Submarine groundwater discharge at Forsmark, Gulf of Bothnia, provided by Ra isotopes

Lindsay Krall, Giada Trezzi, Jordi Garcia-Orellana, Valenti Rodellas,
Carl-Magnus Morth, Per Andersson

► To cite this version:

Lindsay Krall, Giada Trezzi, Jordi Garcia-Orellana, Valenti Rodellas, Carl-Magnus Morth, et al.. Submarine groundwater discharge at Forsmark, Gulf of Bothnia, provided by Ra isotopes. *Marine Chemistry*, 2017, 196, pp.162-172. 10.1016/j.marchem.2017.09.003 . hal-01765616

HAL Id: hal-01765616

<https://hal.science/hal-01765616>

Submitted on 22 Jun 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

**Submarine groundwater discharge at Forsmark, Gulf of Bothnia,
provided by Ra isotopes**

Lindsay Krall^{*1,2,3}, *Giada Trezzi*⁴, *Jordi Garcia-Orellana*⁴, *Valenti Rodella*⁵, *Carl-Magnus
Mörth*², *Per Andersson*³

¹The Swedish Nuclear Fuel and Waste Management Company, Sweden

²Department of Geological Science, Stockholm University, Stockholm Sweden

³Department of Geosciences, Swedish Museum of Natural History, Stockholm, Sweden

⁴Institut de Ciència i tecnologia Ambientals, Universitat Autònoma de Barcelona, Spain

⁵ CEREGE, Aix-Marseille Université, Aix-en-Provence, France

Abstract

Submarine groundwater discharge (SGD) to the Gulf of Bothnia, Baltic Sea, has been believed to be insignificant from hydrological models, yet geochemical investigations of SGD in this basin are limited. In this study, ^{223}Ra , ^{224}Ra , ^{226}Ra , and ^{228}Ra have been complemented by stable $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotopes to characterize and quantify SGD rates from the coast of Forsmark, Sweden to Öregrundsgrepen Strait (Gulf of Bothnia). In shallow bays, SGD has been traced using relations between Ra, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotopes and salinity. Zonal SGD from deformation zones, expressed as hydraulically conductive fractures, overlain by the Börstilåsen esker, a strip of conductive gravel sediment, have been traced through offshore $^{224}\text{Ra}_{\text{xs}}$ and ^{226}Ra trends. On the basis of a $^{224}\text{Ra}_{\text{xs}}$ mass balance, the SGD flow rate ranges from $(5.5 \pm 3.0) \cdot 10^3 \text{ m}^3 \text{ d}^{-1}$ to $(950 \pm 520) \cdot 10^3 \text{ m}^3 \text{ d}^{-1}$. These rates are up to two orders of magnitude higher than those determined from local hydrological models, which consider only the fresh component of SGD. From the divergence between the hydrological and $^{224}\text{Ra}_{\text{xs}}$ models, it is inferred that the site is influenced by a component of recirculated seawater.

1 Introduction

Submarine groundwater discharge (SGD) is defined as the flow of water across the sea floor, including the outward flow of fresh meteoric groundwater and the recirculation of seawater through the coastal aquifer (Burnett, 2003; Moore, 2010). In several areas of the world, this process has been recognized as an important pathway for the transport of chemical compounds, including: nutrients (e.g. Rodellas et al., 2015), metals (e.g. Windom et al., 2006; Trezzi et al., 2016), pollutants (e.g. Boehm et al., 2004), and natural radionuclides (e.g. Garcia-Orellana et al., 2013).

The Ra isotope quartet (long-lived ^{226}Ra and ^{228}Ra and short-lived ^{223}Ra and ^{224}Ra ; $t_{1/2} \sim 1600$ y, 5.75 y, 11.4 d, and 3.66 d, respectively) has been used to trace and quantify the flow of

SGD in several environments, particularly the Pacific, Atlantic, and Mediterranean coasts (Swarzenski et al., 2007; Swarzenski and Izbicki, 2009; Kwon et al., 2014 and references therein). Through application of ^{228}Ra , Moore et al. (2008) determined that the rate of SGD to the upper Atlantic Ocean was similar to that freshwater inputs by rivers. Similarly, Kwon et al. (2014) developed a ^{228}Ra -based model to estimate the rate of SGD to the Atlantic and Indo-Pacific Oceans and showed that SGD was a major source of nutrients to the oceans. However, a noted source of uncertainty in the model was sparsity of ^{228}Ra observations from some areas, for instance the boreal regions, of the global ocean.

From a ^{226}Ra model, Destouni et al. (2008) suggested that the discharge of fresh groundwater accounts for ~4% of the total freshwater inflow to the boreal Baltic Sea. Nevertheless, using natural geochemical tracers off the coast of Poland, Symczycha and Pempkowiak (2016) determined that SGD processes can impact material budgets in the Baltic Sea even alongside low flow rates of fresh SGD. Little is known of SGD-driven material fluxes to the northern and eastern coasts of the Baltic Sea. However, they have been presumed to be less important than to the southern and eastern Baltic coasts (Symczycha and Pempkowiak, 2016).

Ra isotope methodology is typically applied in saline water due to the potential for Ra adsorption to particles in low salinity environments (Li and Chan, 1979; Elsinger and Moore, 1980). However, long- and short-lived Ra isotopes may allow various components of SGD to be discriminated, including relative contributions from fresh groundwater and recirculated seawater (e.g. Charette et al., 2008; Rodellas et al., 2017). Therefore, despite the brackish salinity of the Baltic Sea, it is of interest to characterize SGD to the Gulf of Bothnia using Ra isotopes.

Forsmark (Sweden) lies on the southwest coast of the Gulf of Bothnia, the northern-most basin of the Baltic Sea (Figure 1.a). As a current host of a geologic repository for low-level

radioactive waste and a proposed host of a high-level waste repository, the hydrology and geochemistry around Forsmark have been thoroughly investigated (SKB, 2008). This provides an ideal backdrop to apply Ra isotopes to quantify and characterize SGD in a brackish environment. $\delta^{18}\text{O}$, $\delta\text{-H}$ and major cation measurements complement the $^{224}\text{Ra}_{\text{xs}}$ -based SGD flow estimates. The purpose of this study is to characterize and quantify SGD from Forsmark to the Gulf of Bothnia through integration of the hydrological knowledge of the site with geochemical and isotopic tracers.

2 Site background

Baltic seawater (hereafter “brackish water”) is brackish due to mixing between fresh water sourced from the Scandinavian mainland and saline water from the north Atlantic Ocean. The salinity ranges from one in the northern Gulf of Bothnia to nine near the Danish straits. Since seawater exchange through the Danish straits is limited, tidal sea level fluctuations are minor throughout the Baltic Sea (Voipio, 1981). Symczycha and Pempkowiak (2016) have suggested that groundwater discharge to the Baltic Se occurs mainly along the southern and eastern coasts. Through geochemical methods, the rate of fresh SGD to the Bay of Puck, along the Polish coast, was determined to range from $9 \cdot 10^{-4} \text{ m}^3 \text{ m}^{-2} \text{ d}^{-1}$ to $2.8 \cdot 10^{-2} \text{ m}^3 \text{ m}^{-2} \text{ d}^{-1}$ and was correlated with monthly precipitation. The recirculated seawater component, with a rate ranging from $4 \cdot 10^{-3}$ to $4 \cdot 10^{-2} \text{ m}^3 \text{ m}^{-2} \text{ d}^{-1}$ was found to be important (Symczycha and Pempkowiak, 2016).

Forsmark, Sweden lies along the coast of the Öregrundsgrepen strait, within the Sub-Cambrian Peneplain, a widespread, low-relief landscape within Fennoscandia. The $\sim 6 \times 4 \text{ km}^2$ area investigated for the repositories reaches a maximum elevation of $\sim 20 \text{ m.a.s.l.}$ Several hydraulically conductive fracture zones intersect the bedrock surface of Öregrundsgrepen, through which the discharge of brackish-to-saline groundwater to the strait is possible

(Laaksoharju et al., 2008, Figure 1.b. and 1.c). Jarsjö et al. (2008) developed a hydraulic model for the Forsmark site and attributed up to 20% of the total freshwater input to Öregrundsgrepen ($2.4 \cdot 10^3 \text{ m}^3 \text{ d}^{-1}$ or *ca.* $1.5 \cdot 10^{-4} \text{ m}^3 \text{ m}^{-2} \text{ d}^{-1}$) to fresh SGD from diffuse sources along the coast.

Deposition of glacial sediments, such as glacial sand and clay, both with low hydraulic conductivities, occurred throughout the Forsmark land and seabed during the Pleistocene glaciations (Hedenström et al., 2008). The Börstilåsen esker, a strip of hydraulically conductive gravel sediments deposited directly over the bedrock surface, extends NW-SE across the land and seabed (Figure 1.a). These deposits are overlain by an Fe,Mn-(oxyhydr)oxide-bearing mud (Borgiel, 2004; Voipio, 1981).

Although SGD to the Swedish coast of the Baltic Sea has been presumed low, pockmarks related to permeable layers in glacial clay deposited on the seabed in the Stockholm archipelago, approximately 200 km from Forsmark, have been observed by Söderberg & Flodén (1997) and Jakobsson et al. (2016). These formations mark an area of gas (Hovland, 1985) or groundwater escape (Robb 1984) and in this region range from centimeters to tens of meters in size (Söderberg & Floden, 1997; Jakobsson et al., 2016). Limited geochemical work has been performed alongside the geophysical documentation of pockmarks along the Swedish coast. However, pockmarks on the Baltic coast of Germany were associated with an SGD rate of $9 \cdot 10^{-3} \text{ m}^3 \text{ m}^{-2} \text{ d}^{-1}$ (Schlüter et al., 2004). Symczycha and Pempkowiak (2016) suggest that discharge to the Baltic coast from glacial sediments has been underestimated.

3 Sampling and methods

3.1 Field surveys

Three sampling campaigns were performed at Forsmark, in the strait of Öregrundsgrepen, to collect water and sediment samples for Ra and geochemical analysis. In November 2013, three 25 L samples of seawater were taken directly from the Forsmark shore (S1-S3) and salinities were measured using a YSI-30 probe.

A larger campaign in spring 2014 included the collection of water samples from: three five-station transects (t1-5, t6-10, and t11-15), two stations in the shallow bay Tixelfjärden (TF1-2), four stations in the larger bay Kallrigafjärden (KF1-4), and five piezometers which represent shallow groundwater (SFM0001, SFM0032, SFM0049, SFM0059, SFM0060; ~5 m.b.s.l.). Additionally, deeper groundwater, representative of two of the fracture zones which intersect the bedrock surface of Öregrundsgrepen, was sampled from two boreholes (KFR01, KFR07A; ~50 m.b.s.l.) (Figure 1.a, 1.b). At each sea station, 50 L samples for Ra analysis and 0.5 L samples for $\delta^{18}\text{O}$, $\delta^2\text{H}$, and major cation analysis, respectively, were filtered through a 0.45 μm filter. Salinity profiles were recorded in the field at each station using a YSI-650 probe. Ten-liter groundwater samples were collected for Ra analyses, and 0.5 L for analyses of $\delta^{18}\text{O}$, $\delta^2\text{H}$, and major cations.

In October 2014, a sediment core was collected from Tixelfjärden bay using a Van Veen grab sampler in order to conduct a Ra diffusion experiment following the methodology used by Rodellas et al. (2012). Fifty liters of seawater overlying the sediment core was also collected for use in the experiment.

Figure 1: (a) Topographic map of Sweden, including Forsmark and the Gulf of Bothnia in the Baltic Sea and sampling stations in Forsmark and Öregrundsgrepen, with deformation zones, and Börstilåsen esker. (b) Conceptual illustration of Forsmark fracture network, notable geological formations, groundwater flow (narrow, solid black arrows), and potential Ra supply and removal processes (box model), modified after Follin et al. (2007).

3.2 Methods

3.2.1 Radium

On site, brackish water and groundwater samples were passed through columns loaded with 25 g of manganese-impregnated acrylic fiber (hereafter ‘Mn-fiber’) at a flow rate $<1 \text{ L min}^{-1}$ to extract the Ra isotopes (Moore, 1973; Moore et al., 1995). Two water samples were filtered through a series of two columns to check the efficiency of Ra extraction with Mn-fibers. After the Ra extraction, the Mn-fibers were rinsed with Ra-free deionized water and then partially dried (Sun and Torgersen, 1998). The short-lived Ra isotopes (^{223}Ra and ^{224}Ra) were measured within seven and three days of collection, respectively, using a Radium Delayed Coincidence Counter (RaDeCC) as described by Moore and Arnold (1996). ^{224}Ra activities were corrected for ^{228}Th and uncertainties of ^{223}Ra and $^{224}\text{Ra}_{\text{xs}}$ concentrations were estimated following Garcia-Solsona et al. (2008). Afterwards, the fibers were ashed (820 °C, 16 h), ground and transferred to hermetically sealed counting vials to determine long-lived Ra isotopes (Charette et al., 2001). After aging the vials for three weeks to ensure equilibrium between the ^{226}Ra and its daughters, ^{226}Ra and ^{228}Ra were measured using a well-type germanium gamma detector. ^{226}Ra and ^{228}Ra were determined using the ^{214}Pb and ^{228}Ac photopeaks at 352 and 911 keV, respectively. All Ra activities were corrected for radioactive decay since the time of sampling. The relative uncertainties for ^{223}Ra , $^{224}\text{Ra}_{\text{xs}}$, ^{226}Ra , and ^{228}Ra were respectively 13%, 14%, 7%, and 11% in the brackish water and 5%, 15%, 3%, and 3% in the groundwater.

3.2.2 $\delta^{18}\text{O}$, $\delta^2\text{H}$

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values were determined using cavity ring down spectroscopy on a Picaro Isotope Water Analyser, L2140-i, and is expressed vs. Vienna Standard Mean Ocean Water (VSMOW). $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values were normalized so that the difference between Standard Light Antarctic Precipitation (SLAP) and VSMOW was exactly -55.5‰ for $\delta^{18}\text{O}$ and -428‰

for $\delta^2\text{H}$. The precision for measurements were 0.1‰ for $\delta^{18}\text{O}$ and 0.6‰ for $\delta^2\text{H}$ based on standards run as samples

3.2.3 Major cations and trace elements

Cations were measured on an ICP-OES using a Thermo ICAP 6500 DUO. Calibrations were made from multi-element standards bought from LGC-PROMOCHEM and calibrations were checked with a certified standard, NIST 1640a. The NIST 1640a were within $\pm 5\%$ for all elements. Samples were diluted 100x or 10x for major cations and were run undiluted for trace elements. In some cases, an internal standard was used (Y, approx 2 mg/L) which was added by having a T-Coupling before the nebulizer (an Ultra Sonic nebulizer, Cetac U5000AT+, were used for trace elements and a VGROOVE nebulizer for major elements). After every 20 samples an internal control were analyzed, which was also used to drift correct data if necessary.

3.2.4 Diffusive flux experiments

Quantification of the Ra diffusive flux from the marine sediments was performed in order to check to contribution from of Ra from bottom sediments to the Ra inventory in seawater. The sediment core and 3 L of the brackish water collected from Tixelfjärden were placed in a plastic container and the sediments were allowed to settle. Brackish water above the core was circulated through a Mn-fiber overnight, to ensure that the water was free of Ra at the beginning of the experiment. A closed loop system was assembled using a peristaltic pump and plastic tubing, interconnecting the water overlying the core to a column containing Mn-fiber. Water continuously circulated through the tubing and the Mn-fiber. Fibers were replaced after progressively longer time periods (12, 24, 48, and 72 hours). Diffusive fluxes for each Ra isotope were estimated from the slope of the Ra activity versus incubation time regression line, divided by the core surface area plotted against incubation time to obtain fluxes in $\text{dpm m}^{-2} \text{h}^{-1}$ following the methodology of Rodellas et al. (2012).

4 Results

The measured salinities, Ra isotopes activities, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values, Ba and Ca concentrations and Ca/Mg ratios are shown alongside water column depth and distance from shore for each station in Table 1.

Table 1: Summary of results for the sampled stations. Depth of water column (DPT), distance from shore (m), and salinity alongside Ra activities in dpm 100L⁻¹, Ba in $\mu\text{g/L}$, Na and Ca in mg/L. Uncertainties for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ were ± 0.6 and ± 0.1 , respectively.

ST	DPT (m)	Sal	Dist (m)	²²³ Ra	σ	²²⁴ Ra _{xs}	σ	²²⁶ Ra	σ	²²⁸ Ra	σ	$\delta^2\text{H}$	$\delta^{18}\text{O}$	Ba	Na	Ca	Ca / Mg
t1*	6.2	4.75	220	0.67	0.10	8.1	0.9	12.8	0.6	16.1	1.1	-60.1	-7.9	17.0	1290	59	0.37
t2*	13.4	4.71	1450	0.29	0.06	2.0	0.6	12.0	0.6	15.4	0.9	-60.3	-8.0	16.6	1450	68	0.39
t3*	6.1	4.72	2730	0.22	0.05	3.7	0.5	13.2	0.7	15.9	1.1	-60.9	-7.9	14.8	1490	68	0.39
t4*	11.8	4.63	5490	0.39	0.07	3.0	0.4	15.0	0.6	15.8	0.9	-60.9	-8.0	15.8	1460	70	0.39
t5	33	4.64	7810	0.21	0.05	1.5	0.4	14.5	0.6	15.9	1.0	-60.6	-8.0	15.8	1430	69	0.39
t6*	10.5	4.82	310	0.30	0.07	2.3	0.7	11.6	1.0	15.8	1.0	-60.5	-8.0	16.9	937	42	0.36
t7*	10.6	4.76	1020	0.37	0.06	2.8	0.6	14.0	1.1	15.7	1.1	-60.3	-7.9	16.5	1405	69	0.39
t8	13.5	4.71	3100	0.38	0.06	1.7	0.5	13.3	1.6	15.2	3.4	-60.4	-8.0	16.1	1420	70	0.39
10 m		4.79		0.21	0.03	1.8	0.5					-60.2	-7.9	16.9	1480	69	
t9*	16.3	4.70	4040	0.21	0.05	2.1	0.4	15.2	0.4	16.6	2.6	-60.2	-7.9	16.8	1430	74	0.39
t10	13	4.72	6130	0.24	0.06	1.4	0.4	13.5	1.2	15.7	2.2	-59.9	-7.7	20.3			0.05
t11*	8.7	4.74	255	0.38	0.06	2.3	0.5	13.0	1.6	16.8	3.5	-60.4	-8.0	16.9	1250	55	0.37
t12*	7.89	4.71	1280	0.20	0.05	1.8	0.4	17.6	1.1	16.1	1.0	-60.0	-7.9	17.0	1010	45	0.36
t13	18.5	4.70	2170	0.28	0.06	1.3	0.4	13.8	1.1	15.4	2.4	-60.9	-7.9	18.6	1390	65	0.39
10 m		4.72		0.12	0.02	1.3	0.5					-60.4	-7.9	16.6	1460	69	
t14*	21.5	4.72	2810	0.26	0.06	1.6	0.3	10.0	1.0	17.5	2.7	-60.4	-7.9	15.6	1450	67	0.38
t15	20.5	4.72	4360	0.19	0.06	1.0	0.3	16.0	1.4	16.9	2.4	-60.3	-7.9	15.3	1440	68	0.38
KF1	4	1.71	1590	1.4	0.18	13	1.2	16.4	1.3	22.9	3.6	-64.8	-8.6	17.9	1170	68	0.47
KF2	9.4	4.29	3250	1.2	0.15	11	1.0	21.9	1.4	25.1	3.1	-62.0	-8.1	17.6	1340	69	0.41
KF3	7.2	4.19	4270	0.80	0.11	6.8	0.9	20.7	1.6	19.6	3.8	-63.2	-8.5	16.3	1110	55	0.41
KF4	8.4	4.74	4940	0.41	0.07	2.4	0.6	18.9	1.1	17.7	1.0	-61.8	-8.1	17.4	1390	68	0.38
TF1	3.7	4.84		3.7	0.31	29	2.8	23.5	0.7	38.9	1.4	-58.8	-7.6	19.3	1450	72	0.39
TF2	1.6	4.83		2.8	0.18	17	1.9	14.6	1.6	30.2	3.7	-59.6	-7.8	16.0	1470	70	0.39
S1		4.79				16	2.5	18.1	0.7	28.4	3.8						
S2		4.67				28	3.6	32.2	2.5	48.1	3.5						
S3		4.81				5.0	1.4	15.6	1.6	16.2	1.1						
Shallow groundwater from piezometer (SFM)																	
0001		0.69		8.4	1.25	220	26	328	26	290	23.0	-83.6	-11.5	30.6	165	83	2.8
0032		0.55		9.2	1.12	85	9	203	9.0	182	9.0	-84.0	-11.7	50.8	28	135	9.9
0049		0.21		3.9	0.55	68	5	50.1	2.5	95	5.0	-81.7	-11.1	21.4	18	61	8.8
0059		1.27		5.6	0.74	270	20	262	12.0	287	15.0	-80.5	-11.2	72.5	241	97	3.0
0060		0.37		4.6	0.72	73	8	177	9.0	143	8.0	-89.8	-12.6	53.9	5	98	12.4
Deep groundwater (KFR)																	
07A				288	11	719	240	1670	37	2170	54.0	-70.3	-9.0	32.5	1530	438	3.8
01				359	19	2600	290	3100	70	7200	197	-78.7	-10.3	50.6	1050	620	4.8

4.1 Salinity

In the transects (stations t1-15, 1 m depth) salinity ranged between 4.63 and 4.82. The salinity in Tixelfjärden bay (TF1-2) was slightly higher than in the offshore transects (4.83-4.84). In Kallrigafjärden bay, the salinity was lower near the streams of Forsmarksån and Olandsån (1.7, KF1) and increased toward the opening of the bay (4.7, KF4).

Salinity variation throughout the water column was within the uncertainty of the measurement (± 0.1), thus stations of < 10 m depth exhibited no significant change in salinity with depth (Figure 2). Stations with a deeper water column showed a halocline at ~ 10 m depth, where salinities decreased from ~ 4.8 to ~ 4.6 (Figure 2).

Shallow groundwaters were fresh, with a salinity range 0.4 to 1.3. However, Cl^- concentrations in the deep groundwaters were up to a factor of three greater than brackish Baltic water, thus the deep groundwaters were more saline than the Baltic water.

Figure 2: Salinity profiles for stations t1 (dashed), t3 (solid), and t5 (dotted).

4.2 *Ra isotopes*

In the transects, ^{226}Ra and ^{228}Ra activities ranged 10 – 18 and 15 – 18 dpm 100L⁻¹, respectively (Figure 3.a–b). These values are similar to those reported from the central Gulf of Bothnia, of 13.3 ± 1.2 and 14.7 ± 1.6 dpm 100L⁻¹, respectively (Porcelli et al., 2001). The ^{223}Ra and $^{224}\text{Ra}_{\text{xs}}$ activities ranged 0.19 – 0.70 and 1.0 – 8.1 dpm 100L⁻¹, respectively (Figure 3.c–d). Maximum and minimum activities were found at station t15 and t1, respectively. Gradients were observed within the first 2 km offshore for the short-lived isotopes, particularly $^{224}\text{Ra}_{\text{xs}}$ in transect t1-5 but were not observed for the long-lived isotopes.

In Kallrigafjärden bay, ^{223}Ra , $^{224}\text{Ra}_{\text{xs}}$, ^{226}Ra , and ^{228}Ra activities ranged 0.4 – 1.6, 2 – 14, 16 – 19, and 18 – 23 dpm 100L⁻¹, respectively. Activities were higher in Tixelfjärden bay: 2.7 – 3.7, 17 – 29, 15 – 24, and 30 – 39 dpm 100L⁻¹ for ^{223}Ra , $^{224}\text{Ra}_{\text{xs}}$, ^{226}Ra and ^{228}Ra , respectively.

In shallow groundwaters, long-lived Ra activities were ~2 to 27-times greater and short-lived Ra activities 0.8 – 270-times greater than the brackish water. ^{223}Ra , $^{224}\text{Ra}_{\text{xs}}$, ^{226}Ra , and ^{228}Ra ranged 3.3 – 10, 63 – 290, 48 – 350, and 90 – 310 dpm 100L⁻¹, respectively, in shallow groundwaters. Deep groundwaters were more enriched, with activities 2 – 4 orders of magnitude greater than the brackish water. Deep groundwaters ranged 280 – 380, 470 – 2900, 1600 – 3200, and 2100 – 7400 dpm 100L⁻¹ for ^{223}Ra , $^{224}\text{Ra}_{\text{xs}}$, ^{226}Ra , and ^{228}Ra , respectively. Minimum activities for the four Ra isotopes were found in SFM0049, while maximum activities in SFM0032 (^{223}Ra), SFM0059 ($^{224}\text{Ra}_{\text{xs}}$), and SFM0001 (^{226}Ra and ^{228}Ra).

4.3 $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values

Shallow groundwaters were distinct from, while deep groundwaters were similar to, the brackish water with respect to $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values (Table 1). This is because the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ signature of the deep Forsmark groundwaters was imparted by a component of Littorina Sea (7000 – 9000 BP predecessor to the Baltic Sea), whereas the shallow groundwater

signature was imparted by current meteoric waters (-89.8 to -80.5‰ $\delta^2\text{H}$ and -12.6 to -11.1‰ $\delta^{18}\text{O}$). $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in the transects ranged -60.9 to -59.9‰ $\delta^2\text{H}$ and -8.0 to -7.7‰ $\delta^{18}\text{O}$, respectively. A mixing line between the Forsmark data and results from the central Baltic Sea (Fröhlich et al. 1988) as an offshore end-member, deviate from the local meteoric water line due to the increased influence of evaporation in the open Baltic (Figure 4).

Brackish water in Tixelfjärden bay was enriched in heavy isotopes (maximum -58.8‰ $\delta^2\text{H}$ and -7.59‰ $\delta^{18}\text{O}$) relative to the transects, suggesting a local influence of evaporation, which can produce this heavy signature. Application of the model by Fröhlich et al. (1988) to the Forsmark coast indicates that the rate of evaporation from Tixelfjärden bay is 15% of the rate of water inflow from Öregrundsgrepen to Tixelfjärden bay. This is corroborated by Engqvist et al. (2006), who demonstrated a faster rejuvenation of water towards the center of the strait. The lighter signature (lower isotope values) in Kallrigafjärden bay is reminiscent of influence by current meteoric water.

Figure 3.a–d: ^{226}Ra and ^{228}Ra (a–b) and $^{224}\text{Ra}_{\text{xs}}$ and ^{223}Ra (c–d) activities as a function of distance offshore (m). Circle to indicate systematic increases in $^{224}\text{Ra}_{\text{xs}}$ and ^{226}Ra activity.

4.4 Geochemistry

Geochemical results (Na, Ca, Ca/Mg, and Ba) are presented in Table 1. Ba exhibits chemical behavior similar to Ra due to size and ionic radius. Ca/Mg ratios can be used to trace mixing between groundwaters and brackish water, as Ca in groundwater is predominantly sourced by aquifer solids whereas Mg by the brackish water (Smellie et al. 2008). Therefore, geochemistry may be used to investigate Ra geochemistry and mixing between ground- and brackish Baltic water. Ba concentrations ranged 15 – 20 $\mu\text{g L}^{-1}$ in the brackish water, 21 – 73 $\mu\text{g L}^{-1}$ in the shallow groundwater, and 33 – 51 $\mu\text{g L}^{-1}$ in the deep groundwater. However, Ca is more enriched than Ba in groundwater relative to seawater. Deep groundwater concentrations are particularly high, $\sim 530 \text{ mg Ca L}^{-1}$, while the shallow groundwater concentration ($\sim 95 \text{ mg Ca L}^{-1}$) is only slightly higher than the brackish Baltic water ($\sim 65 \text{ mg Ca L}^{-1}$). Groundwater Ca/Mg ratios are over an order of magnitude higher than brackish water ratios.

Figure 4: $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of groundwater and seawater samples, samples of Fröhlich (1988), and the local meteoric water line (LMWL; Tröjbom et al., 2007).

4.5 Ra diffusion from sediments

Sediment diffusion experiment results were used to derive the flux of Ra diffusion from the fine-grained, Fe,Mn (oxyhydr)oxide-bearing sediments deposited over the Öregrundsgrepen seabed. Calculated ^{223}Ra and $^{224}\text{Ra}_{\text{xs}}$ diffusion rates amount to (2.2 ± 0.02) and (32 ± 2) dpm $\text{m}^{-2} \text{d}^{-1}$, respectively (Figure 5). These represent upper limits because during the experiment Ra was continuously removed from the water overlying the sediment core, thereby forcing diffusion by maximizing the gradient between the porewater and the overlying water. Diffusion-sourced ^{226}Ra and ^{228}Ra fluxes are locally insignificant because the rate of their production by Th parents is slow (Rodellas et al., 2015) relative to the residence time within Öregrundsgrepen. The $^{224}\text{Ra}_{\text{xs}}$ diffusion rate is similar to that reported from the Venice

Lagoon ($32 \text{ dpm d}^{-1} \text{ m}^{-2}$; Garcia-Solsona et al., 2008) and Jamaica Bay ($28 \text{ dpm d}^{-1} \text{ m}^{-2}$; Beck et al., 2007) but lower than that reported from Long Island Sound ($> 127 \text{ dpm m}^{-2} \text{ d}^{-1}$; Garcia Orellana et al., 2014) and the Port of Maó ($110 \text{ dpm m}^{-2} \text{ d}^{-1}$; Rodellas et al., 2015).

Figure 5: Diffusive ^{223}Ra and ^{224}Ra activities as a function of time (not corrected for surface area of core, 0.091 m^2).

5 Discussion

5.1 Geochemical behavior of Ra

Ra exhibits expected salinity-dependent ion exchange behavior, where Ra in fresh water is predominantly adsorbed to particles. When these particles are transported to saline water, the Ra adsorbed to the particles desorbs after exchange for cations that are enriched in seawater relative to fresh water, particularly Na. Thus, Ra isotopes may lead to an underestimation of SGD if utilized in fresh waters, in which Ra is likely by adsorption attached to particles.

The salinity after which Ra behaves conservatively is unclear. Gonnee et al. (2008) and Gu et al. (2012) stated that complete Ra desorption is produced above salinities of 10 – 15, whereas Krest et al. (1999) and Su et al. (2015) suggest a salinity of approximately five. The former authors attributed the variation in Ra adsorption to differences in particle chemistry and size. Experiments in sandy terrains showed that adsorption of Ra to particles is negligible

below ~1.8 (Raanan Kiperwas, 2011). In Öregrundsgrepen, the salinity does not exceed five. Since only the study by Raanan Kiperwas (2011) supports conservative behavior of Ra at salinities less than five, it should be examined whether Ra is an appropriate tracer to apply in the brackish Öregrundsgrepen water.

In seawater, Ra desorption is promoted because it is outcompeted by Na for exchange sites, the latter of which is several orders of magnitude more enriched in seawater than in freshwater. Since exchange of Ra for Na is a heterovalent cation exchange process, the reaction involves exponential terms and is influenced by total ionic strength of the solution. Nevertheless, an ion exchange model can be used to understand competition between monovalent and divalent cations for adsorption sites at a range of salinities, assuming that Ra sorption is controlled by an ion exchange rather than a surface complexation mechanism. Equilibrium between a monovalent and divalent cation is expressed by the mass action equation (1):

$$\frac{X_{Ca-clay}}{X_{Na-clay}^2} = K \frac{m_{Ca^{2+}}}{m_{Na^+}^2} \quad (1)$$

where X represents the fractional equivalents of the mono- or divalent cation in the solid phase, m the dissolved molar concentrations, and K the composition-dependent selectivity coefficient of the particle. Here, the monovalent cations are represented by Na concentrations in freshwater, brackish Baltic water, and seawater because Na is the most abundant cation in brackish and seawater. Divalent cations are represented by concentrations of Ca, which is more similar to Ra than Mg in size and therefore exhibits more comparable ion exchange behavior.

Ca should not exceed 10% of the total Na and Ca adsorbed in brackish water unless $K(Na/Ca)$ exceeds 200 (Figure 6). For reference, $K(Na/Ca)$ values for montmorillonite, a clay with

strong adsorptive properties, range from 2.5 to 6 depending on the ratio of solid to water (25 g L⁻¹ and 2.5 g L⁻¹, respectively; Tertre et al., 2011). Through comparison between these selectivity coefficients, it is inferred that brackish water is more similar to seawater than to fresh water with respect to competition between monovalent and divalent cations. Since adsorption of Ca to particles is not significant in brackish water and the ion exchange behavior of Ra is comparable to that of Ca due to size and ionic radius, adsorption of the Ra to particles should not hinder its application in these brackish waters.

Figure 6: Fractional occupancy of Ca on solid phase for seawater, brackish water, and fresh water as a function of selectivity coefficient (K).

5.2 End-member mixing

To determine an accurate SGD flow rate, an appropriate endmember groundwater Ra activity should be selected. It would be particularly valuable to distinguish between the discharge of deep and shallow groundwater, because the former were found to contain Ra in activities up to two orders of magnitude higher than the latter. Salinity, stable $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values, and $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratios (ARs) have been used to define endmember groundwater components during SGD investigations in the Mediterranean (Povinec et al. 2006; Garcia-

Solsona et al. 2010; Rodellas et al., 2014), while Ca/Mg ratios are potentially useful at Forsmark (Section 4.4).

$^{228}\text{Ra}/^{226}\text{Ra}$ ARs in the Forsmark groundwaters (0.75 – 2.40) do not differ substantially from those in the coastal and offshore brackish Baltic water (0.84 – 2.07; Figure 7.a). ARs in Tixelfjärden are slightly higher than in the transects, but whether this is due to the discharge of deep or shallow groundwater cannot be distinguished from these data (Figure 7.a). Overall, $^{228}\text{Ra}/^{226}\text{Ra}$ ARs are inadequate to define the source of groundwater discharge. Salinity, $\delta^2\text{H}$, and Ca/Mg variations between groundwater and brackish water (Figure 7.b-d) are more significant than $^{228}\text{Ra}/^{226}\text{Ra}$ ARs. No clear mixing relation between groundwater and brackish Baltic water for $\delta^2\text{H}$ and ^{226}Ra is observed. However, the Ca/Mg ratios and salinity versus ^{226}Ra may indicate mixing between groundwater and brackish Baltic water. Provided the elevated Ca/Mg ratio and salinity in Tixelfjärden bay, local discharge of deep groundwater is viable.

5.3 Zonal SGD

5.3.1 Offshore transects

Fractures intersecting the bedrock surface of the Öregrundsgrepen seabed and the Börstilåsen esker described as potential discharge zones (Section 2) are prevalent through the shallow bays Tixelfjärden and Kalligafjärden and up to 6000 m off the Forsmark coast (Figure 1.a). Higher average ^{223}Ra and $^{224}\text{Ra}_{\text{xs}}$ activities were observed around the northern-most transect (t1–5), where the frequency of fractures intersecting the seabed is greatest. Although strong gradients in ^{226}Ra were not observed here, slight increases in offshore $^{224}\text{Ra}_{\text{xs}}$ and ^{226}Ra activities are associated with the occurrence of these fractures ~1000-1500 and 4000-5000m offshore (3.a, 3.c). Systematic increases in Ra are associated with the fracture zones in each offshore transect, and thus may reflect Ra inputs from these zones.

5.3.2 Tixelfjärden bay

Maximum brackish water Ra activities were observed in Tixelfjärden bay. Though the influence of ^{223}Ra and ^{224}Ra diffusion from sediments is more conspicuous in shallow bays due the larger sediment surface area to water volume ratio, ^{226}Ra and ^{228}Ra activities, which are not supplied through sediment diffusion, were elevated in this bay by a factor of two relative to the offshore transects. Given high fracture frequency within the bay and the proximity of the Börstilåsen esker alongside the Ca/Mg ratio (Section 5.3.1), SGD is a plausible local source of Ra enrichment. The rate of evaporation in this bay is ~15% the rate of water inflow from the strait (Section 4.3) and cannot explain the Ra enrichment.

5.3.3 Kallrigafjärden bay

Geochemical relationships in Kallrigafjärden bay are influenced by the streams Forsmarksån and Olandsån, which discharge into the western-most regions of the bay, in addition to possible SGD from local deformation zones and the Börstilåsen esker. Mixing between fresh stream water and brackish seawater is indicated by the relation between salinity and $\delta^2\text{H}$ (Figure 8.a; Fröhlich et al., 1988).

Streams can transport Ra, which is enriched by as great as a factor of six at the outlets as compared to the mouth of Kallrigafjärden bay. Although short-lived ^{223}Ra and $^{224}\text{Ra}_{\text{xs}}$, like $\delta^2\text{H}$, are inversely related to salinity (Figure 8.b), significant Ra input from the streams is not necessarily indicated. A shallow water column is prevalent near the stream outlets, thus ^{223}Ra and ^{224}Ra may be sourced predominantly by sediment diffusion to the shallow water column near the stream outlets. ^{226}Ra and ^{228}Ra , which are not significantly supplied by seabed sediments, are highest toward the center the bay.

Relations between salinity and ^{223}Ra , $^{224}\text{Ra}_{\text{xs}}$, $\delta^2\text{H}$, and $\delta^{18}\text{O}$ values in Kallrigafjärden deviate from a linearity (Figure 8.a-b), which implies an additional source of Ra and $\delta^2\text{H}$. The deviation is apparent around the central stations proximal to the Börstilåsen esker (KF2 and KF3). Likewise, elevated ^{226}Ra and ^{228}Ra activities are found at these stations (Figure 8.c). Despite a salinity increase to > 4 as compared to 1.7 near the outlet of the streams (KF1), Ra desorption from suspended riverine particles would not explain the deviation in $\delta^2\text{H}$ and $\delta^{18}\text{O}$. Therefore, as in Tixelfjärden bay, SGD to Kallrigafjärden bay is a plausible source of Ra.

Figure 8.a-c: (a) $\delta^2\text{H}$ and $\delta^{18}\text{O}$, (b) ^{223}Ra , ^{224}Ra , and (c) ^{226}Ra as a function of salinity in Kallrigafjärden bay. Stations KF2 and KF3, which deviate from mixing trend near Börstilåsen, esker circled.

5.4 Ra mass balance and SGD rate estimation

SGD flow to Öregrundsgrepen can be determined using a steady state mass balance model, which accounts for supply fluxes of Ra through sediment diffusion and removal fluxes through decay and export to the open sea. The difference between the removal and supply fluxes is converted to an SGD flow rate through division by the Ra activity of a discharging groundwater endmember. The Ra mass balance is as follows:

$$J_{\text{sed}} + J_{\text{SGD}} = J_{\text{sea}} + J_{\lambda} \quad (2)$$

where J_{sed} and J_{SGD} denote the input fluxes of a specific Ra isotope through diffusion from seabed sediments and from SGD, respectively while J_{sea} and J_{λ} the output fluxes through export to the open Baltic Sea and radioactive decay. J_{sed} can be constrained using the results of the sediment diffusion experiment (Section 4.5). To constrain J_{sea} requires determination of the excess inventory of the Ra isotope and the residence time of seawater within the investigated area. J_{λ} is simply the mean excess Ra activity observed on the site multiplied by the decay constant. Resulting fluxes are in units of dpm d^{-1} .

Since a $^{224}\text{Ra}_{\text{xs}}$ gradient was observed and more stations were enriched in $^{224}\text{Ra}_{\text{xs}}$ than in ^{223}Ra , $^{224}\text{Ra}_{\text{xs}}$ activities will be used in the mass balance. A mass balance will not be constructed using ^{226}Ra and ^{228}Ra because the average activities found in Öregrundsgrepen (13.7 and 16.0 dpm 100L⁻¹) were not statistically higher than the respective activities reported from the open Baltic Sea (13.3 ± 1.2 and 14.7 ± 1.6 dpm 100L⁻¹; Porcelli et al., 2001).

Contribution of ^{224}Ra from rivers and precipitation are neglected. ^{228}Ra activities of ~ 4 dpm 100L⁻¹ were found at various locations in the Kalix River, which discharges into the northern Gulf of Bothnia (Porcelli et al., 2001). Assuming secular equilibrium between ^{224}Ra and ^{228}Ra , streams would supply only $\sim 10\%$ of the $^{224}\text{Ra}_{\text{xs}}$ than the average shallow groundwater (~ 140 dpm $^{224}\text{Ra}_{\text{xs}}$ 100L⁻¹) could supply if shallow SGD comprises 17% of the total runoff from the Forsmark coast (Section 2).

5.4.1 Site constraints

To develop the mass balance, the surface area and volume of seawater affected by SGD must be constrained. A conservative estimate of the $^{224}\text{Ra}_{\text{xs}}$ activity in the open Baltic Sea is found using the lowest $^{224}\text{Ra}_{\text{xs}}$ activity measured in the studied area (station t15, 1.0 ± 0.3 dpm $^{224}\text{Ra}_{\text{xs}}$ 100L⁻¹). The area affected by SGD is then considered to include only those stations with $^{224}\text{Ra}_{\text{xs}}$ activities statistically higher than the open sea $^{224}\text{Ra}_{\text{xs}}$ activity (stations t1–4, t6–7, t9, t11–12, and t14; denoted by * in Table 1). Thus, the area influenced by SGD is $16 \cdot 10^6$ m². An average depth of 11 m, which represents the depth of the water column averaged over the stations constrained as influenced by SGD, is used to constrain the volume of brackish water influenced by SGD to $180 \cdot 10^6$ m³.

5.4.2 Residence time

A residence time, which represents the time elapsed since Ra isotopes were transferred from their source to the constrained study site, is required to estimate the flux of Ra exported

offshore. One such age model, developed by Moore (2006), is expressed through the equation:

$$\tau = \frac{\left(\frac{^{224}\text{Ra}}{^{228}\text{Ra}_{ex}}\right)_i - \left(\frac{^{224}\text{Ra}}{^{228}\text{Ra}_{ex}}\right)_{obs}}{\left(\frac{^{224}\text{Ra}}{^{228}\text{Ra}_{ex}}\right)_{obs} \cdot \lambda_{224}} \quad (3)$$

where i denotes the initial end-member Ra activity and obs the average $^{224}\text{Ra}_{ex}/^{228}\text{Ra}_{ex}$ activity ratio observed within the constrained site. The subscript “ex” denotes the observed coastal $^{224}\text{Ra}_{xs}$ or ^{228}Ra activity subtracted by the offshore activity (i.e. the Ra signal corrected for mixing with open seawater). An offshore ^{228}Ra activity of 14.7 dpm 100L⁻¹, reported by Porcelli et al. (2001) from the central Gulf of Bothnia, was used to derive $^{228}\text{Ra}_{ex}$, the mean of which was 1.6 dpm 100L⁻¹. ARs involving ^{224}Ra are used because the residence time is likely on the order of days, considering the size of the investigation site. This model relies on the assumption that Ra is removed from the system only through radioactive decay and exchange with open-sea waters. The initial end-member activity, i , will depend on the amount of $^{224}\text{Ra}_{xs}$ and ^{228}Ra supplied to the seawater by SGD and sediment diffusion. Since this term is unknown, the highest $^{224}\text{Ra}_{ex}/^{228}\text{Ra}_{ex}$ AR of (5.9, t1) is here used under the assumption that this ratio is found closest to the Ra source so that minimum decay is expected.

A residence time of 12 ± 14 days was obtained using $^{224}\text{Ra}_{ex}/^{228}\text{Ra}_{ex}$ ARs of the constrained site. The uncertainty is large due to the propagation of analytical uncertainty combined with low Ra activities. However, the Ra-based T_R model agrees with previous hydrological models, which determined a residence time of 9-11 days for the spring season (Engqvist, 1999). Provided the lower uncertainty of the hydrological model, a residence time of 11 ± 2 days is used to reduce the uncertainty propagated to the mass balance calculation.

5.4.3 Contribution from sediments

The experimental $^{224}\text{Ra}_{\text{xs}}$ diffusive flux ($32 \pm 1.8 \text{ dpm m}^{-2} \text{ d}^{-1}$; Section 4.3.3) can be converted to total $^{224}\text{Ra}_{\text{xs}}$ flux from sediments by multiplying them by the surface sediment area of the investigation site ($16 \cdot 10^6 \text{ m}^2$), under the assumption that the core sample represents sediments homogeneously distributed across the seabed of the constrained site. The resulting $^{224}\text{Ra}_{\text{xs}}$ flux from sediment diffusion (J_{sed}) is $(520 \pm 31) \cdot 10^6 \text{ dpm d}^{-1}$.

5.4.4 Selection of SGD end-member

At Forsmark, salinity, $\delta^2\text{H}$, Ca/Mg ratios, and $^{228}\text{Ra}/^{226}\text{Ra}$ ARs can neither be used to define the groundwater source of SGD nor to determine whether the deep or shallow groundwater is discharging (Section 5.3). However, the groundwater end-member can be selected based on the hydrological understanding of the site. For instance, the SFM0059 is a plausible shallow groundwater end-member because it is sampled from the Börstilåsen esker, a potential SGD channel (Section 2). This shallow groundwater probably mixes with some deep groundwater component sourced by the fracture network. To constrain a minimum rate of SGD, the shallow and deep groundwaters which had the highest $^{224}\text{Ra}_{\text{xs}}$ activities (SFM0059 and KFR01, respectively) are used in the SGD rate calculation.

5.4.5 SGD rate estimation

The coastal $^{224}\text{Ra}_{\text{xs}}$ inventory, or the total activity of $^{224}\text{Ra}_{\text{xs}}$ in the volume of brackish water influenced by SGD (Section 4.1.1), must be established for the mass balance (Equation 2). The inventory is determined by 1) multiplying the $^{224}\text{Ra}_{\text{xs}}$ activities of the stations within the constrained site by respective water column depth, 2) averaging the results of (1) (in dpm m^{-2}), and 3) multiplying (2) by surface area of the constrained site ($16 \cdot 10^6 \text{ m}^2$). The resulting inventory, $(4800 \pm 1700) \cdot 10^6 \text{ dpm}$, can then be apportioned into J_{sea} , J_{sed} , J_{λ} , and J_{SGD} (in dpm d^{-1}).

488 J_{sea} , the flux of Ra exported to the open sea, is determined from the excess inventory, i.e. the
 489 difference between the total $^{224}\text{Ra}_{\text{xs}}$ inventory within the site and that supplied by the open sea
 490 (conservatively estimated to $1.3 \text{ dpm } 100\text{L}^{-1}$, Section 5.4.1), divided by the residence time (11
 491 $\pm 2 \text{ d}$). This results in a J_{sea} of $(260 \pm 160) \cdot 10^6 \text{ dpm } ^{224}\text{Ra}_{\text{xs}} \text{ d}^{-1}$.

492 The flux of $^{224}\text{Ra}_{\text{xs}}$ removal through radioactive decay, J_{λ} , is obtained by multiplying the total
 493 $^{224}\text{Ra}_{\text{xs}}$ inventory $(4800 \pm 1700) \cdot 10^6 \text{ dpm}$ by the decay constant of ^{224}Ra (0.189 d^{-1}). The
 494 resulting flux of $^{224}\text{Ra}_{\text{xs}}$ removal by decay is $(900 \pm 310) \cdot 10^6 \text{ dpm d}^{-1}$.

495 **Table 2:** Calculated mass balance inputs* and SGD rate ranges.

	$^{224}\text{Ra}_{\text{xs,offshore}}$		Total Inventory		$^{224}\text{Ra}_{\text{xs}}$ fluxes ($\cdot 10^6 \text{ dpm d}^{-1}$)							
	$^{224}\text{Ra}_{\text{xs,obs}}$	$\sigma_{224\text{Ra}_{\text{xs}}}$	($\cdot 10^9 \text{ dpm}$)		J_{sed}	σ_{sed}	J_{sea}	σ_{sea}	J_{λ}	σ_{λ}	J_{SGD}	σ_{SGD}
	2.8	1.7	4.8	1.7	520	31	270	160	900	310	640	350
	SGD rates ($\text{m}^3 \text{ d}^{-1}$)										Uncertainty	
SFM0049	68	5					9.5E+05				5.2E+05	
SFM0059	270	20					2.4E+05				1.3E+05	
KFR01	2610	290					2.5E+04				1.4E+04	
KFR07A	11800	830					5.5E+03				3.0E+03	

496 *Surface area of $16 \cdot 10^6$, an average depth of 11 m, and a volume of $180 \cdot 10^6 \text{ m}^3$ used to calculate
 497 fluxes.

498

499 Rearranging Equation 2 to $J_{\text{SGD}} = J_{\text{sea}} + J_{\lambda} - J_{\text{sed}}$ yields an SGD-derived $^{224}\text{Ra}_{\text{xs}}$ flux of $(640 \pm$
 500 $350) \cdot 10^6 \text{ dpm d}^{-1}$. The flow rate is obtained by dividing this flux with the $^{224}\text{Ra}_{\text{xs}}$ activity of
 501 the end-member groundwaters (Table 2). The resulting SGD rate ranges from $(5.5 \pm 3.0) \cdot$
 502 10^3 to $(950 \pm 520) \cdot 10^3 \text{ m}^3 \text{ d}^{-1}$ (or $3.4 \cdot 10^{-4}$ to $5.8 \cdot 10^{-2} \text{ m}^3 \text{ m}^{-2} \text{ d}^{-1}$) depending on whether the
 503 end-member is comprised of entirely deep or shallow groundwater, respectively. In reality,
 504 SGD is probably comprised of a mixture between shallow and deep groundwater, thus an
 505 SGD flow between the two estimates is expected. Proportions deep and shallow groundwater
 506 contribution the coastal has not been determined.

5.4.6 Recirculated component of SGD

Previous hydrological models of the Forsmark area determined a shallow fresh groundwater discharge rate of $\sim 2.4 \cdot 10^3 \text{ m}^3 \text{ d}^{-1}$ or $1.5 \cdot 10^{-4} \text{ m}^3 \text{ m}^{-2} \text{ d}^{-1}$ (Jarsjö et al. 2008), which is two orders of magnitude lower than the $^{224}\text{Ra}_{\text{xs}}$ -derived discharge rate of shallow groundwater. Therefore, the SGD rate derived from ^{224}Ra indicates that a component of recirculated seawater, independent of inland hydraulic head, is important in Öregrundsgrepen. When seawater is driven into the coastal aquifer and discharged back into the sea, the generally short residence time in the coastal aquifer allows the water to become enriched in ^{223}Ra and ^{224}Ra , which are rapidly regenerated by aquifer solids, over ^{226}Ra and ^{228}Ra (Leuk & Beck, 2014). Therefore, ^{223}Ra and ^{224}Ra enrichment has been observed in the absence of ^{226}Ra and ^{228}Ra gradients due to the dominance of a short-scale, recirculated seawater component of SGD in Öregrundsgrepen.

Tidal cycles (Robinson et al., 2007), geothermal convection (Wilson, 2005), waves (Li, 2007), currents and irregular bathymetry (Thibodeaux & Boyle, 1987) have been shown to support seawater recirculation. Although tidal cycles are insignificant in the Baltic Sea, the mean sea level change in Öregrundsgrepen is $0.02 \pm 0.2 \text{ m d}^{-1}$ but can change by up to 1.3 m d^{-1} as a result of changes in atmospheric pressure and wind (Aquilonius 2010). The wind speed in the strait is typically higher than 6.5 m s^{-1} and is frequently higher than 10.5 m s^{-1} (Larsson-McCann et al., 2002). Geothermal convection may also drive seawater recirculation in this region, as Söderberg & Flodén (1997) observed contrasting temperatures between warm water seeping from seafloor eskers and cold seawater during early spring in the Stockholm archipelago, 200 km south of Öregrundsgrepen. Finally, the entire Baltic Sea basin has developed irregular bathymetry through glacial erosion and sediment deposition (Voipio, 1981).

The rate of fresh SGD to Öregrundsgrepen ($1.5 \cdot 10^{-4} \text{ m}^3 \text{ m}^{-2} \text{ d}^{-1}$; Jarsjö et al., 2008) is lower than the SGD rates found in the Bay of Puck, Poland (up to $2.8 \cdot 10^{-2} \text{ m}^3 \text{ m}^{-2} \text{ d}^{-1}$) and Eckernförde Bay, Germany ($9 \cdot 10^{-3} \text{ m}^3 \text{ m}^{-2} \text{ d}^{-1}$) (Symczycha and Pempkowiak, 2016; Schlüter et al., 2004, respectively), which are the only two locations in the Baltic Sea where geochemical studies of SGD have been conducted. Consideration of a recirculated component in Öregrundsgrepen increases the SGD rate to $5.8 \cdot 10^{-2} \text{ m}^3 \text{ m}^{-2} \text{ d}^{-1}$, which is higher than that reported from the southern Baltic. While the importance of a recirculated component in delivering nutrients and metals to the Baltic Sea is yet unknown, recirculated seawater is an important source of nutrients to the coastal ocean (Weinstein et al., 2011). Accurate determination of SGD-driven nutrient fluxes to the Baltic Sea represents an important area of future research. Finally, it will be valuable to further understand the impact of geothermal convection, irregular bathymetry, and fluctuations in atmospheric pressure on seawater recirculation, an important route of nutrient transport even in the absence of inland hydraulic head.

6 Conclusions

This study has shown that Ra isotopes can provide estimates of residence time and SGD flow rate at salinities less than five. Ra and stable isotopes have also been used to identify zones of groundwater discharge related to geologic features. Diffusion from seabed sediment is a source of ^{223}Ra and $^{224}\text{Ra}_{\text{xs}}$ to the Gulf of Bothnia, amounting to $\sim 10\%$ of the total $^{224}\text{Ra}_{\text{xs}}$ inventory in Öregrundsgrepen.

The $^{224}\text{Ra}_{\text{xs}}$ -derived SGD flow rate ranged between $(5.5 \pm 3.0) \cdot 10^3$ and $(950 \pm 520) \cdot 10^3 \text{ m}^3 \text{ d}^{-1}$. The precise rate depends on the relative contributions of deep and shallow groundwater, which are unknown. Nevertheless, these rates are higher than would be expected from $\delta^2\text{H}$, $\delta^{18}\text{O}$, and Ca/Mg ratio mixing calculations. Therefore, a component of recirculated brackish

water is significant in Öregrundsgrepen despite a modest, inland hydraulic head. Since this is a potential source of metals and nutrients to the coast, these findings have important implications on mass transport to the Baltic Sea and other low-relief coastal terrains.

Furthermore, hydrological models of the Forsmark site, constructed to understand radionuclide transport from the existing and planned radioactive waste repositories, have not considered a recirculated brackish water component in Öregrundsgrepen. If this can be considered a near-surface process, the effects on radionuclide transport at Forsmark is probably small. Nevertheless, the impact of recirculated seawater should not be overlooked, because coastal regions as prominent locations for nuclear power plants (World Nuclear Association, 2015), are becoming attractive hosts for radioactive waste repositories. Clearly, Ra isotope analysis is a viable and important complement to the models of sites proposed to host repositories.

Acknowledgements

The authors are grateful to Cecilia Berg, Micke Borgiel, Ignasi Puigdomenech, and Karin Wallner for their assistance in field and laboratory work. This article benefitted from critical reviews by Patrik Vidstrand, Emma Johansson, and Lena Evins. This study was supported by the Swedish Nuclear Fuel and Waste Management Company and the European Union's Seventh Framework Programme for research, technological development, and demonstration under Grant Agreement No. 290336. V.R. has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 748896. Support provided by the Generalitat de Catalunya to MERS (2014 SGD – 1356) is also acknowledged.

References

- Aquilonius, K. (Ed.), 2010. The marine ecosystems at Forsmark and Laxemar-Simpevarp. SR-Site Biosphere. SKB TR-10-03. SKB, Stockholm, Sweden.
- Beck, A.J., Rapaglia, J.P., Cochran, J.K., Bokuniewicz, H.J., 2007. Radium mass-balance in Jamaica Bay, NY: Evidence for a substantial flux of submarine groundwater. *Mar. Chem.* 106, 419–441.
- Boehm, A.B., Shellenbarger, G.G., Paytan, A., 2004. Groundwater discharge: Potential association with fecal indicator bacteria in the surf zone. *Environ. Sci. Technol.* 38, 3558–3566.
- Borgiel, M., 2003. Forsmark site investigation: Sampling and analyses of surface sediment in lakes and shallow bays. SKB P-04-05, SKB, Stockholm, Sweden.
- Burnett, W.C., Bokuniewicz, H., Huettel, M., Moore, W.S., Taniguchi, M., 2003. Groundwater and pore water inputs to the coastal zone. *Biogeochemistry* 66, 3–33.
- Charette, M.A., Buesseler, K.O., Andrews, J.E., 2001. Utility of radium isotopes for evaluating the input and transport of groundwater-derived nitrogen to a Cape Cod estuary. *Limnol. Oceanogr.* 46, 465–470.
- Charette, M.A., Moore, W.S., & Burnett, W.C., 2008. Uranium-and thorium-series nuclides as tracers of submarine groundwater discharge, in: Krishnaswami, S., Cochran J.K. (Eds.), *Radioactivity in the Environment*, Vol 13. Elsevier, Oxford, pp. 155–191.
- Elsinger, R.J., Moore, W.S., 1980. ^{226}Ra behavior in the Pee Dee River—Winyah Bay estuary. *Earth Planet. Sci. Lett.* 48, 239–249.
- Engvist, A., Andrejev, O., 1999. Water exchange of Öregrundsgrepen: A baroclinic 3-D model study. SKB TR-99-11. SKB, Stockholm, Sweden.
- Engqvist, A., Döös, K., Andrejev, O., 2006. *AMBIO* 35, 435–447.
- Follin, S., Johansson, P.-O., Levén, J., Hartley, L., Holton, D., McCarthy, R., Roberts, D., 2007. Updated strategy and test of new concepts for groundwater flow modelling in Forsmark in preparation of site descriptive modelling stage 2.2. SKB R-07-20. SKB, Stockholm, Sweden.
- Fröhlich, K., Grabczak, J., Rozanski, K., 1988. Deuterium and oxygen-18 in the Baltic Sea. *Chem. Geol.* 72, 77–83.
- Garcia-Orellana, J., Cochran, J.K., Bokuniewicz, H., Daniel, J.W.R., Rodellas, V., Heilbrun, C., 2014. Evaluation of ^{224}Ra as a tracer for submarine groundwater discharge in Long Island Sound (NY). *Geochim. Cosmochim. Acta* 141, 314–330.

613 Garcia-Solsona, E., Garcia-Orellana, J., Masque, P., Rodellas, V., Mejias, M., Ballesteros, B.,
614 Dominquez, J.A., 2010. Groundwater and nutrient discharge through karstic coastal
615 springs (Castello, Spain). *Biogeosciences* 7, 2625-2638.

616 Garcia-Solsona, E., Masqué, P., Garcia-Orellana, J., Rapaglia, J., Beck, A.J., Cochran, J.K.,
617 Bokuniewicz, H.J., Zaggia, L., Collavini, F., 2008. Estimating submarine groundwater
618 discharge around Isola La Cura, northern Venice Lagoon (Italy), by using the radium
619 quartet. *Mar. Chem.* 109, 292–306.

620 Gu, H., Moore, W.S., Zhang, L., Du, J., Zhang, J., 2012. Using radium isotopes to estimate
621 the residence time and the contribution of submarine groundwater discharge (SGD) in
622 the Changjiang effluent plume, East China Sea. *Cont. Shelf Res.* 35, 95-107.

623 Hedenström, A., Sohlenius, G., Strömgren, M., Brydsten, L., Nyman, H., 2008. Depth and
624 stratigraphy of regolith at Forsmark, site descriptive modelling Forsmark. SKB R-08-
625 07. SKB, Stockholm, Sweden.

626 Jakobsson, M., O'Regan, M., Gyllencreutz, R., Flodén, T., 2016. Seafloor terraces and semi-
627 circular depressions related to fluid discharge in Stockholm Archipelago, Baltic Sea,
628 in: Dowdeswell, J. A., Canals, M., Jakobsson, M., Todd, B. J., Dowdeswell, E. K.,
629 Hogan, K. A. (Eds.), *Atlas of Submarine Glacial Landforms: Modern, Quaternary and*
630 *Ancient*. Geological Society, London, *Memoirs* 46, pp. 305–306.

631 Jarsjö, J., Shibuo, Y., Destouni, G., 2008. Spatial distribution of unmonitored inland water
632 flows to the sea. *J. Hydrol.* 348, 59–72.

633 Krest, J.M., Moore, W.S., Rama, 1999. ^{226}Ra and ^{228}Ra in the mixing zones of the Mississippi
634 and Atchafalaya Rivers: indicators of groundwater input. *Mar. Chem.* 64, 129–152.

635 Kwon, E. Y., Kim, G., Primeau, F., Moore, W.S., Cho, H.-M., DeVries, T., Sarmiento, T.L.,
636 Charette, M.A., Cho, Y.-K., 2014. Global estimate of submarine groundwater
637 discharge based on an observationally constrained radium isotope model. *Geophys.*
638 *Res. Lett.* 41, 8438–8444.

639 Laaksoharju, M., Smellie, J., Tullborg, E.-L., 2008. Bedrock hydrogeochemistry Forsmark,
640 site descriptive modelling Forsmark. SKB R-08-47. SKB, Stockholm, Sweden.

641 Larsson-McCann, S., Karlsson, A., Nord, M., Sjögren, J., Johansson, L., Ivarsson, M.,
642 Kindell, S., 2002. Meteorological, hydrological and oceanographical information and
643 data for site investigation program in the communities of Östhammar and Tierp in the
644 northern part of Uppland. SKB TR-02-02. SKB, Stockholm, Sweden.

645 Leuk, J.L., Beck, A.J., 2014. Radium budget of the York River estuary (VA, USA) dominated
646 by submarine groundwater discharge with a seasonally variable groundwater end-
647 member. *Mar. Chem.* 165, 55-65.

648 Li, L., Barry, D.A., 2000. Wave-induced beach groundwater flow. *Adv. Water Resour.* 23,
649 325-337.

650 Li, Y., Chan, L., 1979. Desorption of Ba and ^{226}Ra from river-borne sediments in the Hudson
651 estuary. *Earth Planet. Sci. Lett.* 43, 343–350.

652 Gonneea, M.E., Morris, P.J., Dulaiova, H., Charette, M.A., 2008. New perspectives on radium
653 behavior within a subterranean estuary. *Mar. Chem.* 109, 250–267.

654 Moore, W.S., Arnold, R., 1996. Measurement of ^{223}Ra and ^{224}Ra in coastal waters using a
655 delayed coincidence counter. *J. Geophys. Res.* 101, 1321–1329.

656 Moore, W. S., Astwood, H., Lindstrom, C., 1995. Radium isotopes in coastal waters on the
657 Amazon shelf. *Geochim. Cosmochim. Acta* 59, 4285–4298.

658 Moore, W., Blanton, J., Joye, S., 2006. Estimates of flushing times, submarine groundwater
659 discharge, and nutrient fluxes to Okatee River, South Carolina. *J. Geophys. Res.*
660 *Oceans* 111, C09006, doi: 10.1029/2005JC003041.

661 Moore, W.S., 2010. The effect of submarine groundwater discharge on the ocean. *Annu. Rev.*
662 *Mar. Sci.* 2, 59–88.

663 Moore, W.S., Reid, D.F., 1973. Extraction of radium from natural waters using manganese
664 impregnated acrylic fibers. *J. Geophys. Res.* 78, 8880–8886.

665 Moore, W.S., Sarmiento, J.L., Key, R.M., 2008. Submarine groundwater discharge revealed
666 by ^{228}Ra distribution in the upper Atlantic Ocean. *Nat. Geosci.* 1, 309–311.

667 Porcelli, D., Andersson, P.S., Baskaran, M., Wasserburg, G.J., 2001. Transport of U- and Th-
668 series nuclides in a Baltic Shield watershed and the Baltic Sea. *Geochim. Cosmochim.*
669 *Acta* 65, 2439–2459.

670 Povinec, P.P., Aggarwal, P.K., Aureli, A., Burnett, W.C., Kontar, E.A., Kulkarni, K.M.,
671 Moore, W.S., Rajar, R., Taniguchi, M., Comanducci, J.F., Cusimano, G., Dulaiova,
672 H., Gatto, L., Groening, M., Hauser, S., Levy-Palomo, I., Oregioni, B., Ozorovich,
673 Y.R., Privitera, A.M., Schiavo, M.A., 2006. Characterisation of submarine
674 groundwater discharge offshore south-eastern Sicily. *J. Environ. Radioact.* 89, 51-
675 101.

676 Raanan Kiperwas, H., 2011. Radium Isotopes as Tracers of Groundwater-Surface Water
677 Interactions in Inland Environments. PhD dissertation, Duke University.

678 Robinson, C., Li, L., Barry, D.A., 2007. Effect of tidal forcing on a subterranean estuary.
679 *Adv. Water Resour.* 30, 851–865.

680 Rodellas, V., Garcia-Orellana, J., Garcia-Solsona, E., Masque, P., Dominguez, J., Ballesteros,
681 B.J., Mejias, M., Zarroca, M., 2012. Quantifying groundwater discharge from different
682 sources into a Mediterranean wetland by using ^{222}Rn and Ra isotopes. *J. Hydrol.* 466,
683 11–22.

684 Rodellas, V., Garcia-Orellana, J., Masqué, P., Font-Muñoz, J.S., 2015. The influence of
685 sediment sources on radium-derived estimates of submarine groundwater discharge.
686 Mar. Chem. 171, 107-117

687 Rodellas, V., Garcia-Orellana, J., Tovar-Sánchez, A., Basterretxea, G., López-García, J. M.,
688 Sánchez-Quiles, D., Garcia-Solsona, E., Masqué, P., 2014. Submarine groundwater
689 discharge as a source of nutrients and trace metals in a Mediterranean bay (Palma
690 Beach, Balearic Islands). Mar. Chem. 160, 56-66.

691 Rodellas, V., Garcia-Orellana, J., Trezzi, G., Masqué, P., Stieglitz, T.C., Bokuniewicz, H.,
692 Kirk Cochran, J., Berdalet, E., 2017. Using the radium quartet to quantify submarine
693 groundwater discharge and porewater exchange. Geochim. Cosmochim. Acta 196, 58–
694 73.

695 Schlüter, M., Sauter, E.J., Andersen, C.A., Dahlgaard, H., Dando, P.R., 2004. Spatial
696 distribution and budget for submarine groundwater discharge in Eckernförde Bay
697 (Western Baltic Sea). Limnol. Oceanogr. 49, 157–167

698 SKB, 2008. Site description of Forsmark at completion of the site investigation phase—SDM-
699 Site Forsmark. SKB TR-08-05. SKB, Stockholm, Sweden.

700 Smellie, J., Tullborg, E.-L., Nilsson, A.C., Sandström, B., Waber, N., Gimeno, M., Gascoyne,
701 M. Explorative analysis of major components and isotopes—SDM-Site Forsmark,
702 2008. SKB R-08-84. SKB, Stockholm, Sweden.

703 Söderberg, P., Flodén, T., 1997. Stratabound submarine terraces and pockmarks—indicators
704 of spring sapping in glacial clay, Stockholm Archipelago, Sweden, in: Cato, I.,
705 Klingberg, F. (Eds.), Proceedings of the Fourth Marine Geological Conference—the
706 Baltic, Uppsala 1995.

707 Su, N., Jinzhou, D., Zonglian, D., Bing, D., Jing, Z., 2015. Radium isotopes and their
708 environmental implications in the Changjiang River System. Estuar. Coast. Shelf Sci.
709 156, 155- 164.

710 Sun, Y., Torgersen, T., 1998. The effects of water content and Mn-fiber surface conditions on
711 measurement by emanation. Mar. Chem. 62, 299–306.

712 Swarzenski, P.W., Simonds, F.W., Paulson, T., Kruse, S., Reich, C.D., 2007. A Geochemical
713 and Geophysical Examination of Submarine Groundwater Discharge and Associated
714 Nutrient Loading Estimates into Lynch Cove, Hood Canal, WA. Environ. Sci.
715 Technol. 41, 7022-7029.

716
717 Swarzenski, P.W., Izbicki, J.A., 2009. Examining coastal exchange processes within a sandy
718 beach using geochemical tracers, seepage meters and electrical resistivity. Estuar.
719 Coast. Shelf Sci. 83, 77-89.

720
721 Symczycha, B., Pempkowiak, J., 2016. *The Role of Submarine Groundwater Discharge as*
722 *Material Source to the Baltic Sea*. Springer.