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Research Paper

A geologically-based approach to map arsenic risk in crystalline aquifers: Analysis of the Tampere region, Finland

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ARTICLE INFO

Article history:

Received 11 September 2017

Received in revised form

22 June 2018

Accepted 8 December 2018

Available online 19 February 2019

Keywords:

Arsenic risk
Crystalline bedrock
Fractured aquifers
Heterogeneity
Finland

ABSTRACT

The study illustrates the critical role of accurate geological structural mapping to delineate crystalline aquifer zones more prone to high health risk due to elevated dissolved As in drinking wells. The analysis revisits the results from more than 1200 groundwater samples collected over ten years from domestic wells across the Tampere region (Finland). It is demonstrated that the highest dissolved As concentrations in the region (up to 2230 µg/L) are exclusively found near major faults and deformation zones (FDZs) detected via geophysical and geological surveys, and that a clear correlation exists between dissolved concentrations and the distance from the FDZs (r). Almost all values exceeding the drinking water limit (10 µg/L) occur at $r < 8$ km, while concentrations above 100 µg/L occur at $r < 4$ km. Solid-phase As concentrations in bedrock show less dependency on FDZ than aqueous concentrations. This behavior is explained considering different mechanisms, which include enhanced sulfide oxidation and fracture connectivity, promoting preferential transport of dissolved As to FDZs and mixing of waters from different redox zones, mobilizing preferentially As(III) or As(V). Fe hydro-oxides may also precipitate/dissolve preferentially because of FDZs, while residence time may influence the contact time between water and As-bearing minerals. It is concluded that the accurate mapping of FDZs, and in general of structural geology, provides an important preliminary information to identify where localized, site-specific characterization of hydrogeology and geochemistry is more urgent to reduce As-related health risk from groundwater intake.

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1. Introduction

Arsenic (As) is a toxic and carcinogenic element that threatens the health of millions of people worldwide (e.g. Ravenscroft et al., 2009; Naujokas et al., 2013; Hunt et al., 2014). The problem is particularly acute for populations exposed through the frequent intake of groundwater enriched in inorganic As. A significant number of studies have been devoted to evaluating the sources, behavior, and distribution of As in groundwater, as well as advanced techniques for its characterization and remediation (e.g. Barringer and Reilly, 2013; Foster and Kim, 2014; Rahman et al., 2014; Baris et al., 2016). A comprehensive review of arsenic in groundwater can be found in Smedley and Kinniburgh (2013).

Arsenic in fractured aquifers has been significantly less studied than in unconsolidated media, yet the number of consumers of groundwater from fractured aquifers potentially exposed to As is still high (Welch et al., 2000). Arsenic in bedrock formations has been found to range from < 1 µg/L to 1160 µg/L in Alaska, USA (Verplanck et al., 2008), and up to about 2000 µg/L in the Northern Appalachian Mountain Belt, USA (Lipfert et al., 2006; Ryan et al., 2011). A list of key studies focusing on arsenic in fractured bedrock aquifers can be also found in Bondu et al. (2016).

Mapping the risk of As in fractured systems is complex and uncertain. The ubiquitous presence of physical and geochemical heterogeneities in fractured media can strongly complicate the expected behavior of dissolved As in the bedrock aquifers. Physical heterogeneity is a result of multiple geological and climatic events controlling fault and deformation zones (FDZs) and resulting in a complex network of fractures. A direct consequence of physical heterogeneity is the spatial variability and scaling of hydraulic and pneumatic aquifer properties, which can vary over several orders of

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Peer-review under responsibility of China University of Geosciences (Beijing).

magnitude (e.g. Pedretti et al., 2016). Geochemical heterogeneity can be attributed to mineralogical variability of the hosting rocks, which could control, for instance, the amount and distribution of As-bearing minerals in the bedrock, i.e. the “geological source” of arsenic (e.g. Ryan et al., 2013). However, geochemical heterogeneity is also closely related to the occurrence of physical processes. For instance, flow heterogeneity controls solute transport dynamics within fractures and the matrix, including the mixing of waters, residence time, the reactivity of solutes and water–rock interaction (e.g. MacQuarrie and Mayer, 2005). Indeed, groundwater mixing has been reported as a key factor in some As-related systems (Yang et al., 2015; Bondu et al., 2017). Gas transport is also limited by fracture and matrix permeability, which may translate into transport-limited conditions for the oxidation of As-bearing sulfides, which has been reported as a key driving factor for elevated As concentrations in bedrock groundwater (Ryan et al., 2013; Mango and Ryan, 2015; O’Shea et al., 2015). Moreover, sulfide oxidation is also a surface-limited mechanism (e.g. Corkhill and Vaughan, 2009), as such sulfide minerals are expected to be more exposed to weathering conditions near FDZs than when locked within the rock matrix.

Quantification of the relationship between FDZs and dissolved As concentrations would be thus needed, for instance, as support for informed mapping of health risks from As intake via groundwater consumption (McGrory et al., 2017). Unfortunately, large-scale field-scale assessments combining a statistically significant amount of spatially distributed data and well-characterized structural geology are limited. This is mainly due to the high costs of characterizing the detailed physical, geophysical, and geochemical properties of groundwater and the hosting bedrock and the ubiquitous limited accessibility to groundwater resources.

In the Tampere region of Finland, the problem of As is particularly acute and important. The crystalline bedrock is a useful groundwater reservoir with multiple drilled wells, mainly used by domestic households or small water cooperatives. Similarly to other parts of the Fennoscandian shield, As is geogenic and a natural element in the bedrock minerals undergoing weathering, including arsenopyrite and other As-bearing sulfides. Investigations in the early 1990s revealed alarming concentrations of dissolved As in local wells. These initial investigations prompted a large-scale regional geochemical assessment that started in 1994 (Backman et al., 1994). Since then, the study has covered more than 1200 samples from an equivalent number of existing domestic wells, sparsely distributed across the region (Fig. 1), resulting in the largest hydrogeochemical survey ever conducted in Finland. A variety of studies and report have been presented since 1994, focusing on multiple aspects of As in the region (e.g. Backman et al., 2006; Loukola-Ruskeeniemi et al., 2007; Ruskeeniemi et al., 2011; Parviainen et al., 2015; Backman and Luoma, 2016), however never before focusing on the relationship between geological structures (and in particular FDZs) and the occurrence of As in the groundwater.

This work revisits the Tampere region geochemical database with the goal of highlighting the geometrical relationships between As concentrations and major FDZs identified via geological and geophysical structural surveys. The aim is to illustrate the importance of combining geological and geochemical mapping to identify where the aquifers potentially pose a greater risk to human health. By using a general methodology, easily exportable to other fractured aquifers, we provide new insights into the evaluation of risk in fractured aquifers combining a reliable statistical database and well-characterized geological mapping. By focusing on regional-scale mapping, our conclusions set the basis for future down-scaling of the analysis towards problem-specific research, as a guide for targeted and site-specific monitoring and assessment of groundwater resources.

The paper is supported by an electronic Supplementary Data (SD) document. Hereafter, figures, tables and text in the SD are referred to as “Figure SX”, “Table SX” and “Text SX”, respectively, being X a sequential number. A list of captions from the SD is found in the appendix of the manuscript.

2. Background

This section provides a summary of the previous key findings on the geological, hydrogeological and geochemical characteristics of the studied aquifer, which enables the reader to understand the problem of As in the Tampere region and to critically evaluate the importance of the findings illustrated in the following section. The interested reader is referred to the referenced works for details and specific aspects of the region not reported in this work.

2.1. Geological background

The Tampere region (Fig. 1) is located approximately 160 km northwest of the capital area of Helsinki. It covers roughly 14,500 km², with currently about 500,000 inhabitants in 22 municipalities. The topography of the area is relatively even in the south, being about 80–90 m above sea level (a.s.l.), and more contoured in the northern parts, ranging between about 150–200 m a.s.l. The metamorphic crystalline bedrock in Finland is part of the Precambrian Fennoscandian craton and mainly consists of Archean domain (>2.5 Ga in age) in the northern and eastern parts and of Svecofennian Paleoproterozoic rocks (1.93–1.8 Ga in age) in the central and southern parts (Vaasjoki et al., 2005). The overburden consists of young glaciogenic Quaternary deposits, mainly of till locally overlaid with gravel, sand, and clay, with an average thickness of 8.5 m (Haavisto-Hyvärinen and Kutvonen, 2007). The east–west-striking Central Finland End Moraine, which was formed within a period of a couple of hundred years about 11,000 years ago (Saarnisto and Saarinen, 2001), is located in the middle part of the Tampere region. The contact between crystalline Precambrian bedrock and Quaternary overburden is generally sharp. The Tampere region can be divided into three distinct geological units (Fig. 1), based on the dominant rock types encountered in the area (Loukola-Ruskeeniemi et al., 2007):

- (1) The Central Finland Granitoid Complex (CFG) in the north, rich in tonalities, granites, and granodiorites, with minor proportions of supracrustal rocks and mafic plutonic rocks (Korsman et al., 1997);
- (2) The Tampere Belt (TB) in the center, mainly composed of turbiditic metasedimentary rocks and felsic-intermediate arc-type metavolcanic rocks, and plutonic intrusions that cut the supracrustal sequence (Ojakangas, 1986; Kähkönen and Leveinen, 1994);
- (3) The Pirkanmaa Belt (PB) in the south, dominated by mafic and ultramafic plutons and granitoids cutting migmatitic metasedimentary rocks, sporadically containing graphite-bearing gneiss interlayers (Nironen et al., 2002).

The volcanic-sedimentary belt (TB and PB) is enriched in Au, As, Ag, Co, Cu, Li, Mo, P, Sb, U, and Zn (Koljonen, 1992). All the rock types encountered in the area are metamorphosed, crystalline hard rocks. Primary sedimentary or volcanic textures have only sporadically been preserved. The distribution of geological sources of arsenic in the bedrock (i.e. solid-phase As or As-bearing minerals; these terms are used synonymously hereafter) of the Tampere region has been reported by Lahtinen (1996). The results based on 603 bedrock samples are presented in Fig. 2 for the area near the city of Tampere, which is highly populated and thus of key

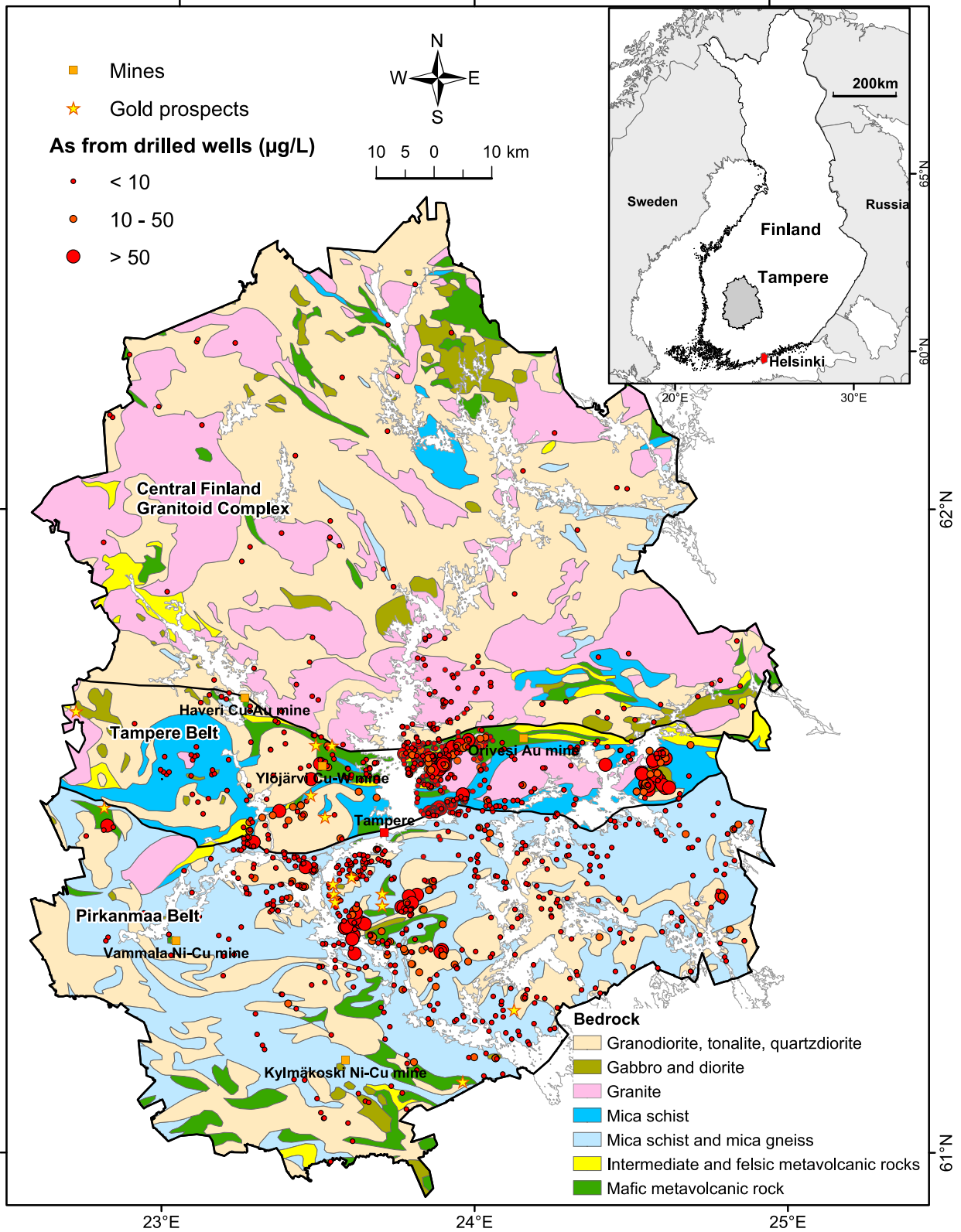


Figure 1. Geological map of the Tampere region, divided into the Central Finland Granitoid Complex (CFG) in the north, the Tampere Belt (TB) in the center, and the Pirkanmaa Belt (PB) in the south, and indicating the seven identified bedrock types (colors). White areas represent lakes and rivers. The black lines indicate the separation between the geological units. (Data: GTK geology database and groundwater database. Base map data copyright © National Land Survey of Finland, 2016).

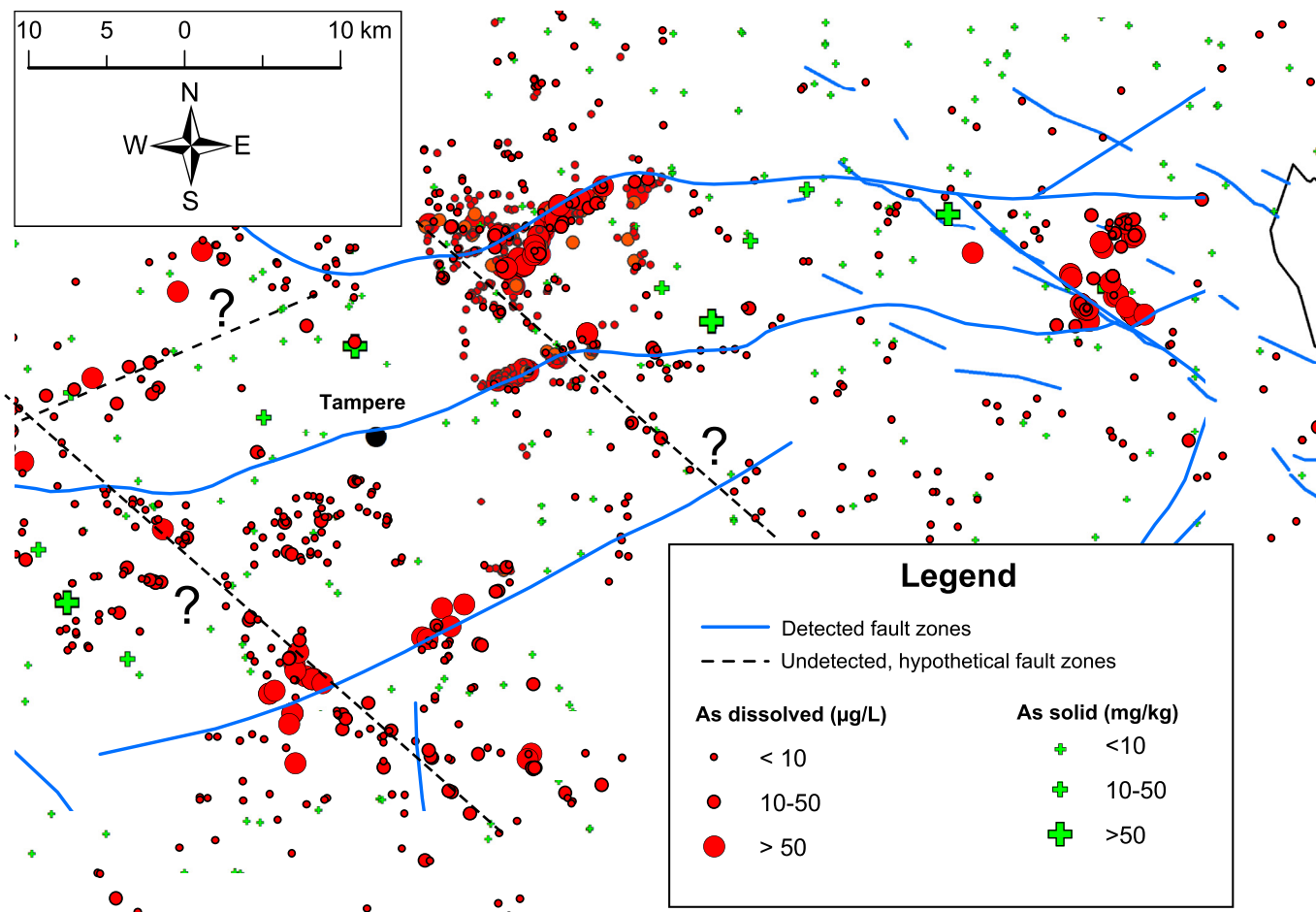


Figure 2. Distribution of dissolved As concentrations ($\mu\text{g/L}$) from samples collected during this study and solid concentrations (mg/kg) in the bedrock reported by Lahtinen (1996) in the southwest Tampere region. Dotted black lines with question marks indicate undetected hypothetical fault and deformation zones (FDZs) in the area inferred from the distribution of high As dissolved concentrations and with orientations similar to the straight blue lines, which represent actual FDZs detected through geological and geophysical surveys (Nironen et al., 2016).

importance for this study, while the results for the entire Tampere region can be found in the SD (Fig. S1). The average As content in the solid phase according to the geological subdivision (CFGC, TB, PB) is also reported in the SD (Table S1). According to the results by Lahtinen (1996), the abundances of the sulfide-forming elements (including As) are above average in the Tampere region in comparison with other sites in Finland. The most prevalent primary As-bearing mineral is arsenopyrite, which is typically randomly disseminated in bedrock or in quartz veins, with the exception of narrow ore-potential zones, where sulfides are enriched. Away from gold-showing areas (Fig. 1), the occurrence of arsenopyrite is reported as occasional in fractures and fault zones (e.g. Eilu and Lahtinen, 2004), i.e. in locations accessible to groundwater.

2.2. Hydrogeological background

In Finland, the compacted till-rich overburden is generally poorly permeable, with a hydraulic conductivity (K) of the order of $K = 10^{-8}$ m/s (Artimo et al., 2003) or lower. The low permeability of the till and the flat topography in the major part of the terrain constrains the mixing of overburden groundwater with bedrock groundwater. Consistently, unpublished sediment investigations performed by the Geological Survey of Finland (GTK) on till profiles have indicated that sulfides are generally lacking from the topmost

layers of the till, but are present in the basal part of the till in contact with the crystalline bedrock. This suggests transport-limited sulfide oxidation due to low permeability and the fine grain size of the till.

The geological units in the Finnish bedrock are mixed due to the long geological history and deformation phases, such as folding. As a result, the lithologies can vary considerably in lateral and vertical directions. Drilled wells are expected to intersect many rock types and hydraulic zones with depth. The fracture network generally occupies various lithologies and it may host chemically different types of groundwater, promoting mixing of waters of different geochemical compositions. Fracturing is relatively abundant within the upper 150 m of the bedrock, and becomes more sporadic with depth. In the topmost part of the bedrock, flow through open fractures is expected, on average, to be faster than flow through till. Hydraulic conductivities of up to $K = 10^{-5}$ m/s have been reported for fractures in Finnish crystalline bedrock near the study area (Stober and Bucher, 2007). Unfractured matrix blocks have very low hydraulic conductivity ($K = 10^{-7}$ m/s and lower, e.g. Mäkelä, 2012) and porosity (generally $<0.5\%$), allowing conductive groundwater flow exclusively along connected networks of open fractures. In the study area, as well as in other regions of Finland with similar geological configurations, it is accepted that recently recharged, shallow Ca-HCO_3 groundwater is expected to evolve in the upper

part of the bedrock into Na-HCO₃ groundwater at increasing depth within a few decades, partially due to Ca-to-Na ion-exchange processes (Pitkänen et al., 2002).

2.3. Geochemical background

The Tampere region database was comprised of 1272 groundwater samples, illustrating the general geochemical conditions suitable for As transport. The data have been collected since 1994 by GTK and the local administrative authorities. Key aspects regarding water sampling and methods used in these geochemical surveys are described in the SD (Text S1 and Table S2); details can be found by accessing GTK internal reports (e.g. Backman et al., 2006).

The samples were exclusively collected from existing pre-drilled domestic wells. Most of these wells had been drilled using the percussion drilling technique and lacked drilling logs. In turn, no quantitative information regarding fracture intensity or orientation of fractures was reported. No specific pumping tests nor tracer tests was performed, such that no local hydrodynamic information or estimation of residence time is available. The total depth of the well, the yield, and the pumping rate were only available for some of the wells. Based on the available data, the average well depth is 81.5 m. The statistics of the results used for the analysis are found in Table 1.

The Piper plots (Fig. S2) reveal that, in general, the sampled bedrock groundwater in the study area is predominantly HCO₃-rich, while Cl-rich waters are only found in a very limited number of samples. Overall, both Ca- and Na-rich water are found in the aquifer, although in the PB region, Na-rich waters appear to dominate over Ca waters. This is consistent with the general geochemical conceptual model of Finnish crystalline aquifers, which suggests that carbonate-rich waters prevail in shallow aquifers while brackish waters generally occur in deeper aquifers (Pitkänen et al., 2002). The relationship between As (meq/L) and the Ca/Na ion ratio (a potential proxy for residence time) is illustrated in Fig. S3, which reports the results from wells where As, Ca, and Na measurements coexisted in all regions. It is important to note that As increases as the Ca/Na ion ratio decreases, and in particular, the highest As concentrations (>10 meq/L) were all recorded in waters with a Ca/Na ion ratio of <4. The majority of observed concentrations exceeding the drinking water threshold (>10 µg/L) are found in a narrow pH window between pH 6.5 and pH 8.5 (Fig. 3 in arithmetic scales, Fig. S4 in logarithmic scales). The Eh–pH diagrams (Fig. S5) revealed that the majority of the groundwater samples fall within the field of arsenate (H₂AsO₄⁻, HAsO₄²⁻), forming under oxic aquifer conditions. Only a few data points from the PB dataset fall into the field of arsenite (HAsO₃), indicating reduced aquifer conditions.

To investigate this last aspect further, As speciation has been analyzed in detail from 14 samples in collected for this purpose, as reported in Table S3. It was found that the total content of As varied between 10.8 µg/L and 1110 µg/L. In 10 out of 14 wells, the groundwater was clearly dominated by arsenate, while arsenite was the major species in only three wells. One sample displayed no clear dominance of either arsenate or arsenite. The proportion of arsenite varied from 0.66% to 73.8% of the near-total arsenic (EDTA concentrated; see SD for more information on the speciation approach). These results are consistent with the expected behavior of Finnish shallow fractured aquifers, in which a progressive trend from oxic conditions to reduced conditions is generally observed as a function of depth. Although the number of speciation samples ($n = 14$) is small considering the heterogeneity of the studied aquifers, the speciation analysis is consistent with the Eh–pH plots and previous understanding of the redox state of the site.

3. Link between As concentrations and FDZs

Dissolved As concentrations in the bedrock groundwater were observed to range between <0.05 µg/L and 2230 µg/L, with a median value of 2.5 µg/L (Table 1). Altogether, As exceeded the drinking water limit of 10 µg/L in 22.5% of the studied drilled well waters. The high concentrations are consistent with the general geochemical composition of the bedrock aquifer, as illustrated above, which suggests that favorable conditions exist to sustain As mobility in groundwater. This is particularly true because of the circumneutral and alkaline pH conditions under oxic conditions (Smedley and Kinniburgh, 2013), and because As is mainly associated with arsenate in the shallow part of the aquifer, as above mentioned. Indeed, limit-exceeding concentrations were recorded with a lower frequency at lower pH values. It is also particularly relevant to note that under alkaline conditions, all samples almost exclusively display very high As concentrations. Ryan et al. (2013) associated high As concentrations under slightly alkaline pH conditions with the desorption of As, a mechanism that could potentially occur in the studied Finnish aquifer and that will be explored in future site-specific studies. Here, however, the aim is to focus mainly on regional scale aspects associated with the aquifer geology.

Elevated arsenic concentrations are found in the drilled well waters in the two southern geological subdivisions, TB and PB, which are predominantly composed of metamorphosed felsic and mafic metavolcanic rocks (including gabbro and diorite), mica schist, and mica gneiss. In the northern CFGC subdivision, where granite is a common rock type, arsenic concentrations were low. A quantitative assessment of the correlation between geological subdivisions and As concentrations is provided in Fig. S6a, in which the three boxplots illustrate the statistical distribution of the log₁₀ concentrations of dissolved As according to the geological subdivision. All the concentrations exceeding the drinking water limit of 10 µg/L (marked by a straight line in the figure) are observed in the TB and PB subdivisions. The maximum concentration (2230 µg/L) was found in the TB subdivision. The boxplots illustrate that for TB, the proportion of values exceeding the drinking water limit is about 25% (i.e. one out of four wells), which reveals the high incidence of elevated As concentrations in this subdivision. It is also noticeable that the 95% (the whisker of the boxplot) falls above 100 µg/L, while the values exceeding 1000 µg/L are outliers of these distributions, suggesting that extremely high concentrations are not frequent in the region.

On a regional scale, the results indicate a general geological influence on the dissolved concentration of As in bedrock groundwater in the Tampere region. The impact of local heterogeneities is, however, notable according to our study. Fig. 1 suggests that closely spaced wells (separated by less than 100 m) within similar geological formations displayed highly variable As concentrations. For instance, low and high arsenic contents were found in wells drilled in rock formations associated with gabbro. No clear relationship was observed between well depth and the As concentration for those wells from which depth information was available (data not reported). Quantitative information on sub-regional heterogeneities can also be inferred from the analysis of Fig. S6b, which presents 21 boxplots, each displaying a quite erratic variability in the statistical distribution of As concentrations according to the bedrock type within each macroscopic geological unit. The corresponding median values are reported in the SD (Table S4).

To provide insight into the factors influencing local heterogeneity in dissolved As concentrations, the analysis focuses on the TB region, where the concentrations were higher than the average. Fig. 2 presents the distribution of dissolved As concentrations along

Table 1
Number of samples and the minimum, median, mean, and maximum of water quality parameters for drilled wells in the Tampere region. The median values for drilled wells in the whole of Finland (*) are obtained from Lahermo et al. (2002). The limits for drinking water (**) are obtained from SMT (2001). Bold text highlights arsenic (As).

Element or variable	Units	Num. samples	Min	Med	Mean	Max	Whole country median*	Ratio Tampere region/whole Finland	Drinking water limit **	Det. limit
Well depth	m	851	10	75	81.5	270	40–60			
pH field	pH	517	5.1	7.4	7.4	9.5	7.2	1.00	6.5–9.5	
EC field	mS/m	522	5.2	26.3	28.8	149	22.9	1.10	250	
T field	°C	714	3.6	7.8	8.2	19.0	8.0	0.90		
CO ₂ field	mg/L	430	0.00	10.0	16.1	165	17.0	0.60		0.0
O ₂ field	%	467	8.4	44.5	46.5	144	39.8	1.10		0.0
Eh field	mV	137	–133	215	207	492				
pH lab	pH	637	5.4	7.6	7.4	9.3			6.5–9.5	
EC lab	mS/m	771	4.7	25.5	28.4	162			<250	
KMnO ₄ consum.	mg/L	639	0.44	3.3	4.3	28.0	3.8	0.90	20	<0.1
Hardness	°dH	823	0.04	4.9	5.3	33.0	3.4	1.4		<0.04
Ag	µg/L	873	<0.01	0.01	0.01	0.10	<0.01			<0.01
Al	µg/L	873	<1.00	2.1	16.9	953	2.5	0.8	200	<0.01
As	µg/L	1272	<0.05	2.5	34.8	2230	0.16	15.60	10	<0.05
B	µg/L	873	2.9	27.1	41.1	1710	27.0	1.00	1000	<0.5
Ba	µg/L	873	0.05	7.3	20.4	858.0	14.2	0.5		<0.05
Be	µg/L	869	<0.10	0.10	0.11	0.50	<0.1			<0.1
Bi	µg/L	869	<0.03	0.03	0.03	0.26	<0.03			<0.03
Br ⁻	µg/L	873	<0.10	0.1	11.6	582				<0.1
Ca	mg/L	873	<0.10	21.8	25.1	162	16	1.4		<0.1
Cd	µg/L	873	<0.02	0.02	0.04	1.5	<0.02		5	<0.02
Cl ⁻	mg/L	873	0.70	7.4	17.2	478	10	0.7	100	<0.2
Co	µg/L	869	<0.02	0.05	0.49	56.5	0.04	1.25		<0.02
Cr	µg/L	873	<0.20	0.20	0.27	2.4	<0.02		50	<0.02
Cu	µg/L	873	0.04	3.5	23.3	873	9.1	0.40	2000	<0.04
F ⁻	mg/L	873	<0.10	0.45	0.65	4.5	0.2	2.25	1.50	<0.1
Fe	mg/L	873	<0.03	0.05	0.57	16.8	0.03	1.67	0.4	<0.03
HCO ₃ ⁻	mg/L	639	6.7	116	117	414	83.3	1.4		<3.6
I ⁻	µg/L	376	2.0	3.7	6.1	44.7	3.0	1.20		<2.0
K	mg/L	873	0.08	2.8	3.6	74.0	3.0	1.2		<0.01
Li	µg/L	869	<0.30	5.3	6.7	84.9	3.3	1.60		<0.03
Mg	mg/L	873	<0.10	7.0	7.9	74.1	4.5	1.5		<0.1
Mn	µg/L	873	0.05	53.8	125	5800	16.3	3.30	100	<0.02
Mo	µg/L	873	<0.03	0.90	2.0	72.3	0.5	1.80		<0.03
Na	mg/L	852	2.2	14.0	19.9	221	9.0	1.5		<0.4
Ni	µg/L	873	<0.06	0.36	1.9	80.3	0.59	0.61	20	<0.06
NO ₃ ⁻	mg/L	873	<0.20	0.20	2.6	66.7	0.3	0.7	50	<0.2
Pb	µg/L	873	<0.03	0.10	0.32	8.9	0.15	0.66	10	<0.03
PO ₄ ³⁻	mg/L	470	<0.02	0.02	0.05	1.1	<0.02			<0.02
Rb	µg/L	835	0.08	2.0	2.7	42.7	1.8	1.10		<0.01
S	mg/L	389	0.30	5.6	7.1	51.1	3.8	1.50		<0.03
Sb	µg/L	873	<0.02	0.03	0.11	3.6	0.02	1.50	5	<0.02
Se	µg/L	848	<0.5	<0.5	0.72	<0.5	<0.5		10	<0.5
SiO ₂	mg/L	819	3.5	18.9	19.3	37.5	13.8	1.4		<0.06
SO ₄ ²⁻	mg/L	873	<0.30	15.9	20.2	143	12.2	1.3	250	<0.3
Sr	µg/L	869	0.11	100.0	122.0	1410.0	81.0	1.2		<0.1
U	µg/L	869	<0.01	0.85	5.2	149	0.64	1.33		<0.01
V	µg/L	869	0.02	0.17	0.47	23.3	0.16	1.10		<0.02
Zn	µg/L	873	<0.20	15.3	75.8	8750	21.7	0.70		<0.02

with the concentration of As in the bedrock near the city of Tampere. The figure also illustrates the major faults and deformation zones (FDZs) detected in the region based on geophysical surveys and geological mapping (Nironen et al., 2016). A visual inspection of the map suggests that the highest dissolved concentrations correlate well with the detected FDZs. In particular, a similarity is noted between the spatial orientation of the highest concentrations and that of FDZs. Two orthogonal systems of FDZs are observed, one oriented NW–SE and the other one oriented NEE–SWW. It can be readily seen that the major dissolved-phase As concentrations tend to cluster along the FDZs. Using this visually based correlation approach, it is possible to postulate the presence of other potential, still undetected FDZs (dotted lines in Fig. 2), consistent in orientation with the confirmed FDZs. On the other hand, the spatial correlation between detected FDZs and solid-phase concentrations is visually less distinct than for dissolved-phase concentrations. This may indicate that the hydrogeological conditions and

transport of As might be more important factors than the actual location of the As source.

The geometrical relationships between detected FDZs and As concentrations were evaluated for both solid and dissolved phases, as follows. A GIS calculation was performed to obtain the closest distance (r) of each sample point from the confirmed FDZs. A map of these distances is reported in Fig. S7 for the entire Tampere region. The dissolved and solid concentrations at each sampling point were then compared against r . From Fig. 4a, we observe that the highest concentrations occur in the proximity of confirmed FDZs. Almost all As concentrations exceeding 100 µg/L are found at $r < 4$ km, while the concentrations tend towards lower values at $r > 4$ km. On the other hand, Fig. 4b appears to confirm that the geometrical control of the confirmed FDZs is weaker for solid-phase As in the bedrock, as noted in the initial visual assessment. While the solid-phase concentrations still show a dependence on r , the data are more scattered than for the dissolved As,

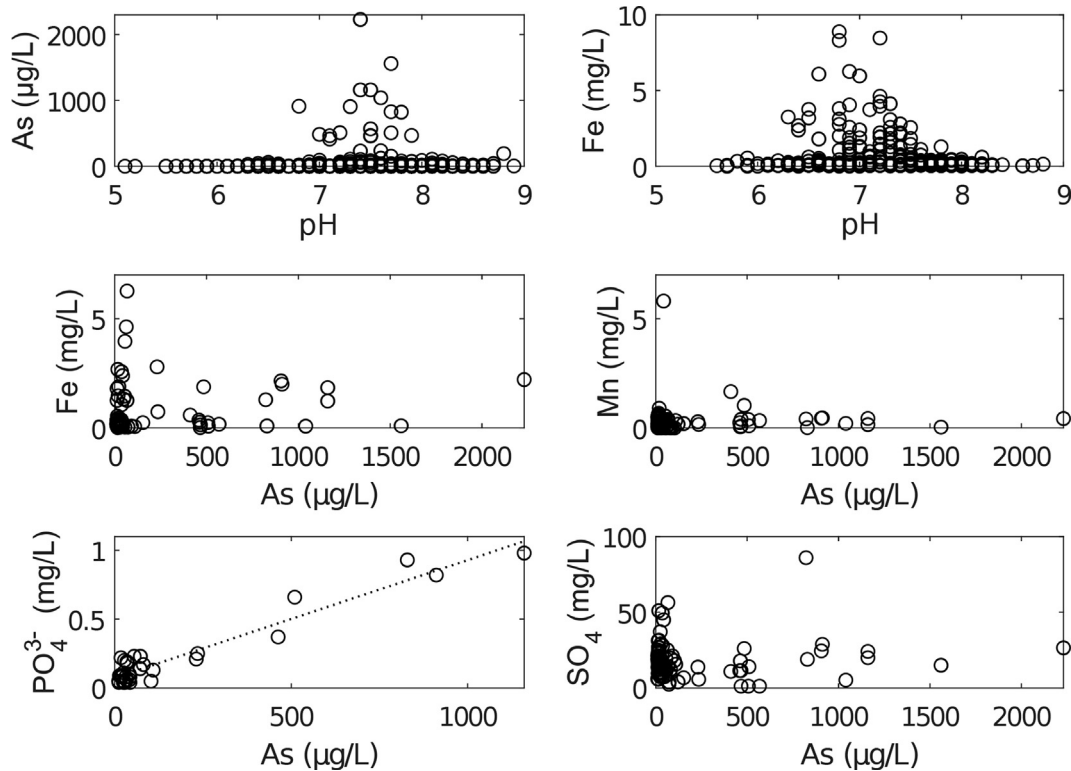


Figure 3. Scatter plots illustrating the correlations among total As, total Fe, pH, Mn, PO_4^{3-} and SO_4 . For PO_4^{3-} , the dotted line represents the best-fit linear regression showing positive correlation between phosphate and arsenic.

and fewer values are found at high concentrations. This evaluation is consistent with the previous analysis by Eilu and Lahtinen (2004).

To quantify the stronger relationship of dissolved concentrations with FDZs compared to solid phase concentrations, Fig. 5 reports the results from the spatial-dependent normalized mean As concentration, $C'(R)$, in both phases. For a specific distance threshold R , we first calculated the mean concentration such that:

$$\bar{C}(R) = \frac{1}{n_s} \sum_{i=1}^{n_s} C_i(r < R) \quad (1)$$

where n_s is the number of samples found within R , and C_i is the concentration of the i th sample. Then, we normalized $\bar{C}(R)$ such that

$$C'(R) = \frac{\bar{C}(R)}{\bar{C}(L)} \quad (2)$$

where L is the maximum distance observed from the datasets (close to $L = 20$ km for both phases). This normalization allows a direct comparison of the two variables. $C'(R) > 1$ can be interpreted as a relative increase in mean concentrations compared to the mean concentration value of all measurements, $\bar{C}(L)$. From Fig. 5, it can be observed that the relative increase of both dissolved and solid phase concentrations show a clear positive dependence with FDZs. However, the normalized mean dissolved As concentrations are higher than solid phase concentrations while approaching the FDZs. For instance, for a threshold $R = 1000$ m, the mean dissolved phase concentrations are 1.7–1.8 times higher than further away from FDZs, while solid phase concentrations are only 1.5–1.6 higher than further away from FDZs. The relative increases of concentrations for the two phases become similar at a distance of about 10 km.

In light of these observations, we conclude that the accurate identification of geological structures, in particular FDZs, can provide key insights to properly map areas with potential risk of elevated As concentrations in bedrock groundwater. It is stressed that FDZs were identified via geological and geophysical approaches (Nironen et al., 2016), and thus independent from the occurrence of As concentrations. While the presence of geological sources is a necessary condition for dissolved As concentrations to occur (Lipfert et al., 2006; Peters, 2008; O'Shea et al., 2015; Yang et al., 2015), our findings suggest that the sole characterization of the spatial distribution of solid phase concentrations without an assessment of structural geology could be insufficient to properly identify areas potentially most prone to health risks. Although previous studies have already reported the need for accurate geological characterization of the bedrock (e.g. Ryan et al., 2013; Mango and Ryan, 2015; O'Shea et al., 2015), to our best knowledge no previous studies on fractured aquifers appear to have reported such as clear and quantitative relationships between the distance from FDZs and occurrence of elevated As concentrations.

4. Potential mechanisms controlling elevated As concentrations near FDZs

A variety of physical and geochemical mechanisms can intervene to control As primary and secondary sources and its mobility in fractured aquifers (e.g. Welch et al., 2000; Peters, 2008). Here, we highlight and discuss four mechanisms potentially controlling the occurrence of elevated As aqueous concentrations near FDZs in the Tampere area. Some of these mechanisms can be identified based on the results from our regional-scale assessment and are consistent with previous observations on the aquifer. Other mechanisms can be only postulated here, lacking detailed information for their proof and requiring more analysis to be confirmed.

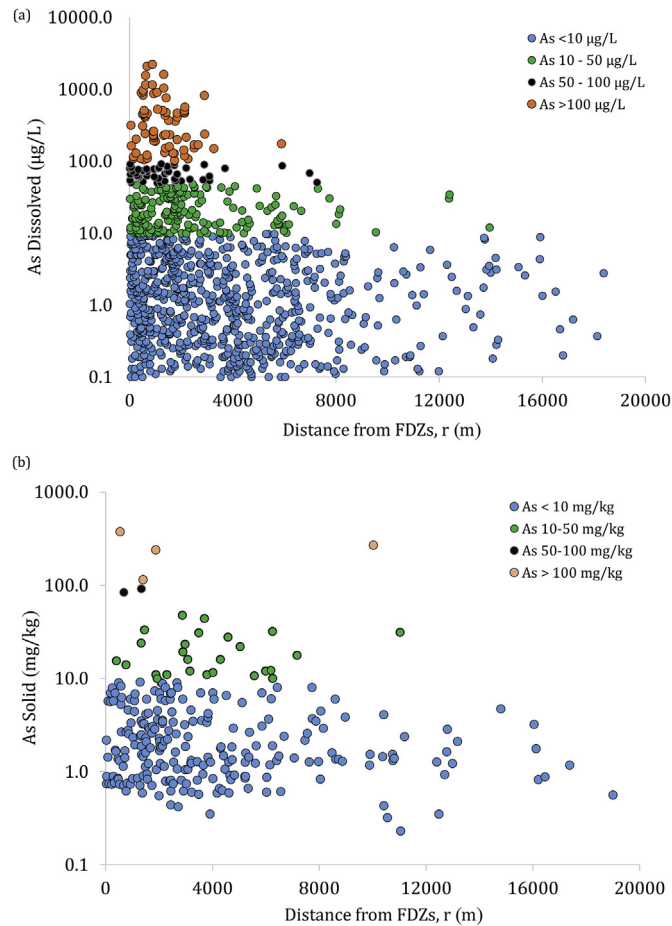


Figure 4. Comparison of concentrations of (a) dissolved As ($\mu\text{g/L}$) and (b) solid phase As (mg/kg) with distance, r (m), from detected fault and deformation zones (FDZs) detected via geological and geophysical surveys, showing the geometrical dependence of As concentrations and major geological features.

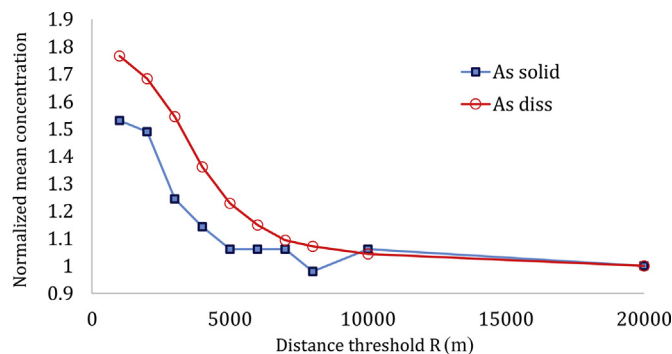


Figure 5. Normalized mean concentrations of arsenic in solid and dissolved phases for samples collected below specific distance thresholds R (m) from fault and deformation zones detected via geological and geophysical surveys.

4.1. Preferential oxidation of As-bearing sulfides near FDZ

It is generally acknowledged that arsenopyrite and similar sulfide-rich minerals are the primary sources of As in the Tampere region (e.g. Backman et al., 2006). We noted however that no preferential accumulation of sulfide-rich minerals has been reported in FDZs of the Tampere region (Eilu and Lahtinen, 2004). Instead, these minerals appear more randomly disseminated in the bedrock, consistent for instance with observations from

meta-sedimentary rocks in Central Maine, USA (e.g. O'Shea et al., 2015), or in narrow Au-bearing shear zones (e.g. Ruskeeniemi et al., 2007). Sulfide oxidation and consequential As leaching is a transport- and surface-limited process, which could be promoted by more intense weathering and fracturing near FDZs. Here, not only oxygen transport and As mobility can be enhanced compared to the weakly permeable bedrock, but fracturing also increases the exposed reactive surface areas subject to increased water–rock interaction. The combination of these processes could boost sulfide weathering and increase dissolved As levels in the bedrock groundwater. This would be qualitatively similar to what occurs at sulfide-rich mining waste sites (e.g. Lorca et al., 2016), where rate-limited sulfide weathering has a key effect on effluent quality. Given that sulfide oxidation generates acidity, a circumneutral pH, as observed in the Tampere region (Fig. 3), would be then consistent with the presence of carbonate fracture infillings (common in the Finnish bedrock) or calcareous lithologies, which buffer the acidity produced by the sulfide oxidation process. Under such conditions, Biswas et al. (2017) highlighted that oxidation of sulfide can precipitate Fe oxides, which could sequester As instead of releasing it into groundwater. However, in the Tampere region we found almost no correlation between As and SO_4 (Fig. 3) with correlation coefficient $\rho < 0.05$. Moreover, SO_4 concentrations remain relatively low (average of 20.2 mg/L, with peaks of 143 mg/L, Table 1) compared to the higher concentrations (hundreds of mg/L) expected for sulfide-oxidation-dominated As-polluted sites (Smedley and Kinniburgh, 2013).

4.2. Fractures-controlled groundwater mixing near FDZs

The expected more intense fracture frequency near FDZs than in the bedrock matrix could create preferential flow routes in the bedrock and increase the lateral flow connectivity of adjacent fractures. Hydraulic connectivity may have a direct impact on the tendency of water bodies to mix. Higher connectivity can be translated into larger potential source areas of dissolved As concentrations. Indeed, As-rich mineral sustaining the dissolved As concentration may also be found both longitudinally and transversally to the main fracture direction. Once formed, dissolved As can be transported towards the FDZs, which can act as a natural receiving boundary of multiple water-bearing fractures. Mixing is particularly emphasized when drilled wells intersect multiple water-bearing fractures and bedrock lithologies (e.g. Ayotte et al., 2011), since the resulting mixed water composition is directly impacted by the flux-averaged concentration of components arriving at the well from different depths (e.g. Pedretti and Fiori, 2013; Pedretti et al., 2014).

To corroborate the impact of mixing on the resulting geochemical composition of the well groundwater, it is first noted that the analysis was based on bedrock groundwater extracted from relatively shallow private wells (average depth about 80 m) with a modest yield ($< 10\text{--}20 \text{ m}^3/\text{month}$) being used by individual households. Such modest pumping rates imply, on average, a limited capture zone near the wells. However, increasing the pumping rates (for instance, for future expansions of the households) may result in a change in the capture zones, and consequently on the geochemical composition of the groundwater. In particular, greater mixing of surficial oxic and deeper reduced waters is expected, as graphically conceptualized in Fig. S8a, highlighting the role of water bearing fractures in the domain.

This conceptual model is consistent with the results reported by Backman et al. (2006), who monitored a selected well (#3) for six months between April and August 2005, and during which period the pumping rates were progressively increased from $0.14 \text{ m}^3/\text{d}$ to about $200 \text{ m}^3/\text{d}$. Speciation and As analyses were conducted on samples collected over time from the well.

The results are presented in Fig. S8b. It can be observed that the increased pumping rates had a minor effect on the total As concentration. However, arsenite became increasingly dominant immediately after the pumping rate was slightly increased, from 0.14 to 5.6 m³/d, and then stabilized as the deeper and reduced part of the aquifer started to feed water in. Interestingly, much more intensive pumping (from 5.6 to 200 m³/d) did not affect the concentration or speciation any further. The outcome from the pumping tests on well #3 under variable discharge rates indicates that mixing of oxic and reduced waters may indeed occur, according to a conceptual model presented in Fig. S8a. Similar conceptual models based on As-rich groundwater mixing have been proposed by others (e.g. Yang et al., 2015; Bondu et al., 2017). It is noteworthy from these results how quickly the increased pumping was reflected in the arsenite/arsenate ratio in this well, demonstrating that even small changes in water consumption would require reassessment of the health risks. The analysis suggests that for the local hydrogeological conditions near the analyzed well, total As concentrations may be insensitive to the pumping rates, in contrast, for instance, to what has been reported from other fractured aquifers (Ayotte et al., 2015) and other observations on Finnish aquifers (Loukola-Ruskeeniemi et al., 2007). However, since the detailed analysis of one well is not sufficient to generalize the behavior of such heterogeneous systems, further investigation is needed in the future to monitor the geochemical response of other sampling points in the domain, and to generalize the conclusions regarding the impact of pumping rates in the Tampere region.

4.3. (De)sorption of As from/to secondary As sources

Secondary As sources can play a key role in the mobility of As in the Tampere region. In particular, desorption of As from amorphous Fe(III) oxyhydroxides (HFOs) (e.g. Peters and Burkert, 2008) could occur in the study area. Previous studies (e.g. Backman et al., 2006; Loukola-Ruskeeniemi et al., 2007) already highlighted that in the oxidized top soils secondary As is bound to HFOs and clayish materials, while in the deep till As is still bound in sulfide fragments. In the upper few tens of meters in the Finnish bedrock, HFOs precipitates are commonly observed on fresh rock surfaces or on top of fracture infillings, evidencing transport and dynamics of the hydrogeochemical cycle with clear connections to the FDZs. Indeed, it has been often suggested that observation of HFOs in fractures would indicate routes for oxic waters and therefore, could also potentially host As-bearing secondary minerals in the flowing fractures. Secondary sources may explain the diverging behavior of As and SO₄ concentrations. From Fig. 3, we observe that Fe tends to reduce as As concentrations increase, a behavior closely followed by Mn, which also forms As-bearing minerals. As indicated by Smedley and Kinniburgh (2013), under oxidizing conditions (i.e. the shallow parts of the Tampere aquifer), desorption of As and other oxyanion-forming elements from metal oxides can occur (especially of Fe and Mn). Under reducing conditions, metal oxides can still occur, although reductive dissolution of Fe oxides could also play a key role in the release of As. Sorption/desorption on HFOs and similar minerals can create a competition between As and other anionic species can occur under these circumstances. Our results indicate for instance a clear positive correlation between As and P at circumneutral pH (Fig. 3), confirming the well-known affinity between these anions.

4.4. Implication of recharge water residence time

The residence time of the recharge water in the aquifer could also have a significant impact on the expected As concentrations

(e.g. Lipfert et al., 2006; Ryan et al., 2013; Bondu et al., 2017). While this study lacks of specific hydrogeological information to quantify such time, we consider that geochemically evolved groundwater should reflect a more prolonged interaction between water and crystalline rock than young water, and therefore contain greater As concentrations as a consequence of the prolonged interaction of water and As-rich minerals. Bondu et al. (2017) observed that high As concentrations were associated with low Ca/Na ratios, which was explained by silicate and carbonate weathering, cation exchange processes, and an extended interaction between As-bearing minerals and recharging water. This observation appears consistent with the behavior of the analyzed Finnish aquifer. Recalling Fig. S3, the highest As concentrations were also found at low Ca/Na ratios. In Finnish crystalline systems, larger Ca/Na ion ratios have been interpreted as representative of shallower water circulations, while lower Ca/Na ratios are interpreted as representative of deeper circulation within the aquifer (Pitkänen et al., 2002). It should be however noted that in shallow crystalline aquifers, the dissolution or weathering of fracture-infilling minerals, including Ca-bearing carbonates and Na-bearing silicates such as plagioclase could also contribute to preferential Ca and Na enrichment of circulating groundwater near FDZs, masking the effects of cation exchange. Quantifying the implications of silicate weathering at such large scales is also not trivial, as several local-scale mechanisms control the rate of weathering of silicates in fractured media (White, 1995; White and Brantley, 2003), in addition to the impact of mineralogical heterogeneity. Fracture-specific investigations are therefore required to elucidate whether these processes control As, Ca and Na enrichment in groundwater near FDZs. In general, additional hydrogeological assessment, including through the support of isotopic dating and mathematical modeling, is needed to clarify the residence time in the system as well as the other abovementioned processes controlling As mobility.

5. Conclusion

Evidence of high dissolved As concentrations in groundwater from fractured bedrock aquifers in the Tampere region led to an extensive geochemical characterization of more than 1200 wells to understand the behavior of As and to evaluate the potential for health risks in the region. The present study revisits part of this dataset, focusing on the link between macroscopic geological patterns and the spatial distribution of dissolved As in the system, with the purpose of illustrating a smart geologically-based approach to delineate aquifer zones more prone to As-related health risk.

Three main conclusions from this study can be listed as follows:

- (1) The strong influence of physical and geochemical heterogeneity on the fate of dissolved arsenic requires quantifying the implication of regional-scale geological patterns in the fractured metamorphic bedrock to adequately control the distribution of As concentrations in both dissolved and solid phases.
- (2) Dissolved concentrations appear to be directly dependent on the distance from faults and deformation zones (FDZs) detected via geological and geophysical surveys. Notably, it was observed that the highest concentrations occur exclusively near FDZs while concentrations tend to be lower as the distance from FDZs increases. Dissolved As exceeding 100 µg/L was found at distances below 4 km from the detected FDZs, while concentrations drop below the drinking limits at about 8 km from the FDZs.
- (3) Geological sources (i.e. the abundance of As-bearing minerals) provide only a partial explanation for this behavior, as we observed a weaker spatial dependence of solid-phase concentrations on FDZs compared to dissolved concentrations.

It is concluded that macroscale relationships between arsenic and geological/geochemical features are of fundamental importance to optimize future studies exploring the local-scale processes controlling the occurrence of As in site-specific wells. In the Tampere area, future investigation will indeed mainly target wells located nearby FDZs, as those mostly prone to high risk from human consumption of bedrock groundwater. Future developments of the study include local-scale analyses focused on the understanding of the key mechanisms explaining the preferential occurrence of As near FDZs. Due to the regional scale of the analysis, such mechanisms remain unclear and multiple hypotheses need to be corroborated with site-specific studies on the aquifer. Postulated mechanisms include: (1) the control of aquifer flow by bedrock fractures near FDZs, where groundwater may preferentially circulate; (2) enhanced oxidizing conditions of sulfides (although low SO₄ concentrations are observed from the experimental database); (3) geochemical dynamics associated to As-bearing secondary minerals, such as HFOs; (4) implication of FDZs on the recharge water residence time in the system.

Acknowledgements

This work was supported by GTK (internal funding), EU Life-Environment Program (RAMAS project) and EU Life+Project focusing on natural aggregate resources (ASROCKS). The cities of Tampere and Orivesi provided As data from their municipalities. We acknowledge Mikael Eklund, Raimo Lahtinen, Arto Pullinen, Roy Siddall, Sirkka Vartiainen, and Labtium Oy staff for their support. The authors acknowledge Francesca Micheletti and another anonymous reviewer, whose comments have contributed to increase the quality of this manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.gsf.2018.12.004>.

References

- Artimo, A., Mäkinen, J., Berg, R.C., Abert, C.C., Salonen, V.-P., 2003. Three-dimensional geologic modeling and visualization of the Virttaankangas aquifer, southwestern Finland. *Hydrogeology Journal* 11, 378–386.
- Ayotte, J.D., Szabo, Z., Focazio, M.J., Eberts, S.M., 2011. Effects of human-induced alteration of groundwater flow on concentrations of naturally-occurring trace elements at water-supply wells. *Applied Geochemistry* 26, 747–762.
- Ayotte, J.D., Belaval, M., Olson, S.A., Burrow, K.R., Flanagan, S.M., Hinkle, S.R., Lindsey, B.D., 2015. Factors affecting temporal variability of arsenic in groundwater used for drinking water supply in the United States. *The Science of the Total Environment* 505, 1370–1379.
- Backman, B., Luoma, S., 2016. Arsenic in bedrock groundwater in Tampere region, South Finland. In: *Arsenic Research and Global Sustainability: Proceedings of the Sixth International Congress on Arsenic in the Environment (As2016)*, June 19–23, 2016. CRC Press, Stockholm, Sweden, p. p31.
- Backman, B., Hiisvirta, L., Ilmasti, M., Lahermo, P., 1994. Arseenin ja muiden raskasmetallien sekä näihin liittyvien anionien esiintyminen porakaivoissa. *Vesitalous* 35, 11–18 (in Finnish).
- Backman, B., Luoma, S., Ruskeeniemi, T., Karttunen, V., Talikka, M., Kajja, J., 2006. Natural Occurrence of Arsenic in the Pirkanmaa Region of Finland, vol. 57. Geological Survey of Finland Report.
- Baris, D., Waddell, R., Freeman, L.E.B., Schwenn, M., Colt, J.S., Ayotte, J.D., Ward, M.H., Nuckols, J., Schned, A., Jackson, B., et al., 2016. Elevated bladder cancer in northern new England: the role of drinking water and arsenic. *Journal of the National Cancer Institute* 108, djw099.
- Barringer, J.L., Reilly, P.A., 2013. Arsenic in groundwater: a summary of sources and the biogeochemical and hydrogeologic factors affecting arsenic occurrence and mobility. In: *Current Perspectives in Contaminant Hydrology and Water Resources Sustainability*. InTech.
- Biswas, A., Hendry, M.J., Essilfie-Dughan, J., 2017. Geochemistry of arsenic in low sulfide-high carbonate coal waste rock, Elk Valley, British Columbia, Canada. *The Science of the Total Environment* 579, 396–408.
- Bondur, R., Cloutier, V., Rosa, E., Benzaazoua, M., 2016. A review and evaluation of the impacts of climate change on geogenic arsenic in groundwater from fractured bedrock aquifers. *Water, Air, & Soil Pollution* 227, 296.
- Bondur, R., Cloutier, V., Rosa, E., Benzaazoua, M., 2017. Mobility and speciation of geogenic arsenic in bedrock groundwater from the Canadian Shield in western Quebec, Canada. *The Science of the Total Environment* 574, 509–519.
- Corkhill, C.L., Vaughan, D.J., 2009. Arsenopyrite oxidation – a review. *Applied Geochemistry* 24, 2342–2361.
- Eilu, P., Lahtinen, R., 2004. Arseeni kallioperässä ja malmituneissa vyöhykkeissä. Summary: anomalous arsenic in bedrock and ores in Finland. In: Loukola – Ruskeeniemi, K., Lahermo, P. (Eds.), *Arseeni Suomen Luonnossa – Ympäristövaikutukset ja riskit (Arsenic in Finland: Distribution, Environmental Impacts and Risks)*. Geological Survey of Finland, Espoo, pp. 29–43 (in Finnish with English abstract).
- Foster, A.L., Kim, C.S., 2014. Arsenic speciation in solids using X-ray absorption spectroscopy. *Reviews in Mineralogy and Geochemistry* 79, 257–369.
- Haavisto-Hyvärinen, M., Kutvonen, H., 2007. Maaperäkartan Käyttöopas. Internal Report. Geological Survey of Finland, Espoo (in Finnish).
- Hunt, K.M., Srivastava, R.K., Elmets, C.A., Athar, M., 2014. The mechanistic basis of arsenicosis: pathogenesis of skin cancer. *Cancer Letters* 354, 211–219.
- Kähkönen, Y., Leveinen, J., 1994. Geochemistry of metasedimentary rocks of the paleoproterozoic Tampere schist belt, southern Finland. In: Nironen, M., Kähkönen, Y. (Eds.), *Geochemistry of Proterozoic Supracrustal Rocks in Finland*. Geological Survey of Finland, Espoo, pp. 117–136. Special paper.
- Koljonen, T., 1992. The Geochemical Atlas of Finland, Part 2 – till. Internal Report. Geological Survey of Finland, Espoo (in Finnish).
- Korsman, K., Koistinen, T., Kohonen, J., Wennerström, M., Ekdahl, E., Honkamo, M., Idman, H., Pekkala, Y., 1997. Suomen Kallioperäkarta – Berggrundskarta Över Finland – Bedrock Map of Finland. 1:1 000 000. Internal Report. Geological Survey of Finland, Espoo (in Finnish).
- Lahermo, P., Tarvainen, T., Hatakka, T., Backman, B., Juntunen, R., Kortelainen, N., Lakomaa, T., Nikkarinen, M., Vesterbacka, P., Väisänen, U., Suomela, P., 2002. One thousand wells-the physical-chemical quality of Finnish well waters in 1999. Geological survey of Finland, report of investigation 155 (in Finnish with English abstract).
- Lahtinen, R., 1996. Geochemistry of Palaeoproterozoic Supracrustal and Plutonic Rocks in the Tampere-Hameenlinna Area, Southern Finland. Geological Survey of Finland Bulletin.
- Lipfert, G., Reeve, A.S., Sidle, W.C., Marvinney, R., 2006. Geochemical patterns of arsenic-enriched ground water in fractured, crystalline bedrock, Northport, Maine, USA. *Applied Geochemistry* 21, 528–545.
- Lorca, M.E., Mayer, K.U., Pedretti, D., Smith, L., Beckie, R.D., 2016. Spatial and temporal fluctuations of pore-gas composition in sulfidic mine waste rock. *Vadose Zone Journal* 15 (10). <https://doi.org/10.2136/vzj2016.05.0039>.
- Loukola-Ruskeeniemi, K., Ruskeeniemi, T., Parviainen, A., Backman, B., 2007. Arseeni Pirkanmaalla – Esiintyminen, Riskinarviointi ja Riskinhallinta. RAMAS-Hankkeen Tärkeimmät Tulokset (in Finnish with English abstract).
- MacQuarrie, K.T.B., Mayer, K.U., 2005. Reactive transport modeling in fractured rock: a state-of-the-science review. *Earth-Science Reviews* 72, 189–227.
- Mäkelä, J., 2012. Drilled Well Yield and Hydraulic Properties in the Precambrian Crystalline Bedrock of Central Finland. Doctoral Thesis. *Annales Universitatis Turkuensis A II* 267. University of Turku, Finland.
- Mango, H., Ryan, P., 2015. Source of arsenic-bearing pyrite in southwestern Vermont, USA: sulfur isotope evidence. *The Science of the Total Environment* 505, 1331–1339.
- McGroarty, E.R., Brown, C., Bargary, N., Williams, N.H., Mannix, A., Zhang, C., Henry, T., Daly, E., Nicholas, S., Petrunic, B.M., et al., 2017. Arsenic contamination of drinking water in Ireland: a spatial analysis of occurrence and potential risk. *The Science of the Total Environment* 579, 1863–1875.
- Naujokas, M.F., Anderson, B., Ahsan, H., Aposhian, H.V., Graziano, J.H., Thompson, C., Suk, W.A., 2013. The broad scope of health effects from chronic arsenic exposure: update on a worldwide public health problem. *Environmental Health Perspectives* 121, 295–302.
- Nironen, M., Lahtinen, R., Koistinen, T., 2002. Suomen geologiset aluenimet – yhtenäisempään nimitykseen. *Geologi* 54, 8–14 (in Finnish).
- Nironen, M., Kousa, J., Luukas, J., Lahtinen, R., 2016. Suomen Geologinen Kartta – Kallioperä – Geologiska Karta Över Finland – Berggrund – Geological Map of Finland – Bedrock 1 : 1 000 000. Geological Survey of Finland (GTK), Espoo, Finland.
- Ojakangas, R.W., 1986. An Early Proterozoic metagraywacke-slate turbidite sequence: the Tampere schist belt, southwestern Finland. *Bulletin of the Geological Society of Finland* 58, 241–261.
- O’Shea, B., Stransky, M., Leitheiser, S., Brock, P., Marvinney, R.G., Zheng, Y., 2015. Heterogeneous arsenic enrichment in meta-sedimentary rocks in central Maine, United States. *The Science of the Total Environment* 505, 1308–1319.
- Parviainen, A., Loukola-Ruskeeniemi, K., Tarvainen, T., Hatakka, T., Härmä, P., Backman, B., Ketola, T., Kuula, P., Lehtinen, H., Sorvari, J., et al., 2015. Arsenic in bedrock, soil and groundwater – the first arsenic guidelines for aggregate production established in Finland. *Earth-Science Reviews* 150, 709–723.
- Pedretti, D., Fiori, A., 2013. Travel time distributions under convergent radial flow in heterogeneous formations: insight from the analytical solution of a stratified model. *Advances in Water Resources* 60, 100–109.
- Pedretti, D., Fernández-García, D., Sanchez-Vila, X., Bolster, D., Benson, D.A., 2014. Apparent directional mass-transfer capacity coefficients in three-dimensional anisotropic heterogeneous aquifers under radial convergent transport. *Water Resources Research* 50, 1205–1224.
- Pedretti, D., Russian, A., Sanchez-Vila, X., Dentz, M., 2016. Scale dependence of the hydraulic properties of a fractured aquifer estimated using transfer functions. *Water Resources Research* 52, 5008–5024.

- Peters, S.C., 2008. Arsenic in groundwaters in the Northern Appalachian Mountain belt: a review of patterns and processes. *Journal of Contaminant Hydrology* 99, 8–21.
- Peters, S.C., Burkert, L., 2008. The occurrence and geochemistry of arsenic in groundwaters of the Newark basin of Pennsylvania. *Applied Geochemistry* 23, 85–98.
- Pitkänen, P., Kaija, J., Blomqvist, R., Smellie, J. a. T., Frapé, S.K., Laaksoharju, M., Negrel, P., Casanova, J., Karhu, J., 2002. Hydrogeochemical Interpretation of Groundwater at Palmottu. EUR 19118, pp. 155–167.
- Rahman, S., Kim, K.-H., Saha, S.K., Swaraz, A.M., Paul, D.K., 2014. Review of remediation techniques for arsenic (As) contamination: a novel approach utilizing bio-organisms. *Journal of Environmental Management* 134, 175–185.
- Ravenscroft, P., Brammer, H., Richards, K., 2009. Arsenic Pollution: A Global Synthesis. John Wiley & Sons, pp. 1–24.
- Ruskeeniemi, T., Kärkkäinen, N., Backman, B., Talikka, M., Vuori, S., Loukola-Ruskeeniemi, K., Parviainen, A., 2007. Arsenic concentrations in groundwater as a potential exploration tool for gold in the Pirkanmaa region, Finland. In: *Digging Deeper: Proceedings of the Ninth Biennial Meeting of the Society for Geology Applied to Mineral Deposits*, Dublin, Ireland 20th–23rd August 2007. Irish Association for Economic Geology, Dublin, pp. 501–504.
- Ruskeeniemi, T., Backman, B., Loukola-Ruskeeniemi, K., Sorvari, J., Lehtinen, H., Schultz, E., Mäkelä-Kurtto, R., Rossi, E., Vaajasaari, K., Bilaletdin, Ä., 2011. Arsenic in the Pirkanmaa region, southern Finland: from identification through to risk assessment to risk management. Special Paper, Geological Survey of Finland. In: *Geoscience for Society: 125th Anniversary*, vol. 49, pp. 21–227.
- Ryan, P.C., Kim, J., Wall, A.J., Moen, J.C., Corenthal, L.G., Chow, D.R., Sullivan, C.M., Bright, K.S., 2011. Ultramafic-derived arsenic in a fractured bedrock aquifer. *Applied Geochemistry* 26, 444–457.
- Ryan, P.C., Kim, J.J., Mango, H., Hattori, K., Thompson, A., 2013. Arsenic in a fractured slate aquifer system, New England, USA: influence of bedrock geochemistry, groundwater flow paths, redox and ion exchange. *Applied Geochemistry* 39, 181–192.
- Saarnisto, M., Saarinen, T., 2001. Deglaciation chronology of the Scandinavian ice sheet from the lake Onega basin to the Salpausselkä End Moraines. *Global and Planetary Change* 31, 387–405.
- Smedley, P.L., Kinniburgh, D.G., 2013. Arsenic in groundwater and the environment. In: *Essentials in Medical Geology*. Springer, Dordrecht, pp. 279–310.
- Stober, I., Bucher, K., 2007. Hydraulic properties of the crystalline basement. *Hydrogeology Journal* 15, 213–224.
- Vaasjoki, M., Korsman, K., Kostinen, T., 2005. In: Lehtinen, M., Nurmi, P.A., Rämö, O.T. (Eds.), *Precambrian Geology of Finland: Key to the Evolution of the Fennoscandian Shield*. Elsevier, Science B. V., Amsterdam, p. 736.
- Verplanck, P.L., Mueller, S.H., Goldfarb, R.J., Nordstrom, D.K., Youcha, E.K., 2008. Geochemical controls of elevated arsenic concentrations in groundwater, Ester Dome, Fairbanks district, Alaska. *Chemical Geology* 255, 160–172.
- Welch, A.H., Westjohn, D.B., Helsel, D.R., Wanty, R.B., 2000. Arsenic in ground water of the United States: occurrence and geochemistry. *Ground Water* 38, 589–604.
- White, A.F., 1995. Chemical weathering rates of silicate minerals in soils. *Reviews in Mineralogy and Geochemistry* 31, 407–461.
- White, A.F., Brantley, S.L., 2003. The effect of time on the weathering of silicate minerals: why do weathering rates differ in the laboratory and field? *Chemical Geology* 202, 479–506.
- Yang, Q., Culbertson, C.W., Nielsen, M.G., Schalk, C.W., Johnson, C.D., Marvinney, R.G., Stute, M., Zheng, Y., 2015. Flow and sorption controls of groundwater arsenic in individual boreholes from bedrock aquifers in central Maine, USA. *The Science of the Total Environment* 505, 1291–1307.