Fluoride in surface water and groundwater in southeast Sweden

– sources, controls and risk aspects
FLUORIDE IN SURFACE WATER
AND GROUNDWATER
IN SOUTHEAST SWEDEN
— sources, controls and risk aspects

TOBIAS BERGER

LINNAEUS UNIVERSITY PRESS
Fluoride in surface water and groundwater in southeast Sweden – sources, controls and risk aspects
Doctoral dissertation, Department of Biology and Environmental Science, Linnaeus University, Kalmar, Sweden, 2016

Front cover: Precipitated secondary fluorite (purple crystals) on an open fracture wall in the reddish Götemar granite. Embedded photos from above: Soil profile in the Kärrsvik catchment, the Kärrsvik stream and a glass of water from the abandoned and water-filled Götebo quarry, exhibiting a fluoride concentration of 5.8 mg/L (maximum permissible limit for drinking water in Sweden is 1.5 mg/L). Photos by the author.
Published by: Linnaeus University Press, 351 95 Växjö, Sweden
Printed by: Elanders Sverige AB, 2016
Abstract


The aim of this thesis is to determine the sources, controls and risk aspects of fluoride in surface water and groundwater in a region of southeastern Sweden where the fluorine-rich 1.45 Ga circular Götemar granite (5 km in diameter) crops out in the surrounding 1.8 Ga granites and quartz monzodiorites (TIB rocks). The materials of this thesis include both primary data, collected for the purpose of this thesis, and a large set of secondary data, retrieved from the Swedish Nuclear Fuel and Waste Management Co., the Swedish Geological Survey and the Kalmar County Council. A characteristic feature of the area is high fluoride concentrations in all kinds of natural waters, including surface waters (such as streams) and groundwater in both the Quaternary deposits (regolith groundwater) and bedrock fractures (fracture groundwater). A number of potential sources and controls of the high fluoride concentrations were investigated, including a variety of geological, mineralogical, mineral-chemical and hydrological features and processes. For the stream waters and regolith groundwater, high fluoride concentrations were correlated with the location of the Götemar granite. This finding is explained by the discharge of fluoride-rich groundwater from fractures in the bedrock and/or the release of fluoride due to the weathering of fluorine-bearing minerals in the Quaternary deposits; however, the Quaternary deposits had considerably lower fluoride concentrations than the underlying bedrock. The high fluoride concentrations in the fresh fracture groundwater (up to 7.4 mg/L) in the TIB-rocks are proposed to be the result of long residence times and the alteration/dissolution of fluorine-bearing primary and secondary minerals along the fracture walls. In terms of risk aspects, this thesis shows that fluoride can add to the transport and inorganic complexation of aluminium in humic-rich, acidic streams. Additionally, 24 % of the children in households with private wells in Kalmar County were assessed to be at risk of excess fluoride intake based on the WHO drinking water guideline value (1.5 mg/L). However, the risk increased significantly when instead the US EPA reference dose (0.06 mg/kg-day) was used, both when all relevant exposure pathways were taken into account as well as water consumption alone. Hence, it is shown that the risk of an excess intake of fluoride is strongly dependent on the basis for evaluation.

*Keywords*: fluorine, fluoride, water-rock interaction, granite, crystalline bedrock, surface water, groundwater, Götemar, drinking water quality, aluminium, speciation, fluorosis, PBA
Sammanfattning

Fluor är ett av få kemiska element som har potential att påverka vår hälsa genom dricksvattnet. Som anionen fluorid (F⁻) förekommer ämnet löst i naturliga yt- och grundvatten över hela jorden. I små doser har det visat sig minska risken för karies, men vid bara något förhöjda halter ökar risken för att inlagringen i tandmalj och skelett istället ska ge hälsoskadliga effekter. I Sverige förekommer flera områden med naturligt förhöjda halter av fluorid i grundvattnet, men få studier har gjorts för att närmare undersöka de geokemiska orsakerna till detta.

I denna avhandling har jag undersökt källorna, kontrollmekanismerna och risikaspekterna av fluorid i yt- och grundvatten i ett område (Laxemar-Simpevarp) i Oskarshamns kommun, Kalmar län (Sverige). Området karaktäriseras av en berggrund med 1.8 miljarder år gamla magmatiska bergarter tillhörande det Transskandinaviska bältet (TIB) och den cirkulära (5 km i diameter) intrusionen av den yngre, fluoranrikade Götemargraniten. Materialen till grund för avhandlingen inkluderar dels primärdatal som samlats in från vatten och fast material specifikt för studierna, men också sekundära data som mottagits från Svensk Kärnbränslehantering, Sveriges Geologiska Undersökning och Landstinget i Kalmar län.

Området karaktäriseras av förhöjda fluoridhalter i alla typer av vatten, vilket inkluderar ytvatten (till exempel bäckar) och grundvatten i de kvartära avlagringarna och i bergets vattenförande sprickor. Ett flertal olika källor och styrmekanismer till de höga halterna har undersökts, vilket inkluderat geologiska, minerallogiska, mineral-kemiska och hydrologiska egenskaper och processer. I ytvatten och grundvattnet i de kvartära avlagringarna korrelerade fluoridhalterna med Götemargranitens utbredning. Detta förklaras av transport av fluorrikt grundvatten i bergssprickor i kontakt med dessa vattendrag liksom vittring av fluorbärande mineral, till exempel biotit, i de kvartära avlagringarna. Det kunde dock konstateras att fluorhalterna i de kvartära avlagringarna var klart mycket lägre än i de underliggande bergarterna. De höga fluoridhalterna i de vattenförande sprickorna i berget (upp till 7.4 mg/L) föreslås vara ett resultat av långa uppehållstider och vittring/omvandling av fluorbärande mineral på sprickväggarna, till exempel fluorit, bastnäsit och apofyllit.

Avhandlingen visar vidare att förhöjda halter av fluor har potentialen att öka mängden aluminium som finns löst i oorganisk form i humusrika, sura bäckar. Ytterligare en risikaspekter av undersöktes var andelen barn i Kalmar län som kan antas riskera få i sig för mycket fluorid i förhållande till satta gränsvärden. Med utgångspunkt från gränsvärdet för fluorid i dricksvattnet på 1.5 mg/L så hade 24 % av hushåll med privata brunns halter som översteg detta. När istället ett gränsvärde för maximalt tolerabelt intag (0.06 mg/kg/dag) användes så bedömdes risken vara klart högre, både då alla exponeringsvägar och dess variabilitet inkluderades men också då endast
vattenkonsumtion togs i beaktande. Detta belyser att den beräknade risken är beroende av vilken metod och gränsvärde som används vid utvärderingen.

Denna avhandling bidrar till en ökad förståelse till orsaken bakom förhöjda fluoridhalter i denna typ av miljöer och vilka riskaspekter detta i sin tur för med sig. Sådan kunskap kan tillämpas när det gäller såväl utvinning av dricksvatten som studier av akvatiska ekosystem, inte minst i områden där förhöjda fluoridhalter är vanligt förekommande och där förekomsten av fluoros är ett utbrett folkhälsoproblem.

*Nyckelord: fluor, fluorid, vatten-berg interaktion, granit, ytvar, grundvatten, dricksvatten, Götemar, aluminium, speciering, fluoros, PBA*
Till mor och far
“Water is the one substance from which the earth can conceal nothing; it sucks out its innermost secrets and brings them to our very lips”
— Jean Giraudoux, The Madwomen of Chaillot
LIST OF PUBLICATIONS

This thesis is based on the following papers, referred to in the text by their roman numerals.


The published papers are reprinted with the kind permission of Springer (Paper I) and Elsevier (Papers II and V).
Author’s contributions to the papers

**Paper I**
Concept and design: Berger T, Peltola P, Åström M.
Material collection and analytical work: Berger T (spatial sampling and analyses of surface waters), Drake H (gathered data on fluorine in rocks and minerals), SICADA Database (SKB) (surface and regolith groundwater chemistry), Geological Survey of Sweden (groundwater data from excavated wells)
Main data analyses and interpretation work: Berger T.
Computer graphics: Berger T.
Original draft: Berger T.
Proofreading and edit: Berger T, Åström M, Peltola P, Drake H.

**Paper II**
Concept and design: Berger T, Gustafsson JP, Åström M.
Material collection and analytical work: SICADA Database (SKB) (stream water chemistry).
Main data analyses and interpretation work: Berger T (incl. MINTEQ modelling).
Computer graphics: Berger T.
Original draft: Berger T.
Proofreading and edit: Berger T, Mathurin F, Gustafsson JP, Peltola P, Åström M.

**Paper III**
Concept and design: Berger T, Mathurin F, Peltola P, Åström M.
Material collection and analytical work: Berger T (collection, preparation, SEM), Drake H (SEM), Yu C (collection, preparation), Svensson D (XRD), Åström M (collection), Activation Laboratories Ltd (additional analytical work)
Main data analyses and interpretation work: Berger T.
Computer graphics: Berger T.
Original draft: Berger T.
Proofreading and edit: Berger T, Changxun Y, Drake H, Peltola P, Svensson D, Åström M.

**Paper IV**
Concept and design: Berger T, Åström M.
Material collection and analytical work: Berger T (SEM-EDS/WDS), Drake H (SEM-EDS/WDS), SICADA Database (SKB) (regolith and fracture groundwater chemistry, drillcore mineral mapping), Geological Survey of Sweden (groundwater data from excavated/drilled wells).
Main data analyses and interpretation work: Berger T, Mathurin F (incl. PHREEQC calculations).
Computer graphics: Berger T, Mathurin F.
Original draft: Berger T.
Proofreading and edit: Berger T, Mathurin F, Drake H, Åström M.

**Paper V**
Concept and design: Augustsson A, Berger T.
Material collection and analytical work: Kalmar County Council
Main data analyses and interpretation work: Augustsson A (incl. PBA Risk Calc calculations), Berger T.
Computer graphics: Augustsson A, Berger T.
Original draft: Augustsson A, Berger T.
Proofreading and edit: Augustsson A, Berger T.
# TABLE OF CONTENTS

LIST OF PUBLICATIONS .................................................................................. 1
Author’s contributions to the papers ................................................................. 2
TABLE OF CONTENTS ...................................................................................... 2
1. INTRODUCTION ............................................................................................ 4
   1.1 Geochemistry of fluorine .......................................................................... 8
       1.1.1 Fluorine in rocks and soils ................................................................. 8
       1.1.2 Fluorine in surface waters and groundwater ..................................... 9
   1.2 Environmental effects of fluoride ........................................................... 10
       1.2.1 Intake of fluoride and human health ............................................... 10
       1.2.2 Toxicological role of fluoride in acidic surface waters .................. 12
   1.3 A Swedish perspective on fluoride ......................................................... 12
2. AIMS .............................................................................................................. 15
3. SETTING ....................................................................................................... 16
4. MATERIAL AND METHODS ..................................................................... 20
   4.1 Sampling and sample treatment .............................................................. 20
       4.1.1 Sampling of surface waters, Quaternary deposits and rock materials ........................................................................................................... 21
       4.1.2 Swedish Nuclear Fuel and Waste Management Company (SKB) .. 22
       4.1.3 Kalmar County Council .................................................................. 24
       4.1.4 Swedish Geological Survey ............................................................ 24
   4.2 Analytical methods ................................................................................. 27
       4.2.1 Water chemistry (primary data) ...................................................... 27
       4.2.2 Water chemistry (secondary data) .................................................. 27
       4.2.3 Minerals in the bedrock (primary data) .......................................... 27
       4.2.4 Quaternary deposits (primary data) ................................................ 28
   4.3 Data analyses .......................................................................................... 30
       4.3.1 Hydrogeochemical modelling ......................................................... 30
       4.3.2 Exposure calculations ..................................................................... 31
       4.3.3 Statistical analyses .......................................................................... 31
5. RESULTS AND DISCUSSION .................................................................... 33
   5.1. Fluoride abundance and spatiotemporal variability in surface waters and groundwater .............................................................. 33
   5.2. Sources and controls of fluoride concentrations in water ...................... 39
5.3. Risk aspects of high dissolved fluoride concentrations .................. 45
5.3.1 Fluoride exposure of children in Kalmar County ...................... 46
5.3.2 Effects on aluminium ............................................................. 49
6. CONCLUSIONS .............................................................................. 52
ACKNOWLEDGEMENTS ................................................................... 55
REFERENCES ..................................................................................... 57
Fluorine is a heavily debated element because it affects the lives of millions of people around the world in a variety of ways. It is ranked as the 13th most common element in the continental crust, and is the most electronegative and reactive of all the elements on the periodic table, reacting with practically all organic and inorganic substances (Kumar Singh et al., 2011; Lahermo and Backman, 2000). In natural waters, fluorine occurs in dissolved form as the univalent anion fluoride ($F^-$) and, as such, has been the subject of wide focus in scientific studies and of public concern for nearly a century.

According to the World Health Organization (WHO), access to safe drinking-water is essential to health, established as a basic human right and a component of an effective policy for health protection (WHO, 2011). In this context, fluoride possesses a double-sided nature, providing the beneficial effects of preventing dental caries but also carrying risks associated with its accumulation in the body, leading to dental and skeletal fluorosis and perhaps even more adverse health effects (Edmunds and Smedley, 2013). Both the negative and positive effects of fluoride have gained increasing attention, starting in the 1930s (Carstairs, 2015). In addition, the role of fluoride in aluminium complexation and the associated toxicological implications has drawn scientific interest (e.g. Gensemer and Playle, 1999; Moore and Ritchie, 1988; Sjöstedt et al., 2010). There are multiple sources of fluoride to which humans can be exposed; of these, the ingestion of drinking water is generally considered to be the largest contributor to daily intake. Other sources include various foods and beverages (e.g. rice, canned fish, tea) and, not least, dental products (i.e. toothpaste, mouthwash and fluoride tablets) (Fawell et al., 2006).

A number of regions around the globe exhibit elevated fluoride levels in natural waters due to the weathering of F-bearing minerals in F-rich geological materials (Brunt et al., 2004). In such areas, the excess intake of fluoride poses a health threat to the public (Bunnell et al., 2007; WHO, 2011). In addition,
anthropogenic activities (eg. phosphorous fertilizers) or volcanic emissions are important sources in some areas, potentially leading to fluoride contamination of soil, surface waters and groundwater (D’Alessandro et al., 2008; Mondal and Gupta, 2015). Elevated levels of fluoride can be found in several large belts across the earth (Figure 1), usually associated with sediments of marine origin in mountainous areas, volcanic rocks or granitic and gneissic rocks (Fawell et al., 2006). Examples of such areas may be found in the Middle-East and North Africa, such as in Iran and Algeria (Battaleb-Looie et al., 2013; Messaitfa, 2008); in the East African Rift system (Msonda et al., 2007; Rango et al., 2009); in South America, such as in Brazil and Argentina (Gomez et al., 2009; Viero et al., 2009); and in parts of China (Li et al., 2011; Su et al., 2015), India (Jacks et al., 2005; Jacks et al., 2009; Mondal and Gupta, 2015) and the USA (Ozsvath, 2006).

**Figure 1.** Larger regions of the world with elevated concentrations of fluoride (above 1.5 mg/L). From Selinus (2010), reprinted with the kind permission of ©Studentlitteratur.

Fluoride concentrations in stream waters and groundwater are low in many European regions. However, areas with elevated concentrations are relatively widespread and are scattered over the European continent (Bårdsen et al., 1999; Fordyce et al., 2007; Lahermo et al., 1991; Salminen et al., 2005). Such areas include southern Sweden and southern Finland where fluoride concentrations are high in stream waters due to F-rich Proterozoic granites (De Vos et al., 2006), and even larger parts of Sweden and Finland where groundwater fluoride levels frequently exceed the guideline value of 1.5 mg/L set by the WHO (Forsman, 1974; Lahermo and Backman, 2000; Selinus, 2010; WHO, 2011).

Although there is a general knowledge of fluoride abundance and main source (bedrock) in natural waters in Sweden and Finland, there are a number of as
yet unanswered questions regarding the geochemistry and risk aspects of this anion: (i) What is the impact of landscape and morphological features on fluoride-distribution patterns in groundwater? (ii) What are the mineralogical sources of high dissolved fluoride levels in natural waters? (iii) Is there a relationship between fluoride concentrations in fresh groundwater in the Quaternary deposits (regolith) and underlying bedrock fractures? (iv) Are there temporal variations in fluoride concentrations in surface waters and groundwater? (v) Are the fluoride concentrations in Quaternary deposits equally high as in the granitoid bedrock? (vi) Does fluoride affect aqueous Al speciation and transport when both these elements and humic substances occur in high concentrations? (vii) What are the risks of an excess fluoride intake among Swedish children in households with private wells and how is the risk characterisation affected by the basis of comparison? Taken together, these questions indicate a lack of information and knowledge that would be useful for various types of environmental and health assessments.

1.1 Geochemistry of fluorine

1.1.1 Fluorine in rocks and soils

The element fluorine is widely distributed in the silicate minerals and rocks of the lithosphere. It is enriched in the late stages of crystallising magmas and, consequently, is concentrated in highly siliceous granitic and alkaline rocks and in hydrothermal mineral deposits. The estimated average abundance of fluorine in the upper continental crust is 557 mg/kg (Rudnick and Gao, 2014). When F-rich late-magmatic fluids are released from crystallising anorogenic (A-type) granites and percolate through the rock, alteration takes place in the vicinity of or within the intrusions, giving rise to greisens (Drake et al., 2009b; Friese et al., 2012; Stemprok, 1987). Greisen typically has a high concentration of fluorine (up to 2–4%), largely due to the presence of fluorite \( \text{CaF}_2 \) and topaz \( \text{Al}_2\text{SiO}_4(\text{F,OH})_2 \) (Lahermo and Backman, 2000). Fluorine occurs in the crystal lattice of minerals in the form of the univalent negatively charged fluoride ion (\( F^- \)) and can replace or be replaced by hydroxyl ions (\( \text{OH}^- \)) in many rock minerals due to the similar ion radius (Saxena and Ahmed, 2001). Common fluorine-bearing minerals are fluorite, fluorapatite \([\text{Ca}_5(\text{PO}_4)_3\text{F}]\), hornblende \([\text{(Ca},\text{Na})_{2.3}(\text{Mg},\text{Fe},\text{Al})_3(\text{Al},\text{Si})_2\text{O}_{22}(\text{OH},\text{F})_2]\), cryolite \([\text{Na}_3\text{AlF}_6]\) and micas such as biotite \([\text{K}(\text{Mg},\text{Fe})_3\text{AlSi}_3\text{O}_{10}(\text{OH},\text{F})_2]\) and muscovite \([\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH,F})_2]\) (Jayawardana et al., 2012; Li et al., 2015; Saxena and Ahmed, 2003). Fluorine is also by far the most abundant halogen in sedimentary rocks, primarily sourced from micas or clay minerals (Brun et al., 2004; De Vos et al., 2006).

Fluorine commonly occurs in soils and regolith, generally explained by the presence of fluoriferous minerals in the parent rock material. Fluoride
concentrations in soils vary widely, but are are seldom > 300 ppm (Groth III, 1975). Lahermo and Backman (2000) suggest that Finnish soils typically have < 100 ppm fluorine. However, extreme values of > 40,000 ppm have been measured in soils derived from phosphate rock (D'Alessandro et al., 2008). In addition to being found in the structure of primary minerals, fluorine can also be present through secondary enrichment, such as adsorption/desorption from a solution onto mineral or amorphous material surfaces (De Vos et al., 2006; Guo et al., 2012; Li et al., 2015; Ramdani et al., 2015). Aluminium- and iron-rich poorly crystalline phases (e.g. amorphous Al(OH)$_3$) are considered to be the most active agents causing the adsorption of fluorine by soils (Omueti and Jones, 1977; Peek and Volk, 1986). Clay minerals, which can be formed in soil through the low-temperature alteration of primary minerals, generally have high anion-exchange capacity and can retain large amounts of fluoride in soils during neutral pH conditions (Kularatne and Pitawala, 2012). In addition, fluorine can reach the soil through deposition from anthropogenic activities such as phosphorous fertilisers, coal burning, irrigation and industrial emissions (e.g. aluminium smelters, brick and glass manufacturing), as well as through volcanic emissions (D'Alessandro et al., 2008; Li et al., 2015; Mondal and Gupta, 2015).

1.1.2 Fluorine in surface waters and groundwater

Unpolluted, fresh (i.e. low salinity) groundwater and surface waters are essential for human society as reservoirs for drinking water, irrigation, various industrial processes and so forth. The chemical composition of natural waters is dependent on factors such as geology (the weathering of minerals present in soil and bedrock), hydrology (e.g. residence time, water mixing), and climate (evapotranspiration/precipitation, including atmospheric deposition) (Ayoob and Gupta, 2006; Gray, 2008). Fluorine is a natural component of all natural waters and occurs in the form of the dissolved univalent anion fluoride, $F^-$, either uncomplexed or complexed with inorganic and/or organic ligands (Deng et al., 2011).

Around the world, fluoride levels in precipitation are generally within the range of 0.05–0.20 mg/L (Lahermo and Backman, 2000). This fluoride is typically retained within the soil, or leached through the soil into aquifers in the saturated zone of the regolith. In surface waters and subsurface waters of the vadose (unsaturated) zone, the fluoride concentrations are also generally low, commonly around 0.1 mg/L. This low concentration is explained by the short residence time and by dilution via overland flow and infiltrating precipitation/snowmelt (De Vos et al., 2006). The source of the fluoride in these water types is typically geochemical processes in the soil, but may also include fluoride-bearing waters discharged from underlying fracture systems. During baseflow, which is frequent in winter and during dry summers, enhanced levels of weathering products, including fluoride, may enter into
streams. In addition, organic acids have been suggested as a control for fluoride leaching from soil minerals (biotite) into waters (Kularatne and Pitawala, 2012). Overall, intense weathering of fluorine-bearing minerals is the main source for easily leachable fluoride in soils and ultimately for the fluoride dissolved in shallow groundwater (Jayawardana et al., 2012).

In bedrock groundwater, the fluoride levels are highly dependent on the chemical composition and physical properties of the bedrock itself, the secondary fracture minerals and the Quaternary deposits. Fluoride gradually dissolves from F-rich minerals and thus becomes one of the main trace elements in groundwater (Saxena and Ahmed, 2001). In deep groundwater, which is characterised by higher pH and low dissolved aluminium, fluoride is expected to be present as the free anion, or to a varying extent depending on the mineralization of the waters, complexed with ligand cations such as Ca$^{2+}$ and Mg$^{2+}$. Saturation with respect to fluorite (CaF$_2$) and, thus, the availability of free Ca$^{2+}$, is an important control limiting the amount of dissolved fluoride in natural waters (Battaleb-Looie et al., 2012; Chae et al., 2006). Fluoride-rich groundwater is frequently associated with alkaline NaHCO$_3$ groundwater with low calcium, favouring fluorite undersaturation and cation exchange with hydroxide ions on mineral surfaces (Ayenew, 2008; Saxena and Ahmed, 2003). Geothermal waters (especially those with high pH) are also rich in fluoride (Deng et al., 2011; Edmunds and Smedley, 1996).

### 1.2 Environmental effects of fluoride

#### 1.2.1 Intake of fluoride and human health

Fluorine is one of the natural elements of greatest health concern according to the WHO (WHO, 2008; 2011). Endemic fluorosis is a widespread health problem in many developing countries or regions where there is a lack of infrastructure to mitigate the impact of high fluoride concentrations in drinking waters. As an example, more than 41 million people in 1,325 different counties in China suffer from dental and skeletal fluorosis (Li et al., 2014 who cite the Ministry of Health of China, 2010). The intake of dissolved fluoride is beneficial in trace amounts and the positive effects in terms of a reduction in dental caries are well known (Featherstone, 1999; Petersen and Lennon, 2004).

However, being a strong calcium-seeking element fluorine has the potential to interfere with all skeletal tissues in the body; and as the dose increases there is an increased risk of negative effects. Fluoride displaces hydroxide ions from hydroxyapatite, Ca$_5$(PO$_4$)$_3$OH, the principal mineral constituent of teeth (particularly enamel) and bones, to form less-soluble fluorapatite, Ca$_5$(PO$_4$)$_3$F. Fluorapatite strengthens the tissue, which gradually becomes denser, harder
and more brittle, causing mottling and embrittlement, a condition known as fluorosis (Mohapatra et al., 2009). Dental fluorosis (Figure 2) is diagnosed either by using the six-graded scale of Dean’s Index (Dean, 1934; 1942) or by more recently developed classifications such as the nine-graded Thylstrup-Fejerskov Index (Thylstrup and Fejerskov, 1978), from normal enamel to severe dental fluorosis. At higher concentrations, severe skeletal damage (such as skeletal fluorosis) and possibly even skeletal cancer and neurotoxicological effects can occur (Bassin et al., 2006; Choi et al., 2012; Hamilton, 1992). In a recent study, Grandjean and Landrigan (2014) referred to fluoride as one of eleven identified developmental neurotoxicants, alongside elements such as arsenic, lead and manganese.

The most common risk management strategy for local authorities is to monitor the fluoride concentration in public drinking water, as this is commonly assumed to be the predominant source of fluoride exposure. However, it is well established that only a narrow margin exists between beneficial and detrimental fluoride intake, meaning that guideline values are hard to estimate. The WHO drinking water guideline value for fluoride is 1.5 mg/L; the same guideline is found in the European Drinking Water Directive (98/83/EC), which is implemented in Swedish legislation. Before this guideline value was set, the commonly recommended maximum concentration was instead 1.0 mg/L, based on an extensive study by Dean et al. (1942), which showed that the severity of fluorosis increased linearly above 1 mg/L on a logarithmic concentration scale, but that even at 1.0 mg/L, a significant proportion of children (between ca. 10–20%) suffered from mild dental fluorosis. The US Environmental Protection Agency (EPA) also provides a toxicological reference value for daily intake – the 0.06 mg/kg-day reference dose (RfD) of the Integrated Risk Information System (IRIS) database. Both these reference values are further discussed in Paper V. In its scientific summary provided for fluoride, WHO highlights the inconsistencies in the different epidemiological estimates of threshold levels in drinking water (WHO, 2002). The organisation further points out that there are few studies that assess the total daily fluoride intake from multiple exposure pathways. Several studies have characterised the risk of excess fluoride intake based solely on water intake (Clark, 1994; Dean, 1942; Fordyce et al., 2007; Indermitte et al., 2009; Rango et al., 2012; Shulman et al., 1995), and some have described the risk from other isolated sources or a combination of a few sources, such as drinking water, fluoridated dental products, infant formula, food and beverages (Chavoshi et al., 2011; Jackson et al., 2002; Jha et al., 2011; Levy, 1994; Riordan and Banks, 1991; Tabari et al., 2000). Erdal and Buchanan (2005) estimate the cumulative intake of fluoride from all significant sources and show that the intake of drinking water is not necessarily the major exposure pathway for fluoride.
1.2.2 Toxicological role of fluoride in acidic surface waters

Modelling work has suggested that fluoride can potentially be important in controlling the abundance and speciation of monomeric aluminium in surface waters (Sjöstedt et al., 2010). Laboratory experiments also point in this direction; that is, it has been demonstrated that increased fluoride pollution increases the mobilisation and leaching of aluminium in acid soils (Harrington et al., 2003; Moore and Ritchie, 1988) and that increasing fluoride concentrations below pH 7.5 cause an increase of dissolved aluminium in water (Wang et al., 2010). The exposure of dissolved inorganic aluminium in acidic water has toxicological implications and can cause unfavourable conditions for biota, such as increased mortality and avoidance behaviour of spawning fish in freshwaters (Andrén and Rydin, 2012; Appelberg et al., 1993; Exley, 2000; Grassie et al., 2013; Poleo and Muniz, 1993; Poleo et al., 1997). In addition, according to Strunecká and Patocka (2002), the synergistic action of aluminium-fluoride complexes in water and in the food chain causes various diseases affecting metabolism, growing processes and homeostasis in living organisms.

In northern Europe (Norway, Sweden, Finland), stream waters are characterised by overall low pH values, due to the widespread occurrence of organic soils and the low acid-neutralising capacity of the soils and regolith (Laudon et al., 2001). In this region, aluminium concentrations are typically elevated (Salminen et al., 2005) because of the well-known fact that aluminium solubility and mobilisation are enhanced under acidic conditions (Gensemer and Playle, 1999). Therefore, in the parts of this region where fluoride concentrations are locally or regionally elevated, fluoride has the potential to significantly affect aluminium geochemistry.

1.3 A Swedish perspective on fluoride

Although the fluoride level in natural waters in Sweden is generally low, several regions in the country have naturally elevated fluoride concentrations. These high concentrations are typically associated with igneous rocks consisting of Proterozoic granites and pegmatites carrying F-bearing minerals such as fluorite and fluorapatite (Lahermo and Bäckman, 2000; Selinus, 2010). Figure 3 visualises fluoride levels in drinking water that is extracted from drilled bedrock wells. Regions with fluoride levels that are above 1.5 mg/L are found throughout the country, including the coastal regions of Kalmar County, the focus of this thesis. Approximately 25 % of all private wells (> 11,000) that are drilled into bedrock and included in the Groundwater Chemistry Archive database, owned and managed by the Swedish Geological Survey, have fluoride concentrations exceeding 1.5 mg/L (SGU, 2013). Stream waters in southern Sweden can also exhibit very high concentrations
(in the context of surface waters) of fluoride (Salminen et al., 2005). De Vos et al. (2006) speculate whether this finding could be partly due to the existence of aluminium- and iron complexes. The incidence of dental fluorosis in three small communities in the Kalmar County and Scania was documented in detail by Forsman (1974). She showed that in districts with fluoride levels ~5 mg/L, 50% of the individuals examined had mild dental fluorosis while 28% had moderate to severe dental fluorosis in their permanent teeth. Fluorosis in primary dentition was milder but only 20% of individuals were completely free from fluorosis. In districts with fluoride levels ~10 mg/L, moderate to severe dental fluorosis occurred in all permanent teeth and in most of the primary teeth in all individuals. Nõmmik (1953) made an important introductory contribution to the study of fluoride in Swedish agricultural products, soil and drinking water. Like Forsman, Nõmmik also highlighted the elevated fluoride concentrations in the coastal parts of Kalmar County, which are more deeply focused on in the work of this thesis.
Figure 2. Drinking water exhibiting high fluoride concentrations causes dental fluorosis. Teeth of an 18-year-old male living in a household with a private well in Kalmar County. Published with the kind permission of the Public Dental Service, Kalmar County Council.

Figure 3. Fluoride in drilled bedrock wells (n = 17,484) in Sweden (source: Swedish Geological Survey). The map shows regions with general occurrence of low (< 0.8), medium (0.8–1.5) and high (> 1.5) fluoride concentrations. Modified from Selinus (2010), reprinted with the kind permission of ©Studentlitteratur.
2. AIMS

This thesis focuses on an area in southeast Sweden that is underlain with rocks of the Transscandinavian Igneous Belt (TIB) and an anorogenic F-rich granite pluton (the “Götemar granite”, approximately 5 km in diameter”). The overall aims of this thesis were:

• To determine and explore the levels and temporal variability in fluoride concentrations in stream waters, in groundwater in Quaternary deposits (regolith) and in fresh groundwater in bedrock fractures;

• To determine and explore fluoride concentrations and solid-phase speciation in Quaternary deposits, including till, sorted sediments (gravel, sand, silt/clay) and organic soil types;

• To assess the geological and mineralogical sources and controls of fluoride in stream waters and in groundwater in regolith and bedrock fractures;

• To model the impact of high dissolved fluoride concentrations on aqueous aluminium speciation; and

• To calculate and model to what extent overconsumption of this potentially toxic element occurs in the children of Kalmar County living in households with private wells and to compare the results obtained using two different kind of reference values (drinking water criteria and total tolerable daily intake).
3. SETTING

The work was conducted in southeast Sweden within the County of Kalmar, which is located in the eastern part of the province of Småland (Figure 4). All the data used in Papers I–IV was collected in the Laxemar-Simpevarp area, which is located between the cities of Västervik and Oskarshamn in the northernmost part of the county (along the mainland coast approximately 250 km south of Stockholm). In this region, the bedrock is dominated by crystalline igneous rock (granitoids). Paper V was based on data from the whole of Kalmar County, including the island of Öland (which primarily consists of sedimentary limestone).

Figure 4. Location of the study area. The catchment areas of the Kärrsvik (upper), Ekerum (middle) and Laxemar (lower) streams in the northern part of Kalmar County are indicated (in text, this is referred to as the “Laxemar-Simpevarp area”). The bedrock around the Götemar granite consists of TIB rocks. The Götemar granite has a near circular shape when cropping out at the ground surface, where it has a diameter of approximately 5 km, but with a greater extent in the subsurface (“punched laccolith”) (Cruden, 2008).
The Laxemar-Simpevarp area have been thoroughly investigated by the Swedish Nuclear Fuel and Waste Management Company (SKB) as part of their site characterisation programme, which had the objective of siting a deep geological repository for spent nuclear fuel. The programme included hydrogeochemical and hydrogeological characterisation, geological mapping and a variety of modeling work (Laaksoharju et al., 2008). Below is a brief summary of some of the main features of the area.

Coniferous and mixed forests cover a large part of the area. In valleys, however, arable land is common. The annual mean temperature is 6.4°C and the annual precipitation generally reaches a total of 600–700 mm (Werner et al., 2006). Wetlands cover only 1% of the area, and lakes and streams are small and shallow, characterised as mesotrophic brown-water systems (Nordén et al., 2008; Söderbäck and Lindborg, 2009). These streams (Figure 4) have strong seasonal variations in water flow, due to snowmelt during the spring flood and to periods of rainfall mainly during the summer and from late autumn to mid-winter.

The bedrock is dominated by 1.8 Ga granites and quartz monzodiorites belonging to the TIB (Wahlgren et al., 2004; 2008). The TIB rocks are dominated by plagioclase, quartz, K-feldspar, and biotite, and have fluorine concentrations of approximately 0.11–0.13 wt% (Drake and Tullborg, 2009b). The main F-bearing mineral is biotite (8–18 vol%). In the northern part of the area, as indicated in Figure 4, the 1.45 Ga granite intrusion referred to as the “Götemar granite” crops out (Friese et al., 2012; Kresten and Chyssler, 1976). The fluorine concentration in the Götemar granite is high, ranging from 0.38–0.54 wt% (Alm and Sundblad, 2002; Alm et al., 2005; Kresten and Chyssler, 1976). The F-bearing minerals in the Götemar granite are biotite and muscovite, which both occur at < 5 vol%, as well as fluorite, topaz, and apatite. Greisen alteration occurs locally in the immediate surroundings of the Götemar granite (Kresten and Chyssler, 1976), and is also found in fractures penetrated by sub-vertical boreholes (down to 600–700 m) at greater distances from the granite (Drake et al., 2009b). This fracture-related greisen has abundant fluorite, muscovite, quartz, pyrite, and topaz.

A number of fracture zones intersect the bedrock in several directions (mainly northwest to southeast, coinciding with the valleys). The most common F-bearing fracture mineral in the TIB-rocks and the Götemar granite is fluorite (Drake and Tullborg, 2006; 2009b). In addition, fluorite occurs as a cement in the Cambrian sandstone found in near-surface fractures in the Götemar granite (Alm and Sundblad, 2002; Drake and Tullborg, 2006; Kresten and Chyssler, 1976; Röshoff and Cosgrove, 2002).
During the Quaternary, several glaciations influenced the area. Ice sculptured
the bedrock surface and removed weathered surface layers. The present
surface was therefore influenced by mechanical erosion and low-temperature
chemical weathering during the Weichselian and the current inter-glacial
period. A characteristic geological feature of the area is a large quantity of
exposed bedrock (or bedrock under a very thin soil, i.e. Leptosol), located
mainly in coniferous forests in the drier, upslope areas (Figure 5). Elsewhere
there are Quaternary deposits of variable thickness, which formed during the
last Pleistocene glaciation and in the Holocene. These deposits include till
(frequently of a sandy nature), glaciofluvial sediments (two prominent eskers
in a NW-SE direction within the Kärrsvik catchment), glacial and postglacial
fine-grained (clay/silt) sediments (containing varying amounts of organic
matter), postglacial sand and gravel, and peat (Figure 5). In the downslope
areas, where the stream tributaries flow, the Quaternary deposits are as
thickest. Histosols (peat) or Gleysols have developed and the land use is
mixed/coniferous forests and arable land. Between the wet (downslope) and
dry (upslope) sites, Umbrisols, Podzols and Regosols occur (Lundin et al.,
2005; Sohlenius and Hedenström, 2008).
Figure 5. Location and distribution of exposed bedrock (or bedrock under a thin soil layer) and Quaternary deposits at a depth of 0.5 m at the study site (the Kärrsvik stream catchment) in southeast Sweden along the Baltic Sea coastline. The Götemar granite pluton is indicated by the circular area to the right (black line). Elsewhere, the bedrock is dominated by granites and quartz monzodiorites of the Transscandinavian Igneous Belt. The map is based on data from the Swedish Nuclear Fuel and Waste Management Co. (Rudmark et al., 2005; Sohlenius and Hedenström, 2008). Profiles through the Quaternary deposits sampled in this study across the catchment are indicated by Id and filled white circles.
4. MATERIAL AND METHODS

4.1 Sampling and sample treatment

The thesis work is based on the analyses and evaluation of different kinds of materials that have been either collected by the author with the help of co-workers (primary data, 4.1.1), or have been made available by an external organisation or authority (secondary data, 4.1.2–4) and explored within the context of these specific studies (Figure 6).
4.1.1 Sampling of surface waters, Quaternary deposits and rock materials

Samplings of stream water in tributaries and other surface waters (i.e. temporary water bodies, bogs, water-filled quarries; Figure 7c, and lake water) within the Kärrsvik catchment area were carried out. A total number of 37 sites were sampled during high flow (300 L/s) conditions in March 2009, and 17 sites were sampled during low flow (10 L/s) conditions in September 2009. The stream water discharge on these occasions was measured with a FP201 Global Flow Probe. Water was filtered through 0.45 μm filters (to exclude particles) and collected in 250 mL polypropylene bottles for measurements of fluoride, pH and electrical conductivity (always within 24 h) in the laboratory at Linnaeus University in Kalmar. This data was further explored as a part of Paper I.

From October to November 2012 and in February 2015, 18 vertical profiles varying in depth from < 1 m to 5 m were sampled from three main areas of the Kärrsvik catchment – the upper reaches (5 profiles), upon the Götemar granite (6 profiles) and the lower reaches (7 profiles) (Figure 5 and 8a) – by manual digging (shallow profiles) or auger drilling. The aim of the sampling was to cover a variety of Quaternary deposits and soil types across the catchment area. Twelve sampling sites were located in a mixed forested landscape and six on arable land in the vicinity of the main stem of the Kärrsvik stream. Subsamples from each profile were collected in the field based on the occurrence of different soil types; in shallow profiles, any visible soil horizons were also sampled. This collection gave a total of 106 subsamples. The subsamples were stored under dark and cold conditions (7.4°C) prior to further handling. Each subsample (500–2,000 g) was oven-dried (60°C), sieved through a 2-mm sieve and thoroughly mixed. For four subsamples, the routine sample (< 2 mm) was split into two size fractions (< 63 μm and 63 μm to 2 mm) for more detailed descriptions, yielding a total number of 114 subsamples. All subsamples were then pulverised in a ball mill prior to further analyses. A portion of each of two non-pulverised subsamples (< 2 mm), a gyttja (KV01_4) and a glacial clay (KV01_10), was mounted in epoxy and then polished in order to obtain a flat surface for energy dispersive spectrometry (EDS) analyses at the Earth Sciences Centre, University of Gothenburg. These 114 subsamples formed the basis for Paper III. A collection of rock samples for further analyses (see 4.2.3) was made from drill cores that had been previously collected and stored by the SKB (see 4.1.2 for more information).
4.1.2 Swedish Nuclear Fuel and Waste Management Company (SKB)

The Site Characterisation Database (SICADA), which is owned, quality-checked, and supervised by the SKB, played a central role in this work, providing spatial and temporal analytical data from a number of materials in the study area: stream waters, regolith groundwater in wells, fracture groundwater in boreholes and drill cores (e.g. Smellie and Tullborg, 2009). This data was initially collected as part of the SKB site investigations from 2002–2009 in Laxemar-Simpevarp with the objective of siting a deep geological repository for spent nuclear fuel (Laaksoharju et al., 2008; SKB, 2009). After the site investigations were finished, monitoring of a number of selected wells and boreholes continued via the hydrogeochemical monitoring programme at the Åspö Hard Rock laboratory. Thanks to Nova FoU (research and development), a collaborative initiative between the municipality of Oskarshamn and the SKB, the database containing all this data (SICADA) is available for scientific research. For this particular thesis, the database was available through the Nova FoU project “Fluorine in surface and groundwaters”. I myself worked part time at the Åspö Hard Rock Laboratory during part of my PhD studies (2011–2012), taking part in the planning and implementation of the hydrogeochemical monitoring programme. This work included field procedures when sampling surface waters and regolith and fracture groundwaters in the Laxemar-Simpevarp area. Although I participated in the work, I treat this data as secondary data here, along with all the data obtained from SICADA that was collected during the site investigations.

Stream water samples were collected monthly (some variables were analysed every second to fourth month) in the main stem of three catchments included in this thesis – Kärrsvik (Papers I–II), Ekerum (Paper II) and Laxemar (Paper II) – following conventional methods as further described in Ericsson and Engdahl (2004). Sampling was performed close to the stream outlets. In the Kärrsvik stream, two sampling points further upstream in the catchment were also included in the dataset. Water-discharge values used in the studies were logged hourly from automatic runoff stations close to the outlet of each stream. Information on the installation of the stations and the measurements is presented in Sjögren et al. (2007).

Regolith groundwater was collected from wells drilled into the terrestrial regolith (Quaternary deposits) overlying the granitoids. Paper I presents data from two wells and Paper IV presents data from 30 wells. The well installations were performed by auger or air-rotary drilling (Ø: 82–90 mm) and the placement of PEH screens (Ø: 63 mm, length: 1–2 m, slot: 0.3 mm) and PEH casings (Ø: 63/50 mm) of different lengths. Filter sand (0.4–0.8 mm) and bentonite clay (Volclay SG40) were filled outside the well while the drill
casing was pulled out. All wells (except eight that were slightly shorter) reached to or just above the bedrock surface. Groundwater was then allowed to enter through the screen, which was adjusted to the depth of the lower end of the well. More information on the installation of wells is presented by Johansson and Adestam (2004a; 2004b). The thickness of the Quaternary deposits was typically less than 10 m; however, they had a min/max depth of 1.4/18.6 m that was characterised in the field. The data used in Paper IV included wells sampled 1–37 (median 5) times during 2004–2012, yielding a total number of 240 observations. The water table was monitored every second hour for more than three years in 20 wells, instrumented with automatic pressure transducers/loggers. An underwater pump (type 12 V Avimex) was used and the water volume of the well was exchanged three times before water sampling was initiated.

Fracture groundwater was collected by regulated pumping from the ground surface using equipment designed for the retrieval of representative groundwater from controlled depths in boreholes. The fracture groundwater presented in this thesis (Paper IV) includes samples representative of 21 individual packed-off sections (length generally \( \leq 20 \) m) and 34 tube units (50 m) along the borehole, with a depth range from 24 m to approximately \( \sim 700 \) m relative to sea level. The principles and routines of sampling from packed-off sections are outlined by Mathurin et al. (2014; 2012), and the sampling equipment and method of hydrochemical logging based on tube units are described by, for example, Lindquist (2007) and Berg and Nilsson (2006). The hydrochemical dataset used is composed of groundwater samples with Cl– concentrations \( \leq 350 \) mg/L and \( \delta^{18}O \) values between –13 and –10 %o versus standard mean ocean water (SMOW). This dataset corresponds with the values of the sampled regolith groundwaters (i.e. brackish to saline fracture groundwaters were excluded), an acceptable charge balance (within the range \( \pm 5 \) %) and a low proportion of drilling water (\( < 5 \) %). Several of the packed-off sections were hydrochemically monitored over time (a week to years).

Water was filtered through 0.45 \( \mu \)m filters (to exclude particles) and collected in 250 mL polypropylene bottles for measurements of pH, electrical conductivity, alkalinity, anion concentrations and levels of dissolved organic carbon (DOC), and in 125 mL acid-washed bottles prepared with 0.8 % Suprapur™ HNO₃ (65 %) for measurements of cation concentrations. For the measurement of total organic carbon (TOC) and oxygen isotopes (\( {^{18}O/{^{16}O}} \)), unfiltered water samples were collected in 250 and 100 mL plastic bottles, respectively.

The mapping of secondary minerals in fractures was carried out routinely by onsite geologists following the drilling of each borehole in 2003–2008, and this data was used in Paper IV. Open, partly open and sealed fractures were
mapped, and up to four minerals for each fracture were identified by visual (hand lens) inspection. For the TIB rocks in the Laxemar area, the total number of fractures mapped was approximately 101,000 (including fractures within deformation zones), of which 67 % were sealed fractures and 33 % were open fractures, from a total length of 19 km of drilled boreholes (about 17 km of drill cores) from 45 boreholes (Drake et al., 2009b). The drill cores cover the upper 1 km of the bedrock.

4.1.3 Kalmar County Council

Data on fluoride concentrations in 4,802 private groundwater wells (one analysis per well) sampled between 1978 and 2007 in Kalmar County was received from the Kalmar County Council (Paper V). About 10–30 % of the residents in this region extract their water from private wells (the exact figure varies between municipalities), and thus lack systematic monitoring of their water quality. During the sampling period, every household in the county with a private well and a new-born child was offered a fluoride analysis for free. The sampled wells hence constitute only a part of the total number of private wells in the county. The long sampling interval may introduce some uncertainty as to whether this data is fully representative of current private water supplies, but although the proportion of the population with private wells has decreased since 1978, there is little to suggest that the water quality has improved significantly for those who still use private wells. Therefore, the available data can still provide an answer to how the fluoride concentration is distributed in the groundwater in this region, and what the chance is of a randomly chosen well having a concentration above a certain level. A larger uncertainty may be associated with the samples being collected by different people and analysed at different laboratories over a rather long period of time. However, the uncertainties in reported results are most critical at low concentrations, where the risk of an excess fluoride intake from water consumption is low.

4.1.4 Swedish Geological Survey

Fluoride concentrations in groundwater extracted from wells and used for drinking water within the study area were retrieved from the Groundwater Chemistry Archive (sampled mainly from 1970–2000) and the Monitoring Project database (sampled from 2007–2009), which are owned by the Geological Survey of Sweden (more information is given in Pousette 1988). The wells were sampled once. The data was divided into regolith groundwater (excavated wells, n = 12, depth 1.1–6.5 m below ground level) and fracture groundwater (wells drilled into the bedrock, n = 9, depth 16–81 m below ground level). In addition, mineral-mapping data was retrieved from three cored boreholes drilled to a depth of 600 m in the Götemar granite in the 1970s. This mapping data is used as a complement to the SKB data in the spatial analyses (Papers I and IV).
Figure 7. Examples of environments sampled for surface and groundwater chemistry, illustrated by (a) the Kärrsvik stream; (b) a regolith groundwater well; and (c) the abandoned, water-filled Götebo quarry, previously used for extraction of reddish Götemar granite. The levels of fluoride in the quarry are up to 3.8 mg/L. (Photo (b) by Lars Andersson, SKB.)
Figure 8. Examples of sampled and analysed solid materials, illustrated by (a) a soil profile within the Kärrsvik catchment; (b) precipitated secondary fluorite on a fracture wall in a Götemar granite quarry; (c) a drill core from TIB rock (Ävrö granite) showing an open fracture coated with secondary fluorite (faint purple), and (d) a back-scattered scanning electron microscopy (SEM) image showing partial dissolution of secondary fluorite crystals (cubical) on an open fracture wall in the Götemar granite (KKR02). Dark crystals are quartz surrounded by chlorite/clay minerals. (Photos (c)–(d) by Henrik Drake.)
4.2 Analytical methods

4.2.1 Water chemistry (primary data)

Fluoride was determined in 54 samples with an ion-selective electrode (ISE) (model ORION 96-09-00) after the addition of a total ionic strength adjustment buffer (TISAB) to complex aluminium and iron (which are strong complexing ligands with fluoride) in order to keep dissolved fluoride as free measureable $\text{F}^-$ in the solution.

4.2.2 Water chemistry (secondary data)

Most of the data on water chemistry utilised for this thesis was obtained as secondary data from the SICADA database. The pH values of the sampled waters were determined with a potentiometer, their electrical conductivity with a Conductivity Meter CDM230 and their alkalinity via titration within 24 h of sampling. Chloride, fluoride and sulphate concentrations were determined by ion chromatography (IC 882, Metrohm), or, for fluoride, by potentiometry (ISE and the addition of TISAB) if the concentration was below 0.5 mg/L. Analyses were carried out at the SKB lab facility (ISO/IEC 17025 accredited) at the Åspö Hard Rock Laboratory in Oskarshamn, Sweden. The $\delta^{18}$O/$\delta^{16}$O ratio of collected groundwater samples was determined by conventional isotope ratio mass spectrometry techniques at the Institute for Energy Technology (Kjeller, Norway). The ratios of these isotopes are reported by the $\delta$ NOTATION per million as a deviation from SMOW. The analytical uncertainty on this $\delta^{18}$O was $\pm 0.1$ unit ($\%$ vs. SMOW) from the measured $\delta$ value. The concentrations of TOC and DOC were determined through combustion catalytic oxidation using a carbon analyser (TOC-5000, Shimadzu) at Ramboll Analytics, Vantaa, Finland or at the former Department of Systems Ecology (current Department of Ecology, Environment and Plant Sciences), Stockholm University, Sweden. Cations included in this thesis were analysed by inductively coupled plasma - atomic emission spectroscopy/sector field mass spectrometry (ICP-AES/SEMS) at ALS Scandinavia, Luleå, Sweden. Fluoride concentrations retrieved from the Kalmar County Council and the Swedish Geological Survey were determined in water samples analysed either by potentiometry (ISE) or ion chromatography at different accredited Swedish laboratories.

4.2.3 Minerals in the bedrock (primary data)

Scanning electron microscopy (SEM) was utilised for the identification and mapping of secondary minerals in 196 open fractures and for the presence and concentration of fluorine in minerals of the TIB rocks (granodiorite, monzodiorite), greisen, Götemar granite and secondary bastnäs site in fractures (Paper IV). SEM uses a focussed electron beam that interacts with the atoms in the sample, producing various signals that can be detected and that contain
information about the sample surface topography (by secondary electrons) and chemical composition (back-scatter electrons). The analyses were performed on a Hitachi S-3400N equipped with an Oxford Instrument Energy Dispersive Spectrometer (for qualitative mineral determination and semi-qualitative SEM-EDS analyses of major and minor elements) and an integrated wavelength dispersive spectrometer (SEM-WDS, for fluorine concentrations), at the Earth Sciences Centre, University of Gothenburg. Calibration was carried out at least twice every hour using a cobalt standard linked to simple oxide and mineral standards, to confirm that the instrument drift was acceptable. X-ray spectrometric corrections were made by an online computer system (INCA).

4.2.4 Quaternary deposits (primary data)

All the subsamples were analysed for Loss on ignition (LOI) by ashing at 500° at Activation Laboratories Ltd., Ontario, Canada. The pH was measured with a pre-calibrated pH probe using a soil/solution weight ratio of 1:5 (5g soil mixed with 25 ml water).

F-bearing mineral phases in a subsample (< 2 mm fractions) of gyttja (KV01_4) and glacial clay (KV01_10) were searched for with a Hitachi S-3400N scanning electron microscope equipped with an Oxford Instruments energy dispersive spectrometer (SEM-EDS) at the Earth Sciences Centre, University of Gothenburg. To obtain a flat surface for the EDS analyses, a portion of each of these samples was mounted in epoxy and then polished. The epoxy mounts were coated with carbon for electron conductivity. Calibration was carried out as described above. Spot size was ~5 μm and the detection limit for fluorine was about 0.3 wt%.

Fluorine concentrations were determined at Activation Laboratories Ltd., Ontario, Canada (ISO/IEC 17025 accredited). The methods are summarised below. Total fluorine concentrations were obtained through fusion with a combination of lithium metaborate and lithium tetraborate in an induction furnace (in samples not leached by sequential chemical extraction, SCE). The fuseate was then dissolved in dilute nitric acid and, prior to the analysis, the solution was complexed and the ionic strength adjusted with an ammonium citrate buffer (TISAB). An automated fluoride analyser (ISE) from Mandel Scientific was used for the analysis, with the limit of detection being 10 ppm.

In total, 32 subsamples (from 10 profiles) with moderate to high fluorine concentrations were applied to a sequential chemical extraction (SCE) analysis. For four of these subsamples (one gyttja and three till), < 63μm and 63 μm to 2 mm fractions were analysed, yielding a total number of 36 samples for analyses. The subsamples were shaken in 1 M sodium acetate (NaAc) adjusted to pH 5 for two hours at room temperature. Thereafter, 23 of the
subsamples were extracted with an 8.9% sodium pyrophosphate (NaPp) solution (pH 9.5–10.5) for one hour at room temperature. The 23 subsamples included in the NaPp step along with the other 13 subsamples were then extracted with an 8.2% hydroxylamine hydrochloride (HaHc) solution for two hours at 60°C. Finally, fluorine was extracted from the residue in a manner similar as the total concentrations were determined. After each of the SCE steps, the remaining material was rinsed with deionized water. The fluorine concentrations in each step were determined by mixing 1 mL of leach solution and 20 mL of TISAB overnight for complexation and then ran on ISE. The total fluorine concentrations (F_{tot}) in these samples were calculated by adding the fluorine concentrations determined in each step. These calculated values were in general similar to the measured total concentrations.

The NaAc step targets water-soluble and exchangeable phases and dissolves carbonates (Tessier et al., 1979), the NaPp step dissolve labile organic material (humic and fulvic acids) (Hall, 1998; Hall et al., 1996) and the HaHc dissolve amorphous and crystalline Fe and Mn oxides and acid-soluble (e.g., Al oxyhydroxides) phases (Virtanen et al., 2013). As fluoride is an anion whose behavior during extraction with NaAc, NaPp and HaHc has not been systematically investigated, the results of the SCE should be interpreted with caution and seen as indicative. In several previous studies acid oxalate has been used to quantify the fraction of fluorine bound to poorly crystalline Al/Fe mineral phases (Begin and Fortin, 2003; D’Alessandro et al., 2008). Here we instead used HaHc, which, as shown in previous studies (Chi et al., 2008; Ross et al., 1985; Wang et al., 1987), targets the same mineral phases as acid oxalate.

The mineralogy was analysed by quantitative X-ray diffraction (XRD) at two laboratories.

1) At Activation Laboratories Ltd., Ontario, Canada, quantitative X-ray diffraction (XRD) was performed on six routine subsamples (< 2 mm) and on the < 63 μm and 63 μm-2 mm fractions of another four subsamples (one gyttja and three till), yielding a total number of 14 analysed subsamples. Semi-quantitative clay speciation was carried out for three of the subsamples, a gravelly sandy till (KV02_8A, i.e. < 63 μm), a glacial clay (KV14_6, < 2 mm) and a gyttja clay (KV12_1, < 2 mm). For clay speciation analysis, a portion of each subsample was dispersed in distilled water allowing clay particles (< 2 μm) to be separated from larger particles by gravity settling. Oriented slides of the < 2 μm size fraction were prepared. In order to identify expandable clay minerals, the oriented slides were air-dry analysed, after saturation with ethylene glycol and after heating at 375°C. The XRD analysis was performed on a Panalytical X’Pert Pro diffractometer equipped with Cu X-ray source and an X’Celerator detector. Intensities were measured at 20 from 2° to 70°.
(random specimens) and from 3° to 30° (oriented specimens) in steps of 0.017 using a 50 s counting time per step. The X’Pert HighScore Plus software along with the PDF4/Minerals ICDD database were used for mineral identification. The percentages of the crystalline mineral phases were determined using the Rietveld method, which utilises a known percent of corundum as an internal standard. Accordingly, the percentage that could not be accounted for by the crystalline phases was considered as poorly-crystalline/amorphous materials and include Fe/Al/Mn oxides/hydroxides, clays that are not crystalline such as allophone and imogolite, poorly crystalline smectite, amorphous silica and organic matter. The semi-quantitative amounts of clay minerals in the < 2 μm size fraction were calculated using ratios of basal-peak areas.

(2) At Äspö Hard Rock Laboratory in Oskarshamn, Sweden, eleven other subsamples (< 2 mm) were analysed. Randomly oriented samples were prepared by backfilling the sample holders. Measurement was done in reflection mode (theta-theta) using a Panalytical X’Pert Pro diffractometer equipped with Co broad focus X-ray source and a PIXcel1D line detector, operating at 45 kV and 50 mA. The interval 4-120° was measured in 1h, programmable divergence slit was used with an irradiated length of 8.5mm. Sample rotation was done at 1 revolution /sec. A 0.016 mm beta-filter of iron was used to decrease the Co k-beta radiation. No monochromator was used to increase the X-ray intensity. Soller slits of 0.04 rad and a fixed incident beam mask of 20 mm was used. Evaluation of the data and quantification of phases was done by the Siroquant software (version 3).

4.3 Data analyses

4.3.1 Hydrogeochemical modelling

Geochemical computational modelling can be used to determine the speciation of dissolved elements in natural waters (Merkel et al., 2008). In this thesis (Paper II), the Windows freeware chemical equilibrium model Visual MINTEQ v3.0, beta (Gustafsson, 2012) was applied to secondary SICADA data on stream water chemistry (from Kärsvik, Ekerum and Laxemar streams) in order to define the speciation of fluoride and aluminium according to an approach developed by Sjöstedt et al. (2010) and recently applied by Köhler et al. (2014). For inorganic complexes, the thermodynamic default database in this program was used; this database is mostly based on the National Institute of Standards and Technology (NIST) compilation (Smith et al., 2003). Input data to the model included a wide range of measured stream water variables: pH, temperature, DOC, alkalinity (as HCO₃⁻) and concentrations of Al, Ca, Fe, K, Li, Mn, Mg, Na, Si, Sr, Cl, F⁻ and SO₄²⁻. Equilibrium constants were corrected for temperature and ionic strength by use of the van’t Hoff and Davies equations, respectively. Following the approach introduced by Sjöstedt
et al. (2010), the aluminium in filtered samples (Al0.45) was allowed to precipitate when the solubility product for Al(OH)₃(s) (log * Kₛ of 8.29 at 25°C, see Appendix A of Paper II) was exceeded. The rationale for choosing this solubility product is that an Al(OH)₃(s) phase with such a solubility was previously found in the B horizons of Podzols (Gustafsson et al., 2001; 1998), a common soil type in the catchments studied here. The model thus calculates the proportion of the Al0.45 fraction occurring as Al(OH)₃(s), that is, as colloidal aluminium. The remaining aluminium was treated as being truly dissolved (Al₆). Aluminium complexation to dissolved organic matter (DOM) was modelled using the Stockholm Humic Model (SHM).

The calcite and fluorite saturation indexes (SI) of fracture groundwater and regolith groundwater were calculated with the PHREEQC geochemical code version 3.06 (Parkhurst and Appelo, 2013) by one of the co-authors (Mathurin) of Paper IV. The WATEQ4F thermodynamic database was used for the calculations (Ball and Nordstrom, 1991).

4.3.2 Exposure calculations
In Paper V, we explored the exposure to fluoride of children in households with private wells in Kalmar County, by using widely acknowledged reference values for fluoride concentrations in drinking water and tolerable daily intake (TDI) of fluoride. In order to assess the variability in exposure to fluoride probabilistically through various pathways, a probability bounds analysis (PBA) was utilised using the software RiskCalc v4.0 from Applied Biomathematics (Ferson, 2002). This analysis was carried out by the first author (Augustsson) of Paper V. In a probabilistic approach variables are given as intervals or probability distribution functions instead of as point estimates (as in deterministic methods) (Cullen and Frey, 1999; Morgan et al., 1990). Monte Carlo analysis is the most common method for probabilistic risk assessments; however, PBA is the most suitable method when a lack of data makes assumptions on the distributions of the input data variables unjustifiable (Binkowitz and Wartenberg, 2001; Bogen et al., 2009; Ferson, 2002; Lester et al., 2007; Sander et al., 2006) With PBA, instead of assuming certain probability distributions from limited data, probability boxes (p-boxes) are drawn to encompass all distributions that meet the statistics that can be determined from the available data (e.g. min, max, mean and a set of percentiles).

4.3.3 Statistical analyses
Environmental chemical data is frequently non-normal in distribution; it may be skewed and contain outliers and values below detection limits (Reimann and Filzmoser, 2000). Consequently, robust and non-parametric methods such as median values and Spearman correlations were used in the analyses in this thesis. However, when the analyses included two chemical variables (i.e.
compositional data), correlation was analysed using an isometric log-ratio transformation (Aitchison, 1982; Buccianti, 2013; Egozcue et al., 2003). The reason is that the appropriate correlation measurement between two compositional variables is the extent to which the ratio of the two variables varies across the samples. This can be expressed as the “stability of ratios” that is favourably measured with the ilr correlation coefficient (Filzmoser et al., 2010). Scatter plots, piper plots and symbol maps (growing symbols/graduating colours) were the primary tools for graphical interpretations of data in this thesis.
5. RESULTS AND DISCUSSION

5.1. Fluoride abundance and spatiotemporal variability in surface waters and groundwater

In summary of the studies presented in this thesis, the Laxemar-Simpevarp area can be recognised, both in a national and global context, as a region showing elevated fluoride concentrations in all types of natural waters.

The Kärrsvik stream runs eastwards just south of the Götemar granite, and the northeast parts of its catchment are located upon this granite (Figure 4). Its position thus makes the Kärrsvik stream particularly interesting and appropriate to investigate in terms of the impact of an F-rich granite on fluoride abundance in stream waters. Fluoride concentration in the lower reaches of the Kärrsvik stream was about one order of magnitude higher than the average fluoride concentration (0.13 mg/L) in 808 European streams (in 25 countries, including Sweden) that are included within the FOREGS Geochemical Baseline Mapping Program (Salminen et al., 2005), all of which are second order streams with < 100 km² drainage basins, comparable with the Kärrsvik catchment.

In the streams investigated in this thesis (Kärrsvik, Ekerum and Laxemar streams), fluoride showed strong flow-dependent variation with reduced transport but strongly elevated concentrations during low flow conditions, that is, during dominance of base flow (Figure 9). For example, the concentrations in Kärrsvik varied between 0.5 and 4.2 mg/L. However, during high flow events, characterised by dilution by meltwater and rainfall and hence decreasing concentrations, the flux of fluoride increased significantly. The correlation between fluoride concentrations and water flow points to a relatively large mechanistic difference between the release and leaching of fluoride from soils, which are hydrologically activated during high flow (yielding an increase in fluoride flux and a decrease in fluoride concentration), and from deeper soil/regolith layers, which are more influential during base
flow conditions (yielding a decrease in fluoride flux and an increase in fluoride concentration). On a smaller scale, Zhu et al. (2007) showed that soil can be expected to contain elevated dissolved fluoride concentrations with depth in an area where granite is the main soil-forming parent rock.

Figure 9. Variation of fluoride concentration and water flow (top) and the flux of fluoride in relation to water flow (bottom) just upstream the outlet of the Kärrsvik stream from 2004–2009. Modified from Berger et al. (2012).

Furthermore, the spatial pattern of fluoride concentrations in surface water within the Kärrsvik catchment was strongly correlated with bedrock geology, that is, with the location of the Götemar granite (Figure 10). The fluoride concentrations increased (usually by 100–200 %) towards the lower stream reaches, which are downstream of the Götemar granite, despite a catchment-wide relatively homogeneous distribution of land use and types of Quaternary deposits and soils. In addition, other surface water bodies, such as wetlands, showed clearly elevated levels upon the Götemar granite (0.23, 0.47, 0.67, 1.1 and 2.0 mg/L) compared to sites in the upper reaches (0.13, 0.16, 0.19 and 0.23 mg/L). Two abandoned and water-filled quarries located within the Götemar granite had fluoride concentrations of 2.5±2.8 and 5.3 mg/L, respectively. Inter-catchment comparisons also showed a spatial decrease from
north to south of fluoride concentrations with distance to the Götemar granite; that is, there was a decrease in the following order: Kärrsvik (median 1.1 mg/L) > Ekerum (1.0 mg/L) > Laxemar (0.48 mg/L) (Berger et al., 2015). This finding is additional evidence of the impact of the Götemar granite on fluoride concentrations in surface waters.

**Figure 10.** Fluoride concentrations (mg/L) in surface waters during high flow conditions in March 2009 (dark grey circles) and in wells in July 1976 (light grey circles). Modified from Berger et al. (2012).

In the groundwater in the Quaternary deposits (“regolith groundwater”), sampled from the deepest parts of these deposits via wells, the fluoride concentrations were stable overall within the sampling sites. This finding shows that in contrast to the stream waters, the subsurface waters deep in the Quaternary deposits have stable conditions and small or non-existent variability in fluoride concentrations. However, there was a large variability in the median fluoride concentration among the groundwater sampling sites (0.3 to 4.2 mg/L). This variability was not random. All sites west of the Götemar granite had low concentrations (< 0.5 mg/L) and several of the sites in the southernmost part of the area had low to relatively low concentrations (≤ 1.0
mg/L) (Figure 11a). In contrast, all sites located on and immediately south of the granite, as well as most sites in the easternmost part of the area, had elevated to high concentrations. These features point to the influence of the Götemar granite on fluoride concentrations in the Quaternary deposits. At several sites, the groundwater was undersaturated with respect to fluorite and calcite, but at some sites it was within the saturation range for one or both of these minerals (Figure 12a-c).
Figure 11. Spatial distribution of fluoride concentrations in regolith groundwater (a) and fracture groundwater (b) in the Laxemar area. The SGU sampling sites are indicated with R (regolith groundwater) and F (fracture groundwater); all others are SKB sampling sites (abbreviation applied for regolith well labelling, e.g. SSM034 = SSM000034). For the SKB sampling sites, the values represent medians of time series. The concentrations over time and with depth (within boreholes) were stable overall; therefore, the maps are a true representation of the spatial distribution. The F-rich Götemar granite pluton (green colour) crops out, surrounded by TIB rocks (white).
Fresh (chloride < 350 mg/L) bedrock groundwater, collected from fractures from close to ground surface to a depth of nearly 700 m, had generally high concentrations of fluoride throughout the area (brackish to saline fracture groundwater was not included in the thesis). The fluoride concentrations (1.2–7.4 mg/L) and pH (6.2–8.9) varied independently of depth and sampling method (Figure 13). The time series for the fluoride concentrations were, in general, short and did not show any systematic patterns. In terms of the spatial variability of the fluoride concentrations, there were no systematic patterns except for relatively low values at all three sites west of the Götemar granite, and no significant increase towards the Götemar granite (Figure 11b). The groundwater was saturated (within error of estimate) with both calcite and fluorite throughout the studied depth interval in the boreholes (Figure 12a-c).

**Figure 12.** Saturation indices (SI) for fluorite and calcite in fracture groundwater with chloride concentrations < 350 mg/L and regolith groundwater. Light blue dots represent fracture groundwater collected from packed-off sections, while connected red dots represent fracture groundwater collected from tube units along a borehole. The SI values are plotted versus depth (a, b) and versus each other (c).
5.2. Sources and controls of fluoride concentrations in water

Although it is well known that crystalline bedrock, which is composed mainly of granitoids and gneisses, is the ultimate source of high fluoride concentrations in Swedish stream waters and groundwater (Selinus, 2010), there are still knowledge gaps in terms of the precise geological and mineralogical sources of fluoride and to what extent various physical landscape features affect fluoride levels in the waters. In this chapter, these gaps are addressed.

The impact of the Götemar granite on the spatial distribution of fluoride in stream waters and regolith groundwaters is obvious. The impact was particularly evident for the surface waters, as the stream running in an easterly direction along the southern border of the granite (the Kärsvik stream) had clearly higher fluoride concentrations downstream than upstream of the granite. In the regolith groundwater, the pattern was slightly less obvious as the fluoride concentrations were high not only upon the granite but also south to southeast of the granite. In the fracture groundwater, in contrast, the fluoride concentrations were not correlated to the Götemar granite. However, this finding may be partly due to the limited number of samples upon and in the immediate vicinity of the granite (Figure 11b).

Taken together, the fluoride-distribution patterns in the stream waters and regolith groundwaters point to Quaternary deposits derived from the Götemar granite, and particularly till, as a major source of high fluoride levels in these...
two water types. The reasoning here is that this source would explain the fluoride pattern in both these water types, that is, the high fluoride concentrations in regolith groundwater south to southeast of the granite would be caused by till formed partly from the Götemar granite as the latest continental ice sheet in the region moved (and thus transported material) from north/northwest to south/southeast. In order to test this hypothesis and to determine fluoride variability spatially and between various soil types, a sampling and analytical campaign of the Quaternary deposits was carried out, with sampling sites located upon the Götemar granite and in reaches both upstream (west) and downstream (south) of the Götemar granite within the catchment of the eastward flowing (Kärrsvik) stream.

The Quaternary deposits (< 2 mm fraction), which included till, sorted sediments (gravel, sand and clay/silt) and organic-rich soils, carried fluorine mainly in relatively resistant phases (a dominance of the “residual fraction” as revealed by sequential chemical extractions) and in low concentrations (maximum 660 ppm, Figure 14) in comparison to those in the underlying bedrock composed of the Götemar granite (0.38–0.54 wt% F) and TIB rocks (0.11–0.13 wt% F). Till was however somewhat hard to sample as it typically was covered by a thick layer of sandy/gravelly deposits. However, in the relatively few till samples collected upon and in the downstream reaches (south) of the Götemar granite, the mineralogical composition of this soil type indicated that it is primarily composed of material derived from the TIB rocks. This is not surprising considering that these rocks cover vast areas of southeast Sweden (Högdahl et al. 2004). Hence, the influence of the Götemar granite seems to be minor, and the low fluorine concentrations in the till is explained primarily by release and leaching of fluoride during alteration of primary minerals from the TIB rocks (biotite, amphibole) to secondary (clay) minerals. For none of the other soil types there were any clear and significant differences between the three subareas within the catchment (Figure 14).
Figure 14. Total fluorine in subsamples of Quaternary deposits sorted according to classification and subarea. Abbreviations: glacial clay, GIci (n = 8); glacial/postglacial clay-silt, GIPCiSi (9); postglacial sand, Pgs (20); fluvioglacial/postglacial sand, Fl/Pgs (10); postglacial sand and gravel, PgsG (12); fluvioglacial sand and gravel, FlsG (2); fluvioglacial/postglacial sand and gravel, Fl/PgsG (10); gyttja, gyttja clay, clay gyttja and peat, Gys, GysCl, GysG, P (27) and till that is gravelly-sandy, gravelly-silty, gravelly-clayey or sandy-silty, GsTa, GsSi, GsIT, SaSiT (8).

Hence, taken together, the solid-phase data presented in this thesis does not support the hypothesis that Quaternary deposits (in particular till) derived from the Götemar granite are a major source of the high fluoride concentrations in surface and groundwaters upon and S/SE of this granite. Elsewhere it has, however, been shown that till upon F-rich granite are clearly enriched in fluorine as compared to till upon nearby less F-rich rocks (Lahermo et al., 1991). Hence, due to the low number of till samples collected and the sampling strategy applied (focus on areas with relatively thick Quaternary deposits) in this thesis, it cannot be excluded that the presented data is not fully representative for the till geochemistry within the catchment. In particular, Leptosols, dominated by till and likely to reflect the underlying bedrock in terms of geochemistry (Lindroos, 2004), were not sampled. Consequently, the till (and any sorted sediments derived from it) upon and south/southeast of the granite may be overall enriched in fluorine, contributing to build up of high fluoride concentrations in nearby waters.

The map of Quaternary deposits (Figure 5) shows that bedrock is extensively exposed (or found under a very thin soil layer) within the area (catchment), which facilitates discharge of fracture groundwater directly into creeks and
aquifers in the Quaternary deposits. The fluoride concentrations of groundwater in fractures in the Götemar granite are poorly known, but are most likely high; this conclusion is based on the high F-concentrations in this granite (Alm and Sundblad, 2002; Friese et al., 2012), visible secondary fluorite precipitates on the walls of fractures in this granite (Figure 8b), and high dissolved fluoride concentrations in quarries within the granite (2.5–5.3 mg/L; Berger et al. 2012) and in samples from two groundwater wells right at the border of this granite (2.4–3.5 mg/L, Berger et al. 2012). Hence, a major source of high dissolved fluoride concentrations in surface waters upon and downstream of the Götemar granite may be fluoride-rich groundwater discharged from fractures running through this granite. Therefore, in addition to release of fluoride as a result of weathering of primary minerals in Quaternary deposits (mainly till) related to the Götemar granite, discharge of fluoride-rich groundwater via fractures in this granite may be a substantial, or even dominating, control of dissolved fluoride levels in surface waters and regolith groundwater (Figure 15).

Figure 15. Along certain stretches in the Kärrsvik stream the water flows in direct contact with the fractured upper bedrock.

Other investigated potential controls of fluoride levels in the regolith groundwater were the well-filter depth and the water table in metres above sea level (masl), the thicknesses of the groundwater column and the regolith, and distribution of soil types at the sites of sampling. The fluoride concentrations
were not significantly correlated with any of these physical variables (Figure 16). Regarding the soil types it shall, however, be noticed that they represent the conditions right at the sites where the groundwater wells were drilled and installed, and thus are not necessarily representative of the entire catchment draining into each well. Hence, a thorough assessment of the impact of soil type on fluoride concentrations cannot be made based on the work included in this thesis.

**Figure 16.** Median fluoride concentrations in regolith wells versus filter depth, median water table, median thickness of the groundwater column and thickness of regolith. The Spearman rank correlation coefficient (rs) is presented in the graphs. The water table was measured in only 19 wells, resulting in fewer points in plots b and c.

The overall high fluoride concentrations in the fracture groundwater are proposed to be the result of alteration and/or dissolution of primary and secondary minerals along the fracture walls. Secondary fluorite, formed from hydrothermal fluids (> 300°C) emanating from the Götemar granite intrusion at 1.45 Ga and from somewhat cooler fluids (70–150°C) circulating in the bedrock in Paleozoic at approximately 400–450 Ma (Drake and Tullborg, 2009a; Drake et al., 2009b), is an obvious source. However, despite that this secondary fluorite is frequent and abundant within and close to the Götemar
granite, the fluoride concentrations did not change systematically with distance to this granite. Also, despite its old age, the fluorite shows mostly fresh surfaces (Figure 17a) with only scattered signs of dissolution features (Figure 17b). Also other minerals were therefore investigated in terms of fluoride release. Bastnäsite (Figure 17c) is a secondary mineral that is mainly of Paleozoic age (400–450 Ma) like the younger generation of fluorite (Drake et al., 2009b). This mineral occurred in a relatively large number of fractures (approximately 30%) and was not enriched in fractures within or in the immediate vicinity of the Götemar granite. Although this mineral generally covers only a small area of a given fracture surface where it is found (< 5 %, frequently below 2 %), it occurred at all depths and contained a significant amount of F (average 1.2 wt%). Apophyllite (Figure 17d) is a secondary mineral likely to be more widespread than was indicated in the drill-core mapping in which it was identified in only 0.6 % of the fractures. In addition to these secondary minerals, also primary minerals may contribute. In particular, biotite, a major mineral in the host rocks, has been heavily altered to chlorite adjacent to the fractures (Drake et al., 2008) under past hydrothermal conditions and most likely also, but to a smaller extent, in the present-day low-temperature environment (Drake et al., 2009a). This process releases fluoride to the groundwater, and may be most active where fracturing causes exposure of fresh bedrock surfaces containing unaltered biotite.
Figure 17. Back-scattered SEM images. Walls of open fractures in the Götemar granite (borehole KKR02: 258 m depth) showing (a) fresh secondary fluorite crystals surrounded by chlorite/clay-minerals and (b) partially dissolved secondary (cubical) fluorite crystals together with quartz (dark crystals) in a matrix of chlorite/clay-minerals. Open fracture walls in the TIB-rocks showing (c) bastnäsite (REE-carbonate) on calcite crystals (KSH01A, 289 m) and (d) apophyllite (KLX03, 970 m). (SEM-images by Henrik Drake.)

5.3. Risk aspects of high dissolved fluoride concentrations

Facing high dissolved fluoride concentrations in natural waters, there are primarily two issues that are recognised from a risk-aspect point of view. Firstly, ingestion of large quantities of fluoride, mainly through drinking water, can have adverse effects on human through the interaction of fluoride with primarily teeth and bones in the body (Bunnell et al., 2007; WHO, 2011). Yet, there are still large uncertainties and ongoing research on whether fluoride also might have the potential to cause additional severe effects on health. Secondly, increased attention has been paid to fluoride in studies
concerning abundance of inorganic aluminium in acidic surface waters. Fluoride and aluminium form strong aqueous complexes that have the possibility to increase the bioavailability of aluminium, and hence to increase the toxicological effects on aquatic biota. In addition, the synergistic effect of such complexes is poorly studied.

5.3.1 Fluoride exposure of children in Kalmar County

It is often assumed that water consumption is the major route of exposure to fluoride; therefore, the analysis of water fluoride content is the most common approach for ensuring that daily intake is not too high. Paper V of this thesis characterised the risk of excess intake for children (aged 4–6 years) in households with private wells in Kalmar County.

Our first aim was to investigate the importance of the approach that was chosen for characterising the risk of an excess intake of fluoride. The risk was characterised in two ways: (1) by evaluating the proportion of the study population that uses drinking water with fluoride concentrations above the prevailing drinking water standard, and (2) by assessing the exposure in the same study group using a probabilistic model and comparing it with reference values of tolerable daily intake (TDI). The ultimate question was how the outcome of the risk characterisation differs between the two approaches. A second objective was to conduct an exposure assessment of fluoride, considering multiple exposure pathways and the variability in these pathways, in order to (1) estimate the variability in each of the chosen exposure pathways, and (2) see how important the intake of drinking water is in comparison to other exposure pathways.

The concentration of fluoride in private wells in Kalmar County varied between < 0.1 and 15 mg/L, with an average of 1.0 mg/L. Of the sampled wells, 24 % showed concentrations above the WHO drinking water criteria of 1.5 mg/L (WHO, 2011). This is the proportion of the study population that was assessed, using this approach, as experiencing a risk of excess fluoride intake. The intake of fluoride is normally controlled by monitoring fluoride concentrations in the municipal water supply, with action being taken if levels exceed applicable drinking water standards. Since there is a narrow margin between beneficial and harmful fluoride levels in drinking water, optimal guideline values are difficult to establish. The scientific basis for the WHO guideline is summarised in a review by McDonagh et al. (2000). All in all, the reviewed studies indicate that concentrations above ca. 1.5 mg/L cause dental fluorosis of aesthetic concern in at least 10 % of exposed individuals, while the risk appears to be significantly lower below this level. Despite some uncertainties, which are stressed in the WHO scientific summary for fluoride (WHO, 2002), a risk assessment that is based only on water fluoride concentrations has the advantage of being very simple. However, it is then
essential that the chosen limit also protects the majority of high-exposure individuals.

When epidemiological data is difficult to interpret, it may make more sense to state the maximum tolerable level as a daily dose per kilogram of body weight. The reference dose (RfD) for TDI represents the no-observed-adverse-effect level (NOEL); and in setting RfD for fluoride (0.06 mg/kg-day), the US EPA refers to Hodge (1950) and Underwood (1977). The US EPA RfDs are often corrected by the use of safety factors. However, this is not the case for fluoride. In 2013, the European Food Safety Authority’s (EFSA) Panel on Dietetic Products, Nutrition and Allergies (NDA) also suggested a reference value for fluoride, expressed as an adequate intake (AI) of 0.05 mg/kg body weight per day from all sources (EFSA NDA Panel, 2013). Without specifying references, the EFSA refers to “epidemiological studies (performed before the 1970s)”, which they describe as indicating that their AI value corresponds to a fluoride intake “at which the caries preventive effect approached its maximum whilst the risk of dental fluorosis approached its minimum”. There are, apparently, some uncertainties associated with this stated thresholds as well and it seems crucial to examine further how relevant the available TDI values are in order to assess the risk of an excess intake.

When only exposure from drinking water consumption was considered, the variability in daily fluoride intake was calculated to range between 0.001 and 0.32 mg/kg-day (with truncation at the 5th and 95th percentiles). In 48 % of the evaluated scenarios the daily fluoride intake exceeded 0.06 mg/kg-day, stated as the TDI limit in the US EPA IRIS database. The daily dose from additional fluoride exposure pathways was also calculated: exposure from beverages and solid food, oral soil intake, inhalation of dust and ingestion of toothpaste. After including all exposure pathways, the total daily fluoride intake was found to increase to between 0.01 and 0.38 mg/kg-day (with truncation at the 5th and 95th percentiles) (Figure 18). For about half of the children concerned (see P50 in Figure 19), the exposure from toothpaste ingestion was actually expected to be the main source of total fluoride intake. However, at higher percentiles water consumption increasingly became the most important exposure pathway (up to 85 % of the daily intake). Because toothpaste ingestion appears to be a major exposure pathway for many children, an easy measure to limit fluoride intake in areas with high natural fluoride concentrations in groundwater would be a recommendation by public health authorities stating at which water concentration the use of fluoridated dental products should be avoided for different age groups. However, the variability in fluoride exposure due to toothpaste ingestion is much lower than that to water consumption from private wells, because of the great natural variability of dissolved fluoride in groundwater, which is not unique for this region. Hence, it is also important to make the public aware of the importance of
controlling fluoride concentrations in private water supplies, and to inform people about measures to reduce fluoride exposure via this pathway, particularly for children.

Figure 18. Probability box (p-box) of fluoride exposure, truncated at the 5th and 95th percentiles, after intake of drinking water, food and beverages, oral soil intake, inhalation of dust, and ingestion of toothpaste. The p-box is drawn by adding a large number of intervals on top of each other (specifically the intervals for each whole number percentile, in the figure between the 5th to the 95th percentiles). When 90 intervals are stacked on top of each other, the minimum values give the shape of the left-hand limiting curve of the p-box, while the maximum values give the right-hand curve. Modified from Augustsson and Berger (2014).
The results showed that there is a significant difference in how the risk of excess fluoride intake is assessed or characterised depending on the risk characterisation approach. When “background exposure” from other sources in addition to drinking water play a major role for the total intake, and indeed play a highly variable role, the risk of excess intake may be judged differently if only drinking water criteria are used or if the total intake via all relevant routes of exposure is compared with a toxicological measure of the total TDI. The risk of excess fluoride intake may be best judged after having quantified all relevant exposure pathways. The inconsistent results between the two risk characterisation approaches indicate either that the WHO drinking water guideline is not conservative enough or that the available values on TDI are too strict.

5.3.2 Effects on aluminium

The overall aim of Paper II was to assess the impact of high concentrations of natural dissolved fluoride on aluminium concentrations and speciation in stream water. Since dissolved fluoride is a ligand that forms strong complexes with aluminium (LaZerte et al., 1997), its effect on aluminium toxicity is complex and ambiguous. Although such complexes are sometimes proposed to mitigate aluminium toxicity to some extent in comparison with other inorganic aluminium complexes, they still represent a bioavailable and thus possibly toxic fraction in comparison with organically bound aluminium (Bi, 2001; Deng et al., 2011; Frankowski and Ziola-Frankowska, 2010; Gensemer and Playle, 1999; Haag et al., 2001).
Analytical data and hydrogeochemical modelling were utilised for three streams (Kärrsvik, Ekerum, Laxemar) in the study area in order to assess the patterns and speciation of aluminium and fluoride. Overall, the concentrations of aluminium were controlled by variations in pH (the solubility of aluminium increased with decreasing pH), which is a well-known phenomenon (Cory et al., 2006; Haag et al., 2001; Lawrence et al., 1988; Neal, 1995). In two of the studied streams (Kärrsvik and Laxemar), as in many other catchments elsewhere in the nemo-boreal zone, there was an overall decrease in pH when stream water discharge increased, caused by consistently high DOC concentrations and a decrease in acid-neutralising capacity when the groundwater table rose during wet periods (Erlandsson et al., 2010; Laudon and Buffam, 2008; Laudon et al., 2001). In addition, the modelling suggested that the amount of $Al_4$ increased, reaching values up to 100% of $Al_{0.45}$ on some occasions. Hence, as high flow conditions set in, the streams are acidified and loaded with an abundance of dissolved aluminium. While organically complexed aluminium was predicted by the model to dominate the dissolved aluminium pool, the inorganically complexed aluminium pool was predicted to be strongly dominated by fluoride complexes in Kärrsvik (98–100%), as well as in Laxemar, where there was, however, a greater variation (26–99%, median 98%). In Ekerum, the corresponding percentages were 0.1–95% and a median of 42%.

For a given pH value, the concentrations of both measured $Al_{0.45}$ and modelled dissolved aluminium were generally considerably higher in Kärrsvik than in Laxemar (Figure 20a-b). This result shows that there is another important factor, in addition to pH, causing a rise in aluminium concentrations in Kärrsvik. The major differences between Kärrsvik and Laxemar are that in the former there were: (i) much higher concentrations of fluoride; and (ii) no inverse correlation between $Al_{0.45}$ and fluoride. In line with these features, the model predicts that in Kärrsvik, at any given pH, aluminium-fluoride complexes occur both in higher concentrations and in higher proportions than in Laxemar. Taken together, these analytical and modelling results indicate that the high fluoride levels in Kärrsvik increase the extent to which aluminium is complexed with fluoride, which in turn increases both the ratio of inorganically to organically complexed dissolved aluminium and the concentrations of dissolved aluminium and $Al_{0.45}$ in stream water.
Figure 20. Concentrations of measured filtered Al$_{0.45}$ (a) and modelled dissolved Ald (b) versus pH in Kärrsvik, Ekerum and Laxemar streams. Modified from Berger et al. (2015).

The result of Paper II supports previous studies (Harrington et al., 2003; Moore and Ritchie, 1988; Sjöstedt et al., 2010; Tagirov et al., 2002) and highlights the role of fluoride in terms of increasing dissolved aluminium levels and the bioavailability (inorganic speciation) of aluminium in acidic stream waters. This finding stresses the importance of reaching consensus regarding the ambiguous toxicological nature of the part of inorganic monomeric aluminium that is complexed with fluoride.
This thesis focussed on the sources, controls and risk aspects of fluoride in surface water and groundwater in southeast Sweden, where the F-rich 1.45 Ga circular Götemar granite (5 km in diameter) crops out in the surrounding 1.8 Ga granites and quartz monzodiorites (TIB rocks). The main results and findings are:

- The fluoride concentrations in stream water (the Kärrsvik stream) increased towards the lower reaches, downstream of the Götemar granite, with outlet concentrations up to 4.2 mg/L and 1.6–4.7 times higher than in the upstream reaches. In addition, fluoride concentrations were particularly high in small surface-water bodies (including quarries) above or in direct contact with the granite, and showed a strong inverse correlation with water discharge in the stream. Taken together, these data and patterns pin-point the granite, or geological deposits derived from it, as the ultimate source of dissolved fluoride in the surface waters in the area.

- In groundwater in the Quaternary deposits (regolith groundwater), the fluoride concentrations varied little in the temporal dimension, but widely in the spatial dimension (the median among 18 groundwater monitoring wells was 0.3 mg/L to 4.2 mg/L). The high fluoride concentrations were not caused by the filter depth or water table in masl, by the thicknesses of the groundwater column or the regolith, or by the distribution of soil types at the sampling sites. The fluoride concentrations were, however, correlated with the spatial distribution of erosional material (till) derived from the F-rich Götemar granite.

- In the fresh fracture groundwater (brackish to saline groundwater was not included in the thesis), the fluoride concentrations were generally higher (up to 7.4 mg/L) than in the surface waters and regolith groundwater, and were uncorrelated with depth (from just beneath the ground surface to nearly 700 m) and with location relative to the Götemar granite. Two mechanisms
explaining the overall high fluoride levels in the fresh fracture groundwater were addressed: first, the weathering/dissolution of fluorite, bastnäsite, apophyllite and biotite; and second, long water-residence times, which favour water-rock interaction and the build-up of high dissolved fluoride concentrations in groundwater.

- Fluorine concentrations in Quaternary deposits, including till, were considerably lower than in the underlying bedrock that is dominated by granitoids. The low fluorine concentrations in the till, as compared to the bedrock, are explained by the release and leaching of fluoride during the alteration of biotite and amphibole to secondary minerals. In addition, the till is likely to be partly composed of rock material that lost some of its fluorine content during hydrothermal events in the Proterozoic. Hence, the original fluorine concentrations in the till are likely to have been slightly lower overall than in the fresh (unaltered) source bedrock.

- In the Quaternary deposits, fluorine resided mainly in the residual fraction. However, it was also present, to a substantial extent, in phases extractable with HAc solution in the till, and in phases extractable with NaPb solution in organic-rich soil types. This finding indicates that after release via the alteration of primary minerals, fluoride has been largely scavenged by Fe/Al (and perhaps Mn) oxyhydroxides in the till and by organic matter in organic-rich soil types.

- It is likely that a major source of dissolved fluoride in surface waters and groundwater in the area is Quaternary deposits (till) containing erosional products derived from the F-rich Götemar granite. However, as the bedrock is widely exposed (or overlain only by very thin soils), the discharge of fluoride-rich groundwater from bedrock fractures may be of particular importance in terms of the dispersion of dissolved fluoride in the surface environment in this area.

- Modelling predicted that with declining pH of stream waters, the proportion of aluminium complexed with fluoride (relative to aluminium complexed with organic substances) is either maintained or increased, indicating that fluoride is an important complexing agent for aluminium, particularly at low pH conditions. In addition, both the analytical data and the modelling point to fluoride as an important control of elevated aluminium concentrations in stream water in the area.

- A high proportion (24%) of the children in households with private wells in Kalmar County were assessed to be at risk of excess fluoride intake based on the WHO drinking water guideline value (1.5 mg/L). However, the risk increased significantly when the US EPA reference dose (0.06 mg/kg-day)
was used instead, both when all relevant exposure pathways were taken into account and when water consumption alone was taken as the exposure pathway. Hence, the risk of an excess intake of fluoride is dependent on the basis used for evaluation.

Taken together, the results and findings presented here draw attention to southeast Sweden as a fluoride hotspot area in a global context. This conclusion is shown, for example, by the widespread occurrence of dissolved fluoride concentrations above the stated thresholds for drinking water. More specifically, this thesis contributes to the understanding of where and when to expect elevated fluoride levels in surface water and groundwater, which in turn is important in terms of current and future extractions of water for consumption purposes. The thesis also highlights the role of fluoride in terms of increasing dissolved aluminium levels and the biological availability (inorganic speciation) of aluminium in acidic stream waters. This finding calls for further studies of the geochemistry, bioavailability and toxicology of aqueous aluminium-fluoride complexes in such environments. In terms of human exposure to fluoride, it is important that both drinking water and other sources are considered and included in assessments. It is notable that the inconsistent results between the two risk characterisation approaches used here indicate that either the WHO drinking water guideline is not conservative enough or that the available values on tolerable daily intake are too strict.
ACKNOWLEDGEMENTS

First and foremost, I owe my deepest gratitude to my main supervisor Professor Mats E. Åström. You inspired me to start explore the world of environmental geochemistry more in-depth. Since the very beginning of this journey, you have been there with continuous optimism, enthusiasm and encouragement. At times when I doubted myself, I still felt you believed in me. Your professionalism, knowledge and supervision have been essential in order for me to complete this thesis, thank you.

I am sincerely grateful to co-supervisors Dr Pasi Peltola and Dr Henrik Drake. Despite living in different parts of Sweden, both of you have always been just a click or phone call away whenever I have had any questions, ideas or doubts. Your knowledge in your respective scientific fields, and willingness to share, has been very valuable throughout my PhD-studies. Pasi, thank you for being so open-minded and supportive, always up for a laugh, relaxed yet skilled in science. Throughout the years, we have discussed almost all topics related to fluoride in any way, I think. Thank you, Henrik, for all the support and patience when it comes to mineralogy-related issues and the invaluable assistance during analyses at the Earth Sciences Centre, University of Gothenburg.

Fellow PhD-students (most of you now entitled Dr) of our research team; Changxun, Olga, Frédéric, Lina, Linda and Mikael. I feel blessed getting to know you and you have all, in different ways, contributed to and inspired me to finally reaching the end of this adventure. I have enjoyed sharing offices or having you by my side during courses, seminars, conference trips, field and laboratory work.

The Swedish Nuclear Fuel and Waste Management Co. (SKB) and Joint Research and Development Platform at Nova Centre for University Studies (Nova FoU) in Oskarshamn are acknowledged for providing the opportunities to process existing data and materials owned by the SKB. The site
investigations in Laxemar-Simpevarp constitute a crucial foundation for the work of this thesis. Nova FoU is also thanked for providing financial support for Paper III. I spent almost two years during my PhD-studies working at the SKB facility Äspö Hard Rock Laboratory (ÄHRL), and would like to take the opportunity to thank the staff there. Especially thanks to Assen Simeonov and Ann-Sofie Karlsson, head of the departments TDU and TDK, respectively, with co-workers, where I spent my time at Äspö. Also at the ÄHRL, thank you Daniel Svensson for the XRD analyses in Paper IV.

I would like to thank first-author of Paper V, Anna Augustsson, for your professionalism and willingness to carry out this study together with me. This study truly made me broaden my knowledge on fluorine in a wider, health-related context.

Joon and Sara, it was a pleasure hanging out with you during the conference in Chiang Mai. I hope to meet you again in the future.

The staff at the Department of Biology and Environmental Science at the Linnaeus University, thank you all who I have gotten to know during my years here! Thank you current and former Head of Department, Per-Eric Betzholtz, and Tommy Claesson. Special thanks to Anders and Henrik for helping out on any practical issues and thank you Sara for everything laboratory-related. Also great thanks to the administrative personnel, Boel, Margareta, Anna G, Lena P and others. I also would like to express my gratitude to all the nice PhD-students, professors, post-docs, research assistants and others colleagues at the department. I have had a wonderful time getting to know all of you people; Petter, Olof, Oscar, Kocken, Johanna, Jon, Hanna, Einat, Magnus K, Lena, Anders, Pelle, KB, Christofer, Swapnil, Magnus E, Fredrik, Terese, Sarfraz, Fabio, Mireia, Jonas, Andreas among many others. With my office being “wedged in” between evolutionary ecologists and fish ecologists I couldn’t ask for a better corridor to stay in at the department.

To my friends outside of the university world, you know who you are. Whenever we hit the road in pursuit of new adventures I feel so alive.

My parents, Olle and Kerstin, and my sister Emma, thank you for supporting me spiritually throughout the writing of this thesis and in life in general, I love you. Brother Henrik, every time we meet is a moment I enjoy and value a lot! My beloved brother Daniel, you will always be an inspiration to me in everyday life even though you left us all way to early... You lived life to the fullest. My “second family”, Kjell, Harriet, Malin, Viktor, Martin and Erik. I am so happy you have become a part of my life. Last but not least, I would like to thank you, Anna. For being there, being who you are, always supporting and encouraging. I love you so much.
REFERENCES


Fawell, J. et al., 2006. Fluoride in Drinking-water, World Health Organization (WHO).


genesis of some high-fluoride groundwaters in India. Applied Geochemistry,
20(2): 221-228.

Jacks, G., Harikumar, P.S., Bhattacharya, P., 2009. Fluoride mobilisation in

Jackson, R.D. et al., 2002. The fluoride content of foods and beverages from
negligibly and optimally fluoridated communities. Community Dentistry and
Oral Epidemiology, 30(5): 382-391.

soils in districts of fluoride-rich and fluoride-poor groundwater, north-central

from fluoride exposure through ingestion of vegetables and cereal crops in
Unnao district, Uttar Pradesh, India. Ecotoxicology and Environmental Safety,
74(4): 940-946.

of groundwater monitoring wells in the Laxemar area. Swedish Nuclear Fuel

of groundwater monitoring wells. Swedish Nuclear Fuel and Waste

Kresten, P., Chyssler, J., 1976. The Götemar Massif in south-eastern Sweden:
A reconnaissance survey. Geologiska Föreningen i Stockholm Förhandlingar,
98: 155-161.

Biotite Mica in Soil: Implications for Fluoride in Shallow Groundwater. ISRN

Kumar Singh, C. et al., 2011. Geochemical modeling of high fluoride
concentration in groundwater of Pokhran area of Rajasthan, India. Bulletin of
Environmental Contamination and Toxicology: 86 (2) 152-158, 86(2): 152-
158.

Köhler, S.J., Lidman, F., Laudon, H., 2014. Landscape types and pH control
organic matter mediated mobilization of Al, Fe, U and La in boreal
Laaksoharju, M. et al., 2008. Hydrogeochemical evaluation and modelling performed within the Swedish site investigation programme. Applied Geochemistry, 23(7): 1761-1795.


Smellie, J.A.T., Tullborg, E.-L., 2009. Quality assurance and categorisation of groundwater samples from the Laxemar-Simpevarp area. In Background Complementary Hydrogeochemical Studies. Site Descriptive Modelling SDM-

Smith, R.M., Martell, A.E., Motekanis, R.J., 2003. NIST critically selected stability constants of metal complexes. NIST standard reference database 46, version 7.0, Gaithersburg, MD, USA.


