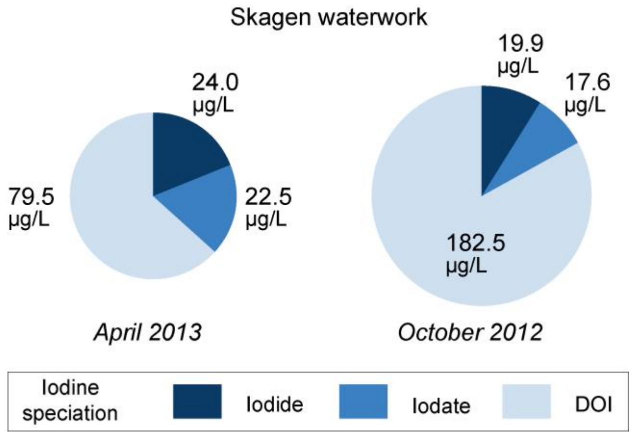
Therefore, this difference could be explained either by a temporal variation of TI in the GW, or by difference in the GW pumping scheme at the time of sampling. Skagen waterwork mixes GW abstracted from max 31 wells with varying abstraction volumes per well depending on the DW consumption (seasonal and daily variation). Details on the GW iodine concentrations at Skagen can be found in **Paper III.** Further studies are needed in order to explain the difference presented on Figure 5.

The TI speciation was also found to vary over the country, with no apparent trend. There were six different combinations of iodine species in the samples; the two most common combinations were: all species were detected in the sample (I^-, IO_3^-, DOI), and only inorganic iodine was detected (I^-, IO_3^-). The DOI containing samples were generally with higher TI concentration, however there were also exceptions. Andersen, *et al.* [17] stated that iodine in Danish GW is bound in humic substances based on results from six waterworks. However, our results (**Paper II**) demonstrate a considerable complexity with respect both to the presence/absence of DOI but also the proportion of DOI at different locations (*Fig. 4*, **Paper II**)

Overall, the higher spatial resolution of our study presented a more complex picture for the DW iodine than previously reported. The Local Moran's I analysis for TI revealed two *high-high cluster* areas (Zealand and North Jutland) and one *low-low cluster* area (Jutland). However, spatial outliers were present even though these parts were classified as areas with predominantly high TI or low TI. There was no substantial difference between the large-scale trends for inorganic iodine (I^- + IO_3^-I) and TI. The spatial variation was attributed to both the geology (GW composition and its variation) and the treatment of the raw GW.

In **Paper II** it was also demonstrated that the current and widely accepted conceptual model of iodine in DW in Denmark (Zealand and Funen – high iodine, Jutland – low iodine) [57] is misrepresenting the smaller scale variability of DW iodine on Jutland. The conceptual model proposed in **Paper II** incorporates the observed variations. Five areas with different iodine content in DW were separated on Jutland based on the interpretation of Local Moran's I results.

Figure 5: Comparison between the results for Skagen waterwork based on two sampling campaigns (DW 2013 and DW&GW 2012) (October 2012 sample has not been reported previously)



According to this model, the two areas with the highest and lowest average TI concentration are located on Jutland. However, the monitoring of populations iodine status (DanThyr) is done based on two cohorts, which were chosen so they reflect the differences in DW iodine: Copenhagen representing the high iodine in DW on Zealand and Funen, and Aalborg, representing the low iodine in DW on Jutland [11], which is according to the old model. Thus, our findings suggest that DanThyr may not offer a sufficiently accurate picture due to the chosen generalisation of the spatial variation of DW iodine. The local variations should be mapped and incorporated into future adjustments of the DanThyr monitoring and/or the USI programmes, and in future epidemiological studies. Further, the proposed new conceptual model can be refined to reflect the factors governing the spatial variation of TI concentrations.

4.1.2. Health implications

The topic with the potential health implications of iodine variation in Danish DW was only briefly touched upon in this PhD study. Only the first step has been made, i.e. the importance of DW iodine to the dietary intake of the population was investigated in **Paper II.**

Based on the iodine data from DW 2013 dataset and reference values on the DW consumption, it was estimated that DW (incl. coffee and tea) contributes with 0 to > 100% of RNI for adults and with 0 to >50% of RNI for adolescents in different parts of the country. A simplified risk assessment, based only on DW iodine concentrations and the new conceptual model, allowed for pointing at potentially iodine deficient, mildly excessive, or areas with optimal iodine status. Our results show that despite the believe that water has a negligible contribution to the dietary iodine intake [10] and that the average dietary iodine intake from beverages for Denmark is set to 14% [12], DW iodine concentration and spatial variation can be an important factor. On a global scale, it is important to study thoroughly the iodine concentrations in DW and their geographical variation, especially in parts of the world where the DW is of GW origin (or at least partially of GW origin). **Paper II** demonstrated that regional variations in DW can exist and may be important for the population's intake not only in the large scale of China, but also in the relatively small Denmark (43 000 km^2).

4.2. Groundwater iodine

The GW iodine subjects (Figure 3) are covered in **Paper I, III, and IV**. A summary on the GW concentrations and speciation for the different datasets is presented in Table 3. **Paper I**, based on GW 1933-2011 dataset, and **Paper IV**, based on sub-set 1 of GW 2011-2014, focus on the GW iodine characterisation on a large scale (entire Denmark) (Figure 4). Whereas, **Paper III**, based on the GW data from DW&GW 2012 dataset, and **Paper IV**, based on sub-set 2 of GW 2011-2014, are case-studies covering different local scales. In order to explain the spatial variation of iodine in DW in Denmark (discussed in the previous part), the spatial variation of GW iodine has to be better understood. Therefore the main focus in this PhD thesis (regarding GW iodine) was on mapping GW iodine, describing the observed spatial patterns, and which factors are governing it.

4.2.1. Spatial variation

At the time of conducting the study, reported in **Paper I**, no other investigation on GW iodine data from Denmark had been published. Therefore, **Paper I** served the purpose of giving a first overview on the spatial variation of iodine in Danish GW. The mapped iodine concentrations did not show a clear pattern, however it seemed as there were more samples with high iodine concentration on Zealand than on Jutland (**Paper I and IV**). Thus, the GW 1933-2011 dataset was divided in groups of samples from wells located in different administrative or geographic areas and the descriptive statistics parameters of these groups were compared. When using the conceptual model for DW iodine by Andersen and Lauberg [57], dividing Denmark in East (Zealand + Bornholm) and West (Jutland + Funen), it was demonstrated that indeed East Denmark is characterised by GW with higher iodine concentrations (mean 21.02 µg/L, median 8 µg/L, n=1058) than West Denmark (mean 8.77 µg/L, median 4 µg/L, n=1504) (**Paper I**). However, the iodine concentrations were far from homogeneous throughout the administrative and geographical regions, as both high- and low-concentration samples were clustering together (**Paper I**). Thus, it was concluded that Danish GW is characterised by both large scale spatial trends and small scale heterogeneity. This was confirmed also by the data from sub-set 1 of GW 2011-2014 dataset (**Paper IV**), which consists of more recent iodine analyses, and the data quality of this dataset is more homogeneous than GW 1933-2011 dataset.

Iodine variation on a local scale was studied at two sites located on Jutland and two sites located on Zealand (**Paper III**) and at four multiscreen wells (**Paper IV**), two of which located on Jutland and two on Zealand. A difference in the concentrations at the wells from a single well field (0.1-0.2km) and on a 5-10 km local scale were detected (**Paper III**), and also at different depths for the four multiscreen wells (**Paper IV**). These findings lead to the conclusion that GW iodine concentrations are not homogeneous at the given geographical scales either and further attention was paid to the potential factors which could explain the observed geographical variation.

4.2.2. Factors governing the spatial variation

One of the conclusions from **Paper III** is that the processes governing the iodine concentration in GW are site- and depth-specific and that most probably at different concentration levels different processes (sources) are dominating. The results presented here are only focused on the relation between iodine concentrations and aquifer type (geology), depth of extraction, groundwater age and the geochemical association with other elements.

Paper I, III, and IV provide information on the GW iodine concentrations at different aquifers. The overview on the ranges of iodine concentrations from different aquifer types in Denmark (Table 4), show no obvious difference. However, it should be kept in mind that these results come from very different investigations – in **Paper I** a large amount of samples is overviewed, while having limited information on the geology at each location, whereas, **Paper III** focuses on very few locations, but in greater detail. The results from **Paper III** show that there is an apparent difference in the TI concentrations from Post-glacial marine sand and from Danian/Selandian chalk. In **Paper I**, the highest 75^{th}, 90^{th}, and 95^{th} percentiles were found for samples representing Paleocene to Late Cretaceous limestone/chalk. However the late-, inter-, and postglacial marine sediments were not very well represented in the GW 1933-2011 dataset (<1%, n=17).

Further, when the general trend of iodine concentrations' distribution in depth was studied (**Paper I**), it was found that the relatively higher concentrations start to be observed sharply at depths of about 40 mbt (to 80 mbt). It was hypothesised that this difference is due to shift in the geological settings (e.g. glacial deposits vs. limestone/chalk deposits) or the GW chemistry (different GW type). It was found that at depths of 40-50 mbt there were twice as many samples representing limestone/chalk aquifer than at depth 30-40 mbt, which could be causing the depth-concentration relation, observed on Fig. 3 of **Paper I**. For one of the study sites (**Paper III**), where the extremely high TI concentrations (1.12-14.5 mg/L) were seen, there was pronounced increase of TI with depth. This was attributed to diffusion of old saline water in the Campanian-Maastrichtian chalk aquifer. In **Paper IV**, the relation between depth, GW age, and TI concentration was investigated based on sub-set 1 of GW 2011-2014 dataset. Elevated TI concentrations were present at different depths, however samples with TI > 27 µg/L were representing GW older than 25 years. This could be explained by the longer residence times which would provide longer time for interaction between the GW and the aquifer material, or by mixing between fresh GW and old saline and enriched in iodine GW (**Paper IV**).

Table 4 Overview on the total iodine concentration (min, max) for samples from different aquifer types/geological setting based on the papers included in this PhD thesis

Aquifer type or dominating geological setting at the screen length	Samples (n)	Total Iodine (µg/L) min	max	mean	median	Paper
Post glacial marine (Quaternary)	4	167	308	x	x	III
Glacial melt-water (Quaternary)	70**	1	48	x	x	IV
	3	9.1	12.5	x	x	III
	916	0.75	533	10.54	5	I
Glacial moraine (till) (Quaternary)	135	0.75	160	11.61	7	I
Paleogene deposits (excl. limestones)	140	0.75	1100	26.78	2.8	I
Limestone/Chalk: Paleocene or Late Cretaceous	439	0.3	1220	26.77	7	I
Danian-Selandian chalk	11	5	19	x	x	III
Campanian-Maastrichtian chalk	4 (3)*	23 (1120)	198 (14500)	x	x	III

*one well
**sub-set 2, four wells, 10-23 samples per well

An association between iodine, Li, B, Ba, and Br (PCA analysis, **Paper I**), lead to the conclusion that there is a common source or governing process, pointing in the direction of saline water influence. Additionally, most of the samples with elevated iodine concentrations were representing reduced and alkaline GWs (GW 1933-2011 dataset, **Paper I**). The hydrogeochemical characterisation of the GWs based on Piper and Pratt diagrams (DW&GW 2012, **Paper III**) showed respectively that TI concentrations >160 µg/l are found in GW samples with Cl^- being the dominating anion, and, that samples with elevated TI concentrations plot at or close to the saline zone of the Pratt diagram. However, for the same study, Cl/Br vs. TI plot did not show any apparent relation between the two parameters. Similarly to **Paper I**, in **Paper III** the elevated TI concentrations were found in reduced GWs. A positive relation between TI and the iodine species and DOC was also observed, pointing at the importance of the organic matter (**Paper III**).

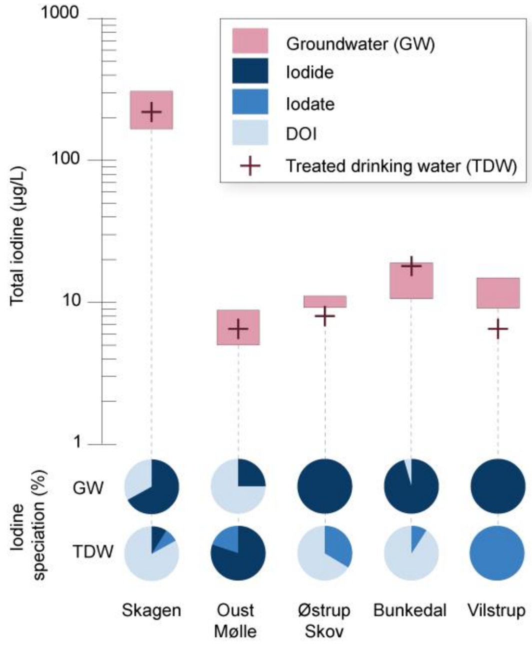
The results from the four multiscreen wells (sub-set 2 of GW 2011-2014 dataset, **Paper IV**) provided the insight into what is happening at different depths with respect to iodine concentrations. It was suspected that the small changes in the concentration in depth (±1-2 µg/L) are due to geochemical processes occurring at the sampling depth, which could be explained by localised differences (at depth) in the organic matter content, the metal hydroxides, redox conditions, and the pH. While, the larger changes in the TI concentration in depth (±10-20 µg/L) could be representing complex hydrogeological conditions at this aquifer. However, further studies are needed in order to accept or reject these theories (see **Paper IV** for details).

4.3. Groundwater-Drinking water differences

DW in Denmark originates from GW, which normally is subjected to only simple treatment, consisting of aeration and sand filtration. Details on the general GW treatment practices in Denmark are summarised in **Technical Note I**. The alteration of the GW composition in the treatment process could affect the iodine concentration and speciation in the DW. Thus, as part of the DW&GW 2012 sampling campaign, DW samples from five waterworks and GW samples from the production wells of these waterworks were obtained. The purpose was to compare the iodine concentration and speciation in GW and DW. The treatment at Oust Mølle is only aeration, while at Østrup Skov, Bunkedal, and Vilstrup is aeration and filtration, whereas at Skagen is more advanced (see **Paper II** for more details on the treatment at Skagen). All production wells were sampled at Østrup Skov, Bunkedal, and Vilstrup, but at Skagen and Oust Mølle four wells were chosen randomly per waterwork.

Figure 6 presents a comparison between the DW- and GW-TI concentrations, showing that DW-TI concentration falls in the range of GW-TI for three of the waterworks (Skagen, Oust Mølle, and Bunkedal). Whereas, for two of the waterworks (Østrup Skov, Vilstrup), DW-TI is lower than GW-TI concentration, suggesting that some iodine has been lost during the treatment, Figure 6. Changes in the speciation due to the treatment are observed at all of the sites, but no obvious pattern can be seen Figure 6.

Figure 6: Comparison of total iodine concentrations and speciation in drinking water (DW) (n=1) and groundwater (GW) for five waterworks.



Note: GW concentrations are presented as range, whereas the speciation is presented as average % from the wells at each site (source: DW&GW 2012 dataset, DW data not reported before, GW data is reported in Paper III)

Iodate (IO_3^-) was detected only in two of the GW samples (most probably due to post-sampling oxidation) and in all of the treated DW samples (8-100% of TI). Iodide (I^-) was detected in the treated DW at two of the waterworks only (Oust Mølle (80%) and at Skagen (9%)), whereas it was present and dominating in the GW samples from the wells at all sites. DOI dominates in the treated DW samples from three waterworks (Skagen (83%), Østrup Skov (66%), Bunkedal (91%)). Expected change in iodine speciation during the aeration process is that the reduced form (I^-) will be converted (at least partially) to IO_3^-. The potential effect of the treatment procedures on the dominating form of iodine is also discussed in **Paper II.**

5. General conclusion and perspectives

The main objectives of this PhD study were 1) to map iodine concentration and speciation in DW and GW in Denmark, 2) to study the spatial patterns of iodine concentration (and speciation) and to elucidate the factors governing them, and 3) to evaluate the importance of the spatial variation of DW iodine to the populations' nutrition (health). This PhD project provides the Danish perspective on these issues; nevertheless, the outcomes illustrate the importance of and the need for a thorough description of the spatial patterns of DW and GW iodine, especially in places where the drinking water originates (at least partially) from groundwater.

Throughout the Summary Chapter of this PhD thesis, the findings from the single papers, addressing the three PhD objectives, were jointly discussed by grouping them into the subjects from Figure 3. Iodine concentration and speciation in DW and GW were mapped, the spatial variation was studied on different scales, the health implications and the factors governing the iodine variability were also discussed. However, these topics are far from exhausted from scientific point of view. This PhD is a starting point for further, more comprehensive studies regarding iodine in DW and GW and the health implications in Denmark. Throughout this project knowledge gaps were identified, hypotheses were formulated, and the fundament for further research was laid.

This work can be continued in various directions. Here, only few of the perspective for future research work packages are listed:

- *Temporal variation of iodine in DW and GW.* Virtually all information on temporal variation of iodine in Danish DW is limited to the inconclusive results in Paper II and part 4.1.1. of this *Summary Chapter*, and the results from few other studies. Thus, there is evidence that the day-to-day variation (10 days) of iodine in tap water at two locations was *small [?]* [15], there was *no significant [?] difference* between iodine in tap water samples collected in January and June [13], and iodine concentration in DW obtained at the Skagen waterwork was *unaltered* [?] in the period 1997-2000 (one sample every second month for six months and one sample every year for four years) [17]. Therefore, some of the questions awaiting answer are:
    - Is there a short term (daily, weekly) or long term (seasonally, yearly) variation of iodine in DW?
    - If there is variation, what triggers it: is it due to treatment practices, changes in GW abstraction and mixing, or GW iodine variability?
    - If the GW iodine varies temporally at a single location, what are the governing factors?

  Answering these questions for different locations (as many as possible) will help elucidating the importance of drinking water as an iodine source for the long term iodine exposure.

- *Iodine hydrogeochemistry.* The discussion of possible sources, processes, and factors for iodine enrichment of the GW (**Paper III and IV**), have opened the topic. However, there is need for further data collection and analysis in order to answer conclusively what causes the spatial variability of iodine in Danish GW. The four multi-screen wells, presented in **Paper IV**, are especially perspective for a field studies on iodine hydrogeochemistry in glacial meltwater aquifers. Some possibilities for future research with respect to this topic are outlined in part 4 of **Paper IV**.

- *"Follow the watercourse",* i.e.: how does the iodine concentration and speciation change from the raw GW through the different treatment steps, to the treated DW and the supply system, to the tap water of the single households. This topic was touched upon briefly in the discussion of iodine speciation in DW (**Paper II**) and a comparison between GW iodine and DW iodine at five waterworks was presented in part 4.3 of this *Summary Chapter*. A study, specially designed for these purposes, would provide the missing link between GW→DW→tap water iodine concentration and speciation, and, will allow quantification of eventual iodine loss to the atmosphere (I_2), conversion inorganic-organic iodine, etc. It has to be stressed that chlorination is not practiced in Denmark, thus iodinated disinfection by-products (I-DBPs) are not a concern.
- *Health implications.* As mentioned in **Technical Note I**, the nationwide DW sampling campaign was designed, as to enable the investigation of potential health implications due to the geographical variation of iodine in DW. Such study could be divided in two parts: estimating lifelong exposure of iodine in DW, and testing for association between the geographical distribution of various IDD and the variation of iodine in DW. The Danish Civil Registration System (CRS, established in 1968) provides information on present and past addresses, date and place of birth, vital status, and identity of parents and spouses for all people, who live in Denmark [58]. By combining the CRS data with 1) the data from the existing health registers on all cases of various IDD, with 2) the supply areas of the waterworks (compiled in [59]), it becomes possible to perform representative population- based epidemiological study(ies) with respect to (lifelong) exposure to DW iodine.

Next to these topics, it should be mentioned that further investigations incorporating both temporal and spatial aspect of iodine variation in GW and DW on different time and space scales are needed. However, it is anticipated that such massive data collection is hard to fund, organise, and implement. Therefore, one of the recommendations (**Paper II**, **Technical Note I**) is to include iodine in the routine DW-quality investigations of the waterworks (n>2500). Iodine was included in the national GW monitoring programme (GRUMO) in 2011 and the first results are reviewed in **Paper IV**. However, the recent DW iodine data (for the last 10 years) are limited to the study presented in **Paper II** and **Technical Note I** (n=144, one time point). Monitoring iodine in both GW and DW is crucial for accumulating enough data to enable data-based informed decision-making for future adjustments of USI and/or the monitoring programme following up on the iodine status of the population (DanThyr).

6. References

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Paper I

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Iodine concentrations in Danish groundwater: historical data assessment 1933–2011

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Assessment of spatial variation in drinking water iodine and its implications for dietary intake: A new conceptual model for Denmark

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Paper IV

Work in progress

High resolution depth profiles of iodine concentration in groundwater at four multi-screen wells in Denmark: possibilities for future research

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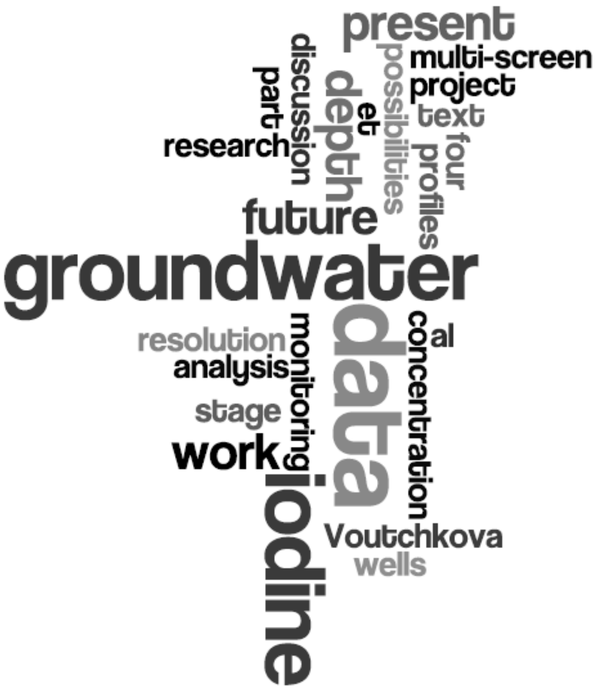

Preface

The hydrogeochemical data obtained as part of the Danish groundwater quality monitoring programme is fully accessible and offers various opportunities for data mining and data exploratory analysis. The purpose of this text is to present the most recent data relevant to the iodine topic, which can be used for elucidating depth related changes in iodine concentrations in groundwater. Especially promising is the data from four multi-screen monitoring wells. A unique dataset of high resolution depth profiles of iodine concentration in relation to redox conditions, pH, and groundwater age is presented here.
The results and the following discussion should be seen as a first overview, which can supplement or continue the work that has been done in the previous two studies on groundwater iodine (Voutchkova et al., t.b.s.; Voutchkova et al., 2014). The present work is in a preliminary stage, thus none of the discussed hypothesis have been accepted/rejected yet. The possibilities for future research, both based on existing data, and on further sampling and laboratory analysis are discussed in the last part of this text. However, due to the late stage of the present project, it is only possible to outline them here. This can serve as foundation for discussion and planning of future project application, as additional funding is needed in order to continue this work.

Keywords: multi-screen wells, hydrochemistry, groundwater, iodine,

1. Methods and Materials

1.1. Data

The water chemistry data used here are from the GRUMO 2014 dataset. GRUMO stands for Groundwater Monitoring Programme and is one of the sub-programmes for systematic data collection and reporting on groundwater quality in Denmark (Thorling et al., 2013). The GRUMO 2014 dataset covers data on water chemistry for the period 1989-2013. The data are downloaded from the nationwide publicly accessible hydrogeological database, Jupiter (GEUS).

Iodine is included in the analytical programme of GRUMO since 2011. The groundwater sampling is in compliance with the technical guide on groundwater sampling (Thorling, 2012). The reference laboratory for chemical and microbiological analysis of Danish Nature Agency has provided a Method Data Sheet for dissolved iodine in groundwater (RefLab, 2011). According to RefLab (2011), ICP-MS or other similar method for measuring the total dissolved iodine (all species), has to be used in the GRUMO monitoring. For the sub-sets used here, all laboratory analyses have been handled by Eurofins Danmark A/S and the used method for detecting iodine in the groundwater is ICP-MS (CEN, 2004). Thus, the sub-sets consist of data on the total

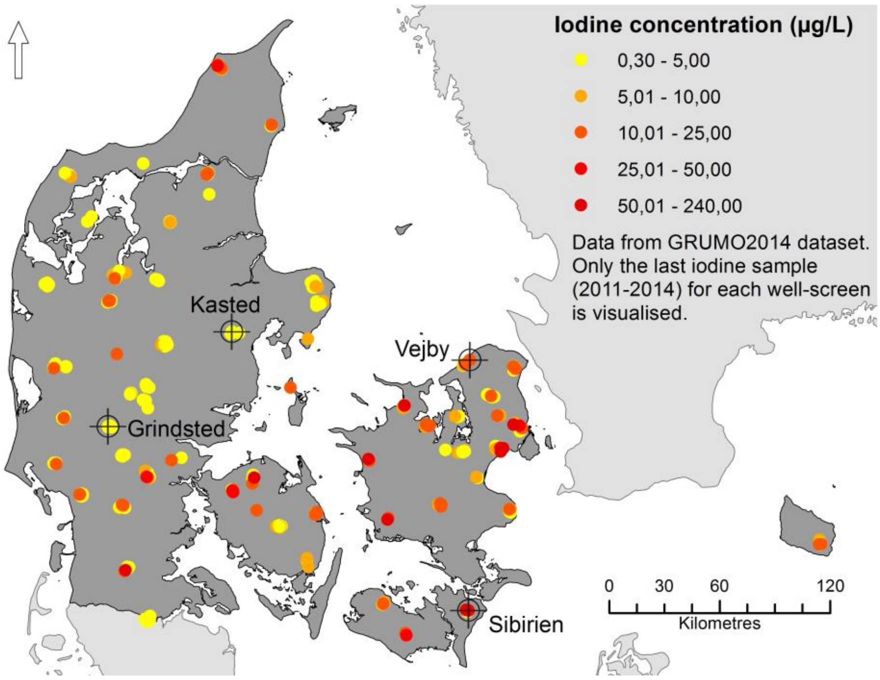

Figure 1
Location of the four multi-screen wells (Kasted, Grindsted, Vejby, Sibirien) and the GRUMO 2014 sub-dataset including the last sample analysed for total iodine (2011-2014)

Note: the higher concentrations have priority in this visualisation, i.e. they are plotted over the lower ones dissolved iodine (TI) concentrations. No information on the iodine speciation is present.

Further information on sampling procedures, analytical methods, and details on the GRUMO programme can be found in the annual report on groundwater (Thorling et al., 2013). The latest annual report (based on the GRUMO 2014 dataset) is under preparation at the time of PhD thesis submission.

The two sub-sets that have been used for the purposes of this paper contain:

I. The last TI analyse (2011-2014) and the last chlorofluorocarbon (CFC) dating (1997-2013) for each GRUMO location (well screen) where a sample was analysed for TI in that period. Only one sample per well screen is included. The CFC-dating and the TI analysis may be based on groundwater samples obtained from the same well screen, but at a different date.

II. Depth profiles of TI concentration (sampling 2012) in groundwater from four of the multi-screen wells, part of GRUMO, are also shown here.

The multi-screen wells are used primary for monitoring of the redox conditions. The monitoring purpose is to better describe and understand the variation over time of the redox zones in depth and consequently to improve the understanding of the time series for different redox-sensitive elements, e.g. nitrate (Thorling et al., 2013). Thorling et al. (2013) report time-series on redox conditions for the four multi-screen wells, as well as, some analyses on the depth profiles of redox-sensitive elements. The redox sensitive compounds are analysed on a regular basis, but not every year in the period 2011-2015.

The GRUMO dataset (the sub-sets too) provides information also about geographical location, depth and length of the screen, purpose of sampling, additional sampling information, e.g. field filtration/no filtration, even a geological information.

1.2. Sites description

The location of all samples used in sub-set 1 and subset 2 are visualised on Figure 1. Technical description of the multilevel wells (Kasted, Grindsted, Vejby, Sibirien) can be found elsewhere. All wells (well screens too) have unique identification numbers (DGU no.) by which all the information on geology, groundwater levels, and chemistry can be found in the online publicly accessible Jupiter database (GEUS). The monitored screens are shown in depth in meters below terrain (mbt) together with the depth profile of TI and other elements on Figure 4-7. The well screens are 10cm long. The geology at each well together with classification of the water type at each depth (coloured red, yellow, green dots) are also visualised on Figure 4-7 (source: Thorling et al. (2013)). The groundwater samples from all four wells represent glacial melt-water aquifers. The geology at Kasted, Sibirien and Vejby is characterised by local heterogeneity: interchanging sand, gravel, stones, and clay/silt lenses/layers. A predominantly horizontal groundwater movement is suspected at the four well locations.

2. Results and Discussion

2.1. Iodine concentration and groundwater age

Sub-set 1 is used for the analysis on the relation between groundwater age and TI concentrations. The last measured TI concentration for each well screen is mapped on Figure 1. The estimate of groundwater age is based on CFC dating. The CFC age estimate is directly obtained from the dataset, no further calculations and assumptions have been made. A new dating method (tritium/helium) for young groundwaters has been employed in GRUMO programme since 2012. However, not all the locations have been dated with the new method, thus the CFC is used here. The CFC method cannot provide information on groundwater recharged after the start of the new millennium.

The relation between groundwater age, depth of extraction (mid. screen) and TI is visualised on Figure 2. The bubble size indicates the TI concentration. The elevated TI concentrations are present in different depths; however, they are predominantly in groundwaters older than 25 years. There is only one exception – a sample representing young groundwater (12 years old) with TI = 240 μg/L. The sample is extracted from the shallowest screen (1.5-2.5 mbt) of well with DGU no. 159. 982. The screen is located in sand aquifer and overlaid by lacustrine gyttja (0.65 - 1.25 mbt) and a plough layer (0 - 0.65 mbt). Most probably the high TI concentration can be explained by the influence of the overlying high in organic matter layer.

The sub-dataset 1 was divided in 3 parts depending on the groundwater age: <15 years old, 15 - 24 years old, 25->60 years old. Box plots with outliers for the TI concentrations for these 3 groups of samples and for the whole sub-set 1 are plotted on Figure 3. A Mann-Whitney (or other similar) test is need to test if there is a significant difference between these groups of samples.

The overall first impression is that the samples with TI > 27 μg/L are representing groundwater older than 25 years (Figure 2 and Figure 3). This could be explained by the longer residence times which would provide longer time for groundwater-sediment material interaction. It is possible also that older saline groundwaters with elevated iodine are influencing the fresher groundwater. Further investigations are needed: 1) to test for significant difference and then 2) to explain the observed relation and to test different hypothesis.

2.2. Depth profiles of iodine concentration at four multi-screen wells

The TI depth profiles for Kasted, Grindsted, Vejby, Sibirien are presented on Figure 4-7. Together with TI concentrations, other elements and parameters (O2, NO3, NO2, Fe, Mn, SO4, pH, Al, As, Cl, CFC age) are shown to facilitate (or complicate) the discussion on TI variation in depth.

The redox conditions at Grindsted, Vejby and Sibirien change in depth multiple times (interchanging oxic, anoxic and slightly reduced zones), whereas at Kasted there is clear separation between oxic, anoxic and slightly reduced redox zones. A comprehensive overview on the time series (1999-2012) of the redox conditions for these wells is presented in (Thorling et al., 2013). The groundwater at Grindsted is acidic (range pH 4.5 – pH 5.5), whereas at the other three wells the groundwater is near neutral to slightly alkaline. At all four locations pH varies with depth. Also, based on the CFC dating and abrupt changes in the groundwater age at some depths, it can be assumed that groundwaters with different sources (different recharge area) are present at different depths in the same aquifer for Kasted, Vejby, Sibirien.

Figure 2: Relationship between depth of extraction (depth of screen middle point in mbt), groundwater age (CFC) and iodine concentration (bubble size)

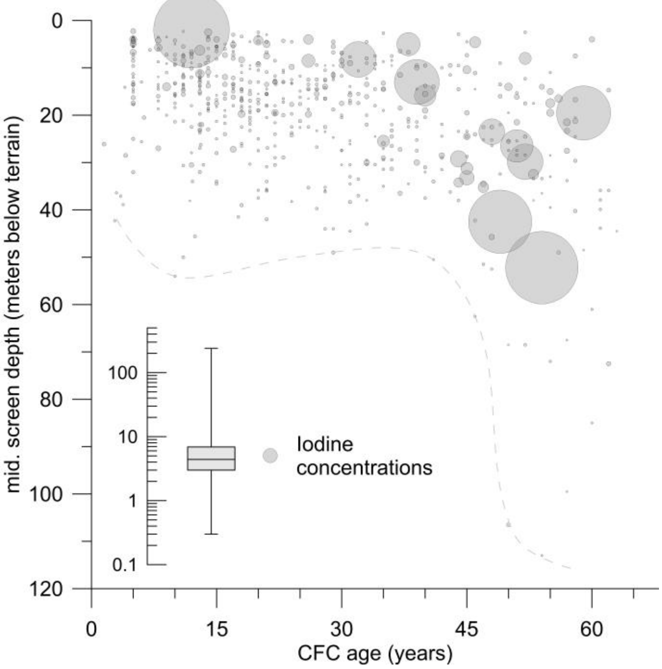

Figure 3 Box-plots of samples divided in 3 groups by the groundwater age: younger than 15 years, 15-24 years old and older than 25 years. Box-plot of all samples is given for comparison.

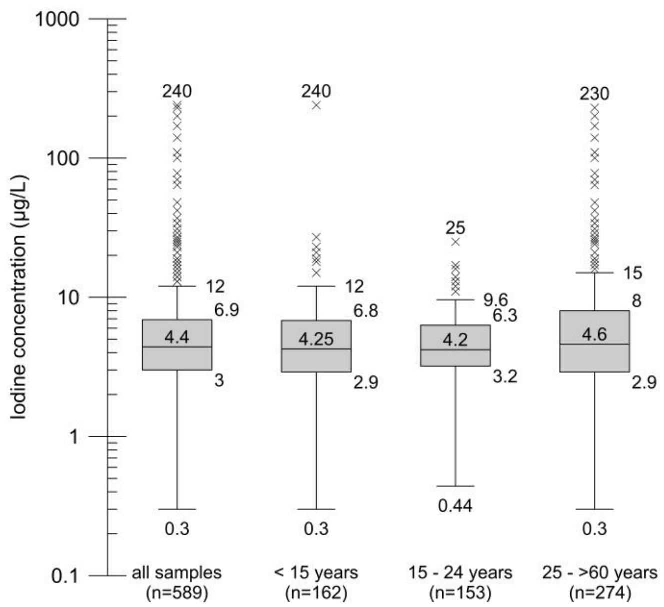

Table 1: Descriptive statistics of TI concentrations (samples at different depths) at Kasted, Grindsted, Vejby, and Sibirien multilevel wells

TI	Kasted	Grindsted	Vejby	Sibirien
sampling (2012)	26 June	10-12 July	14-16 Aug.	20-21 Aug.
Mean	3.85	2.15	13.45	13.68
Standard Error	0.270	0.211	2.634	3.762
Median	3.8	2.1	14.5	4.2
Mode	3.9	1	#N/A	4.2
Standard Deviation	1.205	1.010	8.330	15.511
Sample Variance	1.453	1.020	69.392	240.587
Kurtosis	2.078	-1.205	-1.555	0.105
Skewness	1.289	0.336	0.005	1.241
Range	4.9	3.2	22.8	46
Minimum	2.2	1	2.2	2
Maximum	7.1	4.2	25	48
Sum	76.9	49.5	134.5	232.5
Count	20	23	10	17
Confidence Level for mean (95.0%)	0.564	0.437	5.959	7.975

The descriptive statistics for TI concentrations for each well, based on the depth profiles, is given in Table 1. The concentrations at Vejby and Sibirien have the largest range span over depth: 2.2-25 µg/L for Vejby and 2-48 µg/L for Sibirien. Whereas, at Kasted and Grindsted the TI concentrations vary over depth in a narrower range: 2.2-7.1 µg/L for Kasted and 1-4.2 for Grindsted.

The low TI concentrations at the shallowest parts of the depth-profiles reflect most probably the iodine content in precipitation, including the subsequent up-concentration due to evapotranspiration and/or immobilisation in the topsoil or upper layers.

The small changes in TI in depth (±1-2 µg/L) are most probably result of the geochemical processes occurring at the sampling depths. This can be explained by localised difference (at depth) in the organic matter content, metal hydroxides, redox conditions, and pH. Redox conditions will affect the iodine speciation: it is expected that iodate will be dominating in the oxidised waters (possibly also in the anoxic), while in the reduced water, iodide will be the stable inorganic species. The pH changes will affect the sorption/desorption processes, which may be important for iodine concentration too.

Based on the CFC ages, TI concentrations at Vejby and Sibirien could be explained with the presence of other (older) groundwater source at certain levels. The change in the concentrations in depth at these two wells (±10-20 µg/L) could be representing complex hydrogeological conditions. However, it is also possible that there is a geochemical process which is responsible for the elevated concentrations. At Vejby TI and Cl do not follow the same trend, which rules out saline water influence, as Cl elevation would have been expected. The TI concentration peek at Vejby coincides with As, Fe, and Mn peaks too, as well as with change in the redox conditions from slightly reduced water to anoxic one. However, this change in the redox conditions in depth is not present at all 3 sampling periods in 2012, but only for the sampling when also TI was analysed. At the deepest part of Sibirien, however, the TI and Cl concentrations seem to follow the same trend. The TI peak coincides with a peak in Fe concentrations at screen no.6.

It is also possible that local differences in dry precipitation of iodine at the groundwater recharge can also be governing for the observed small or not so small differences in the TI concentrations. Further site description (incl. land use at the groundwater catchment) is needed. Further geochemical analysis and also data collection are also needed in order to elucidate the sources, processes and the mechanisms governing these concentration-depth changes.

3. Possibilities for future research

The multilevel wells part of GRUMO monitoring network present an opportunity to design future studies on high resolution depth profiles of iodine (but also other trace elements). The data presented here visualises the potential of these four wells to be used as study sites in future comprehensive geochemical investigations.

With respect to iodine, these four study sites are suitable for testing different hypothesis on the mechanisms governing the iodine concentrations and their variation in glacial melt-water sediments, e.g.:

- Evaporative up-concentration of precipitation
- Organic matter degradation and reductive dissolution of iron (or other metal) hydroxides.
- Diffusion of older saline waters and/or sea water intrusion (not very likely based on the presented

here data, but still further studies are needed to exclude this as possibility).

In order to do that, though, further work is needed. This can constitute of:

- Hydrogeochemical modelling of the data from the GRUMO dataset, e.g. calculating SI of different minerals, iodine speciation, and even testing different scenarios on vertical and/or horizontal transport of solutes through the sediment column.
- Additional data mining based on existing chemical, geological and hydrogeological data for the areas, where these four wells are located, in order to describe better the study sites.
- Designing of new sampling campaigns to obtain groundwater samples for additional analysis on iodine speciation, iodine isotopes, dissolved organic matter characterisation, major elements that currently are not measured, etc.
- Further sediment characterisation based on the existing and stored at GEUS sediment samples from the four multilevel wells: sequential extraction for water-soluble-, exchangeable -, metal-oxide-, humic and fulvic acid iodine fractions and TI from the sediment samples (example for of similar investigation: Li et al. (2013)), TOC, % composition of major elements (XRF), LOI, etc.

4. Appendix

The depth profiles for the four wells are presented on the next two pages

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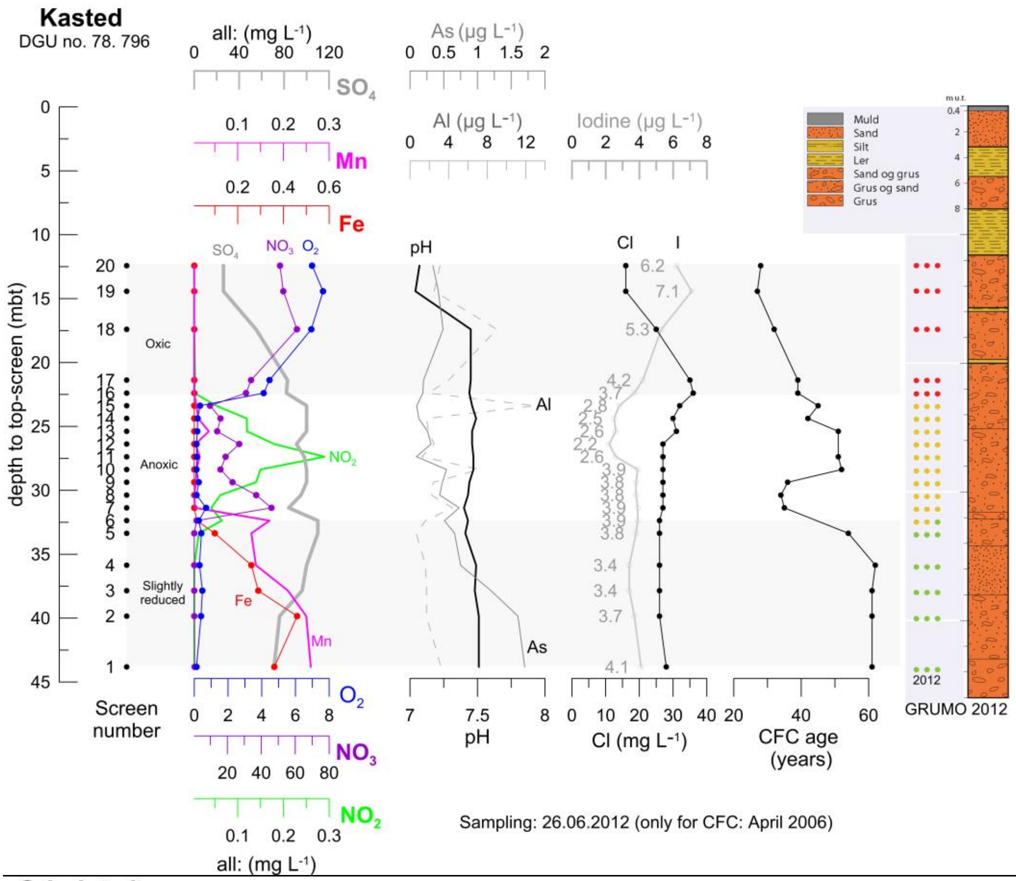

Figure 4: Kasted

Depth profiles for SO4, Mn, Fe, O2, NO2, NO3, Al, As, pH, Cl, I, CFC age and geology; the middle point of the screens (10 cm length) is shown; The data is from GRUMO programme, the geology profile is from the GRUMO report

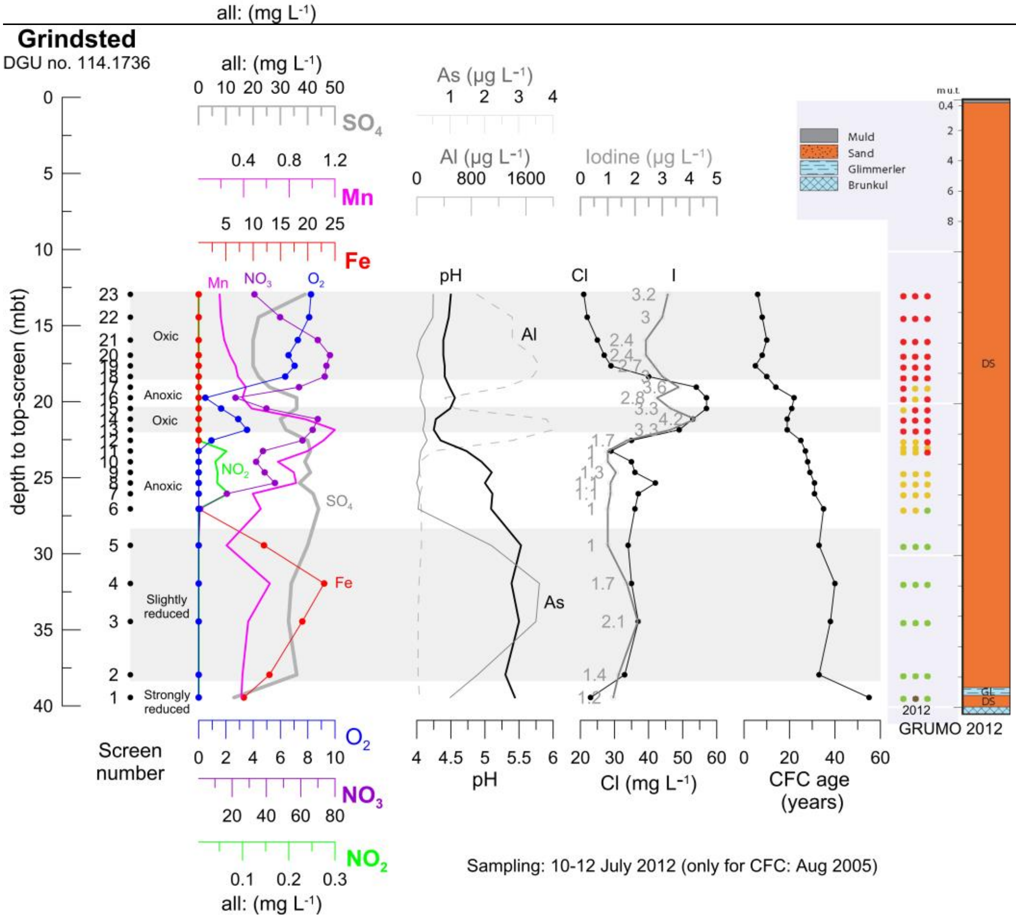

Figure 5: Grindsted

Depth profiles for SO4, Mn, Fe, O2, NO2, NO3, Al, As, pH, Cl, I, CFC age and geology; the middle point of the screens (10 cm length) is shown; The data is from GRUMO programme, the geology profile is from the GRUMO report

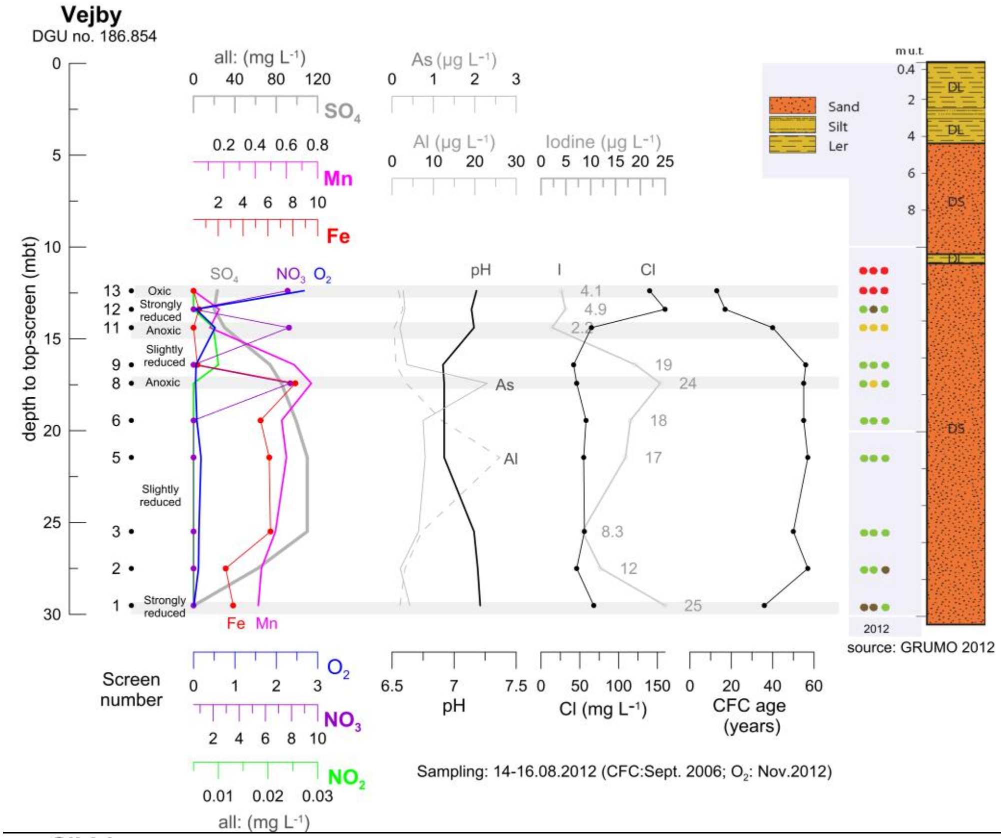

Figure 6: Vejby

Depth profiles for SO4, Mn, Fe, O2, NO2, NO3, Al, As, pH, Cl, I, CFC age and geology; the middle point of the screens (10 cm length) is shown; The data is from GRUMO programme, the geology profile is from the GRUMO report

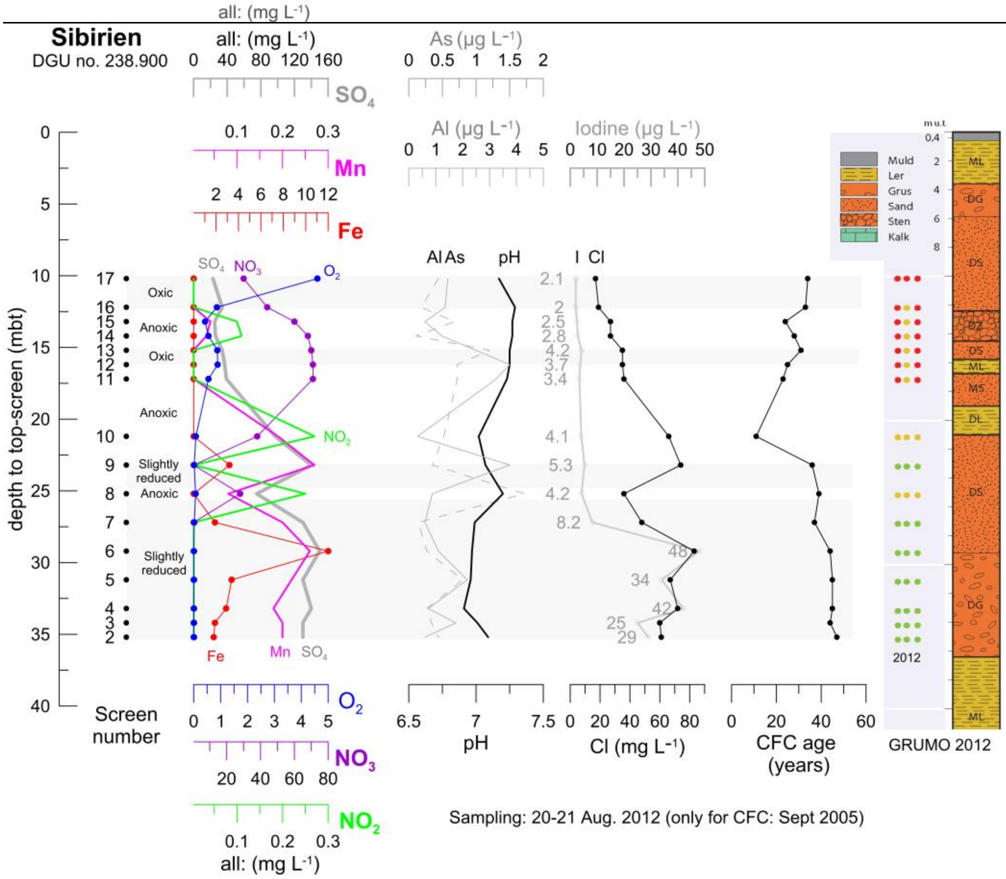

Figure 7: Sibirien

Depth profiles for SO4, Mn, Fe, O2, NO2, NO3, Al, As, pH, Cl, I, CFC age and geology; the middle point of the screens (10 cm length) is shown; The data is from GRUMO programme, the geology profile is from the GRUMO report

Technical Note I

To be submitted to Hydrogeology Journal

Design of a nationwide drinking-water sampling campaign for assessment of dietary iodine intake and human health outcomes

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Edit 4 (Sep. 2018):

1. Revised version of Technical Note I was published in 2018 in International Journal of Environmental Research and Public Health, under new title ("*Nationwide Drinking Water Sampling Campaign for Exposure Assessments in Denmark*"), thus the manuscript is removed from this e-book (14 pages);
2. Cite article as: Voutchkova, D.D. et al. Int. J. Environ. Res. Public Health (2018) 15: 467.
3. DOI: https://doi.org/10.3390/ijerph15030467

Appendix: Publication list

Papers included in the PhD thesis

D.D. Voutchkova, S.M. Kristiansen, B. Hansen, V. Ernstsen, B. Sørensen, K. Esbensen. *Iodine concentrations in Danish groundwater: historical data assessment 1933-2011.* In: Environmental Geochemistry and Health, (2014) DOI 10.1007/s10653-014-9625-4

D.D. Voutchkova, V. Ernstsen, B. Hansen, B. Sørensen, Z. Chaosheng, S.M. Kristiansen. *Assessment of spatial variation in drinking water iodine and its implications for dietary intake: A new conceptual model for Denmark.* In: Science of the Total Environment, Vol. 493 (2014) p. 432–44. DOI 10.1016/j.scitotenv.2014.06.008

D.D. Voutchkova, B. Hansen, V. Ernstsen, S.M. Kristiansen. *Hydro-geochemical characterisation and interpretation of selected Danish groundwaters in relation to iodine* (to be submitted at Hydrogeology Journal)

D.D. Voutchkova, B. Hansen, V. Ernstsen, S.M. Kristiansen. *Technical note: Design of a drinking water sampling campaign for nationwide assessment of drinking-water importance for dietary iodine intake* (to be submitted at Hydrogeology Journal)

D.D. Voutchkova, L.T. Sørensen, V. Ernstsen, S.M. Kristiansen, B. Hansen. *High resolution depth profiles of iodine concentration in groundwater at four multi-screen wells in Denmark: possibilities for future research* (work in progress)

Manuscripts not included in the PhD thesis

D.D. Voutchkova, *Iodine in Danish Groundwater and Drinking Water: Interdisciplinary Study on Hydrogeochemistry and Human Health,* PhD progress report handed in December 2012, Qualifying exam passed successfully on 28th of January 2013

D.D. Voutchkova, B. Hansen. *Report on Arsenic levels in Danish Groundwater and Drinking water: Historical Data Assessment 2001-2013* (in preparation)

Conference abstracts

B. Hansen, V. Ernstsen, B. Sørensen, K. Esbensen, S.M. Kristensen, **D.D. Voutchkova**. *Iodine in groundwater and human health in Denmark; Issue of medical geology - relating natural geological factors and health, 2011* MEDGEO 2011

D.D. Voutchkova, S.M. Kristiansen, B. Hansen, V. Ernstsen, B. Sørensen, K. Esbensen, *Iodine in* **Groundwater in** *Denmark; Implications for Human Health*, 2012. abstract and oral contribution from Medical geology workshop (GEUS)

D.D. Voutchkova, S.M. Kristiansen, B. Hansen, B. Sørensen, V. Ernstsen, K. Esbensen. *Iodine in Groundwater in Denmark and Implications for Human Health,* 2012. Abstract and oral contribution from ATV Jord og Grundvand, Gentofte, Denmark

D.D. Voutchkova, S.M. Kristiansen, B. Hansen, V. Ernstsen, B. Sørensen, K. Esbensen. *Multivariate Analysis of Danish Historical Hydrogeochemical Data with Respect to Iodine in Groundwater*, 2012. Abstract and oral contribution from SESEH 2012, Galway, Ireland.

S.M. Kristiansen, **D.D. Voutchkova**, B. Sørensen, B. Hansen, V. Ernstsen, K. Esbensen, *Iodine in Danish ground and drinking water – preliminary speciation results and design of a nationwide sampling campaign*, 2013. Abstract from DWRIP2013, DTU

D.D. Voutchkova, S.M. Kristiansen, B. Hansen, V. Ernstsen, B. Sørensen, K. Esbensen, *Dietary Iodine Intake from Drinking Water in Denmark,* 2013. Abstract and oral contribution from 5th International Conference on Medical Geology (MEDGEO2013), Arlington, Virginia, United States.

D.D. Voutchkova, B. Hansen, B. Sørensen, C.L. Larsen, S.M. Kristiansen. *Arsenic Levels in Danish Groundwater and Drinking Water: Historical Data Assessment 2001-2013*, 2013. Abstract and poster from 5th International Conference on Medical Geology (MEDGEO2013), Arlington, Virginia, United States.

D.D. Voutchkova, V. Ernstsen, S.M. Kristiansen, B. Hansen, *Spatial variability of drinking water iodine in Denmark: implications for future policy making.* Abstract and poster from European Geoscience Union General Assembly 2014 (EGU2014), Vienna, Austria.

D.D. Voutchkova, B. Hansen, V. Ernstsen, K. Esbensen, B. Sørensen, S.M. Kristiansen. *High spatial variability of iodine in Danish groundwater and drinking water: geochemical factors and human health implications*. Abstract and oral contribution from 30th International Conference of the Society of Environmental Geochemistry and Health - European Section (SEGH2014)

Completed courses as part of the PhD

"The Hydrogeochemical Cycle", Department of Geoscience, Aarhus University – **10 ECTS**
"Geoscience Data Analysis", GEUS – **5 ECTS**
"Searching databases of scientific literature" GSST, Aarhus University – **1 ECTS**
"Groundwater sampling course" , School of Technology and Business, VIA University College – **1 ECTS**
"Representative sampling of Heterogeneous System in Science, Technology & Industry: Theory of Sampling (TOS)", Faculty of Energy and Science, Aalborg University (held in GEUS) – **5 ECTS**
"Health and Earth – Building a Safer Environment", short course on medical geology sponsored by IMGA and SESEH 2012 (held in Galway, Ireland) – **2 ECTS**
"Scientific Writing and Presentation", GSST, Aarhus University (held in Foulum) - **2 ECTS**
"The world of research", GSST, Aarhus University – **1 ECTS**
"Advanced GIS", NUI Galway, Ireland.

Obligatory salaried PhD work:

487 hours: teaching at the Department of Geoscience (AU):

- Field course in hydrology and geomorphology ("Hydrologisk og Geomorfologisk Feltkursus, Klim) - 2 weeks 2012, 6 days 2013, 5 days 2014), where instructing students 1) to perform stream discharge measurements using different instruments, 2) to measure groundwater levels and 3) to delineate and characterise the topographic and groundwater catchment areas.
- Assisting at the course "Hydrologi, jordbund og dynamisk geomorfologi" in 2012 and jointly supervising 2 small student projects.

280 hours: working on project not related to the PhD thesis (Arsenic in Danish groundwater and drinking water) at the Department of Groundwater and Quaternary Geology Mapping (GEUS)

Research environment

Department of Geoscience, Aarhus University (AU) and Department of Groundwater and Quaternary Geology Mapping at the Geological Survey of Denmark and Greenland (GEUS) – main research environments.

Research visit (3 months) at NUI Galway, visiting Dr. Chaosheng Zhang

Appendix: Supplementary materials

Edit 5 (Sep. 2018): This section contained the Supplementary materials for Papers I, II, and III. Since those can be found on-line together with the corresponding publications, I have removed them from this e-book (27 pages).