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ORIGINAL

^{228}Ra, ^{226}Ra, ^{224}Ra and ^{223}Ra in potential sources and sinks of land-derived material in the German Bight of the North Sea: implications for the use of radium as a tracer

Caroline Schmidt · Claudia Hanfland · Pierre Regnier · Philippe Van Cappellen · Michael Schlüter · Ulrich Knauthe · Ingrid Stimac · Walter Geibert

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Abstract Activities of the naturally occurring radium nuclides ^{228}Ra, ^{226}Ra, ^{224}Ra and ^{223}Ra were determined in waters of the open German Bight and adjacent nearshore areas in the North Sea, in order to explore the potential use of radium isotopes as natural tracers of land–ocean interaction in an environment characterised by extensive tidal flats, as well as riverine and groundwater influx. Data collected at various tidal phases from the Weser Estuary (^{228}Ra: 46.3±4.6; ^{226}Ra: 17.1±1.1; ^{224}Ra: 26.1±8.2 to 36.5±6.1; ^{223}Ra: 1.8±0.1 to 4.0±0.4), tidal flats near Sahlenburg (^{228}Ra: 39.3±3.8 to 46.0±4.5; ^{226}Ra: 15.5±1.5 to 16.5±1.7; ^{224}Ra: 34.3±2.2 to 85.3±6.3; ^{223}Ra: 3.6±0.5 to 8.0±1.2), freshwater seeps on tidal flats near Sahlenburg (^{228}Ra: 42.1±4.1; ^{226}Ra: 21.3±2.2; ^{224}Ra: 5.1±0.9; ^{223}Ra: 2.6±1.3) and also in permanently inundated parts of the North Sea (^{228}Ra: 23.0±2.3 to 28.2±2.8; ^{226}Ra: 8.2±0.8 to 11.8±1.2; ^{224}Ra: 3.1±1.0 to 10.1±0.9; ^{223}Ra: 0.1±0.02 to 0.9±0.05; units: disintegrations per minute per 100 kg water sample) reveal that, except for the fresh groundwater, the potential end-members of nearshore water mass mixing have quite similar radium signatures, excluding a simple discrimination between the sources. However, the decreasing activities of the short-lived ^{224}Ra and ^{223}Ra isotopes recorded towards the island of Helgoland in the central German Bight show a potential to constrain fluxes of land-derived material to the open North Sea. The largest source for all radium isotopes is generally found on the vast tidal flats and in the Weser Estuary. Future work could meaningfully combine this so-called radium quartet approach with investigations of radon activity. Indeed, preliminary data from a tidal flat site with fresh groundwater seepage reveal a ^{222}Rn signal that is clearly lower in seawater.

C. Schmidt · P. Regnier · P. Van Cappellen
Department of Earth Sciences—Geochemistry, Utrecht University,
3508 TA Utrecht, The Netherlands

C. Schmidt · C. Hanfland · M. Schlüter · U. Knauthe · I. Stimac · W. Geibert (✉)
Alfred Wegener Institute for Polar and Marine Research,
Am Handelshafen 12,
27570 Bremerhaven, Germany
e-mail: walter.geibert@ed.ac.uk

Present Address:
W. Geibert
School of GeoSciences, University of Edinburgh,
West Mains Road,
Edinburgh EH9 3JW, UK

Present Address:
W. Geibert
Scottish Association for Marine Science,
Oban, UK

Present Address:
C. Schmidt
Geomicrobiology Group, Centre for Applied Geosciences,
University of Tübingen,
Sigwartstrasse 10,
72076 Tübingen, Germany

Present Address:
P. Van Cappellen
School of Earth and Atmospheric Sciences,
Georgia Institute of Technology,
Atlanta, GA 30332-0340, USA

Introduction

The German Bight in the south-eastern North Sea, including the Wadden Sea that is listed as a UNESCO

World Heritage Site, is a coastal region of enormous ecological and economical importance, extensively used for transportation, fishing, tourism and, more recently, energy generation by offshore wind parks. Environmental conditions depend strongly on the exchange between land and sea, in particular on the balance between particle deposition and erosion, and dissolved land–sea fluxes of freshwater, nutrients and contaminants. Such fluxes can be difficult to constrain, however, as the tracking of diffuse sources is often complicated (Gallardo and Marui 2006; Burnett et al. 2006). Naturally occurring radiotracers could conveniently be used for this purpose, as their loss due to radioactive decay with increasing distance from the source can be used to constrain the rates of supply, as well as the transport away from the source by mixing and advection.

Hydrological restoration represents a major current challenge along the south-eastern North Sea coast (Reise 2005; van der Hagen et al. 2008). Moreover, weather-dependent fluctuations in the residence time of Wadden Sea tidal water masses have recently been hypothesised as pivotal in controlling regional eutrophication (van Beusekom et al. 2008), and is has been shown that pore waters from tidal flats represent an important part of the nutrient and carbon cycle in the North Sea (Billerbeck et al. 2006a, b). Therefore, additional tracers that could improve evaluations of groundwater and pore water discharge, water mass residence times or exchange rates would be a useful tool in this environment.

The suite of naturally occurring radon (^{222}Rn) and radium isotopes (^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra) have been widely used to quantify estuarine and ocean mixing processes, as well as submarine groundwater discharge to the coastal zone (e.g. Rama and Moore 1996; Moore 2000a, b; Charette et al. 2003; Burnett et al. 2006). All four natural Ra isotopes are produced by the decay of different isotopes of thorium (Th), a highly particle-reactive element. The decay of Th sorbed to particles represents a continuous source of the more soluble Ra to seawater. In turn, ^{222}Rn is produced by the decay of ^{226}Ra. It has been shown to be a powerful tracer of submarine groundwater discharge, especially if losses to the atmosphere can be quantified (Cable et al. 1996; Burnett and Dulaiova 2003; Stieglitz et al. 2010).

The distribution, enrichment and depletion of Ra and Rn isotopes in the water column depend on their production and radioactive decay, as well as the ambient hydrodynamic and physicochemical conditions (e.g. Key et al. 1985; Burnett et al. 2006; Ku and Luo 2008). In freshwater, Ra tends to sorb to particles, whereas in seawater it is found primarily in the dissolved form (Li et al. 1977). Therefore, desorption occurs during estuarine mixing, due mainly to the effect of increasing ionic strength (I) at higher salinity—that is, the partition coefficient of Ra varies inversely with I (Li et al. 1977; Moore et al. 1995; Webster et al. 1995; Krest et al. 1999; Charette et al. 2008). A similar effect takes place within freshwater aquifers, where radium adsorbed onto the surface of particles (Porcelli 2008) becomes mobilised when seawater infiltrates and replaces freshwater in the pore spaces. This process takes place frequently in aquifers within the tidal zone, as found in our study area.

Due to their short half-lives, both ^{224}Ra ($t_{1/2}$=3.7 days) and ^{223}Ra ($t_{1/2}$=11.4 days) can serve as tracers of hydrological processes over relatively short timescales (days, weeks), characterising exchange fluxes along the river–estuary–coastal zone continuum, or the movement of water masses over continental shelves. On such short timescales, radioactive decay does not significantly affect the activities of ^{226}Ra ($t_{1/2}$=1,600 years) and ^{228}Ra ($t_{1/2}$= 5.8 years). Therefore, the combined activities of all four radium isotopes, the so-called radium quartet, can be used to study the exchange of water masses between different compartments of the coastal ocean on various temporal and spatial scales (Rama and Moore 1996).

The German Bight unifies several key processes that would be expected to be mirrored in the distribution of Ra and Rn isotopes, including sediment–water exchange in estuaries and on extensive tidal flats, some influenced by freshwater seepage, as well as mixing between nearshore and offshore water masses. Despite a wealth of information dealing with this subject matter for this region, to date there exist only very localised data based on the Ra approach (Schnetger et al. 2001; Shaw 2003) and, to our knowledge, no Ra data from the North Sea are available in the peer-reviewed literature.

In order to close this gap and to explore the potential use of Ra and Ra isotopes as tracers of land–ocean exchange in the North Sea, we studied the concentrations of all four naturally occurring radium isotopes in potential nearshore mixing end-members, and in the open German Bight. Our study aims at finding possibly distinctive isotopic signatures of the potential end-members and, based on the results, we explore the possibilities to disentangle contributions of individual hydrological compartments of the Wadden Sea to the German Bight.

Materials and methods

Study areas

Water samples were collected in three main study areas in the German Bight (Fig. 1a, b), these being a corridor extending from the barrier islands of Langeoog and Spiekeroog (East Frisian Wadden Sea) offshore to the island of Helgoland (Fig. 1c), an open tidal flat site influenced by freshwater seepage near the settlement of Sahlenburg (Fig. 1d), and the outer Weser Estuary (Fig. 1e).

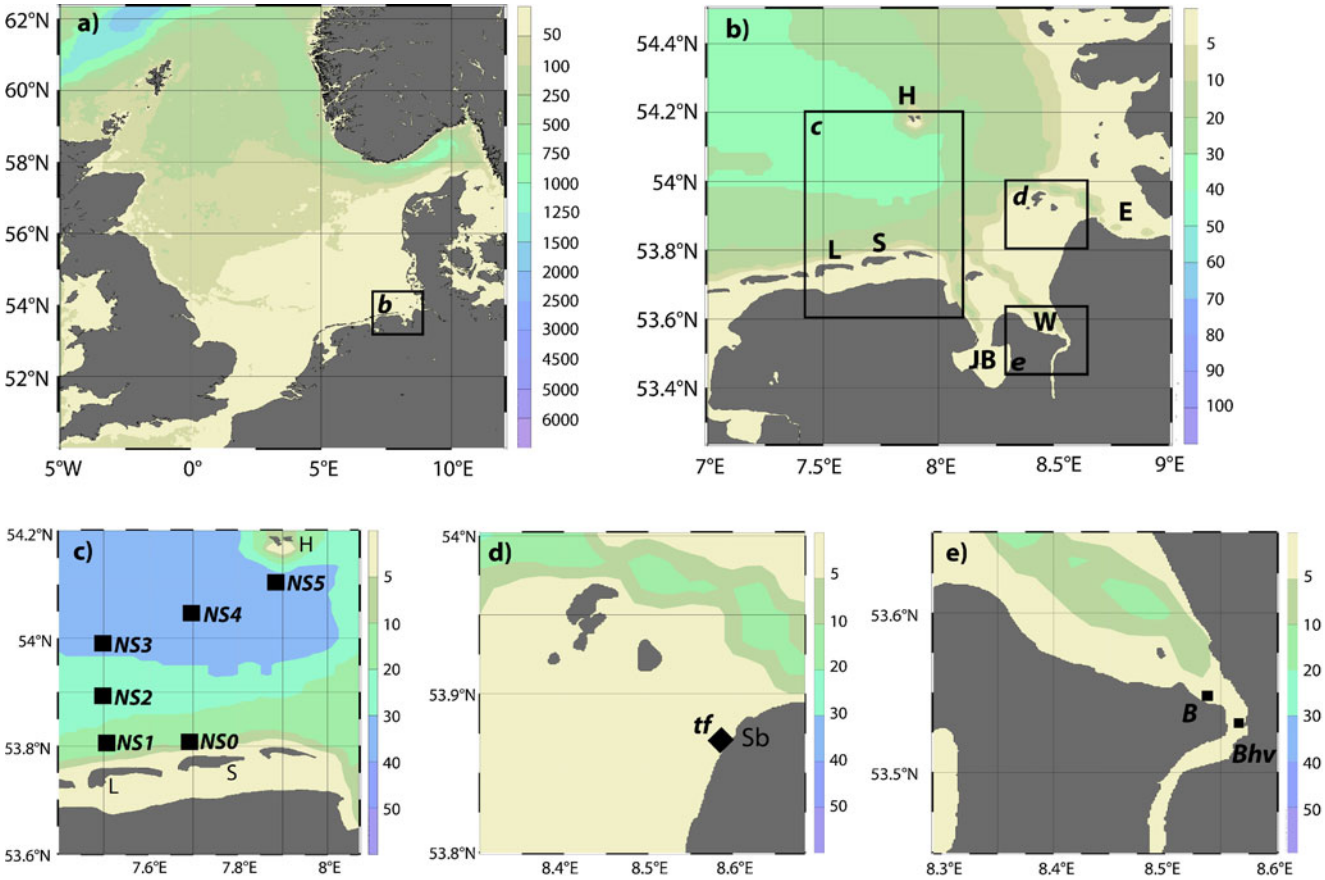

Fig. 1 Location maps of the North Sea (**a**) and the German Bight (**b**), as well as sampling locations (*squares*) in the open North Sea (**c**), the Sahlenburg intertidal flats (**d**) and the Weser Estuary (**e**). The bathymetry is shown in metres. *NS* North Sea transect sites, *tf* tidal flat site, *B* Blexen, *Bhv* Bremerhaven, *E* Elbe Estuary, *W* Weser Estuary; *JB* Jade Bay, *L* Langeoog, *S* Spiekeroog, *H* Helgoland, *Sb* Sahlenburg

The Wadden Sea covers approximately 9,300 km^2 of the Southern North Sea (Grunwald et al. 2009). The tides are semidiurnal, and the region can be divided into two mesotidal sections (tidal range <3.5 m), characterised by barrier islands and back-barrier tidal flats, and a macrotidal section (tidal range >3.5 m) consisting of open, unprotected tidal flats lining the inner German Bight. The back-barrier tidal flats, including estuaries, have been estimated to cover 3,364 km^2 (Grunwald et al. 2009). Century-long diking activities and land reclamation have resulted in an overall paucity of true mudflats in the region (sediments with mud contents exceeding 95%; mud= <63 μm fraction), and a dominance of sand flats (mud contents of <5%) and so-called mixed flats (for various sediment classification schemes, see Flemming 2000). The effects of this Wadden Sea squeeze (Delafontaine et al. 2000; Mai and Bartholomä 2000) are less pronounced in protected embayments (e.g. Jade Bay) that can accommodate fine-grained sediment deposition, and in tidal flats nourished by estuarine silts and clays (e.g. Sahlenburg tidal flats). Sediment reworking and destabilisation are caused by burrowing organisms and deposit feeders (bioturbation), as well as physical disturbance by tidal currents and storm events (e.g. Widdows et al. 2000; Volkenborn et al. 2009).

The main freshwater input to the German Bight originates from the Elbe and Weser rivers and a number of smaller streams, draining through sluice gates in the dikes. Very localised, fresh groundwater discharge occurs, for example, near Sahlenburg (cf. Gabriel et al. 2003) or near the island of Sylt (cf. Zipperle and Reise 2005). At the site near Sahlenburg (Fig. 1b), a mainland aquifer extends ca. 0.5 km onto the tidal flats, discharging fresh groundwater at scattered springs ("sand boils", according to Li et al. 1996). Those at the Sahlenburg site are 10^{-2} to $3*10^{-1}$ m in diameter. During flooding tide, when the pressure gradient increases due to the overlying body of water, the punctual groundwater discharge at the sample site decreases to a minimum value of 21 mL minute^{-1} (30 L day^{-1}), but the hydraulic gradient never allows the seawater to penetrate the freshwater aquifer. At low tide, the discharge increases to about 35 mL minute^{-1} (50 L day^{-1}; Kurtz 2004).

To the south of the Sahlenburg tidal flats, the Weser River estuary is associated with a mean discharge of

323 m^3 s^{-1} (Schuchardt et al. 1993), representing the second-largest freshwater source for the German Bight, after the Elbe River. The outer estuary is characterised by a funnel-like morphology with extensive open tidal flats. The mean tidal range exceeds 3.5 m, but water levels are also influenced by strong winds. Due to high current velocities in the estuary (Schuchardt et al. 1993), the water is generally well mixed and highly turbid, with a weakly stratified salt wedge. Highly mobile fluid mud layers >1 m in thickness have been observed, particularly at slack water (Schrottke et al. 2006). Average salinities near the city of Bremerhaven (Fig. 1c, own data) were found to range from 3–15 psu, decreasing to 1 psu at the tidal freshwater reach further upstream.

Sampling

Open North Sea transect

During cruise 234 of the RV *Heincke* (18–22 July 2005), water samples were taken at six locations (NS0 to NS5) along an open North Sea transect of ~60 km (Fig. 1c). Locations NS0 and NS1 were east and west respectively of the Otzumer Balje tidal inlet, on the shoreface of the islands of Spiekeroog and Langeoog. Locations NS2 to NS5 extended N–NE further offshore up to Helgoland. The water samples were analyzed for ^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra isotopes (albeit long-lived isotopes not on all samples). It should be noted that the wind situation changed drastically during the sampling period, with calm conditions during the sampling of NS0 and NS1, and a storm event during the following transect to Helgoland.

Tidal flat

On 18 June 2004 and again 18 June 2006, surface seawater samples were collected from the Sahlenburg tidal flat near the permanent coastline (rectangle d in Fig. 1b; label tf in Fig. 1d) immediately after low and high tide (samples tf in Table 1, taken at flooding and ebbing tide). Groundwater samples were taken from nearby scattered freshwater springs at low tide on 18 June 2004. Here, all the samples were analyzed for ^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra isotopes, as well as ^{222}Rn.

Weser Estuary

In the Weser Estuary, water samples were collected near the city of Blexen from aboard the RV *Heincke* on 21 July 2005 (Fig. 1e). An earlier batch of samples had been taken on 3 July 2002 near the city of Bremerhaven, directly from the shore (Handelshafen). In both cases, sampling was every 1–2 h over one tidal cycle, i.e. including high, low, flooding and ebbing tide phases.

Activities of ^{223}Ra and ^{224}Ra were determined in all samples from the two locations. ^{226}Ra and ^{228}Ra activities were determined only in the Blexen samples taken at high tide, as the high suspended particle loads from low tide samples hampered filtration, and high particle loads interfere with subsequent analysis by gamma spectroscopy.

^{226}Ra and ^{228}Ra measurements

From each sample, 40 L of water was filtered through a 1 μm pore size filter (Hytrex filter cartridges, 12 inch length). Radium was co-precipitated as $Ba(Ra)SO_4$ and stored sealed for 3–4 weeks to enable the short-lived daughters ^{214}Pb, ^{214}Bi and ^{228}Ac to equilibrate with their parent radionuclides ^{226}Ra and ^{228}Ra (Moore 1984). The activities of ^{226}Ra and ^{228}Ra were then determined by gamma-ray spectrometry using a high-purity germanium well-type detector. Standard aliquots of known activities analyzed under conditions identical to those of the water samples were used as reference material.

^{223}Ra and ^{224}Ra measurements

Radium was extracted usually from 40 to 90 L of sample water in each case, these volumes having been shown to be in the optimum range for minimising counting errors (Garcia-Solsona et al. 2008). Occasionally, lower volumes were processed because of high particle loads or limited availability (fresh groundwater). The samples were passed through a manganese-oxide-impregnated acrylic fibre at flow rates <0.5 $L minute^{-1}$, which results in a good quantitative adsorption of Ra (Reid et al. 1979). Activities of ^{223}Ra and ^{224}Ra were then determined using a radium delayed coincidence counter (RaDeCC), a nuclear counter system suitable for low-activity measurements in natural waters (Moore and Arnold 1996). Analyses of the Bremerhaven (2002) estuarine samples were performed in air as carrier gas. The decay of these samples was monitored by repeated (every 2–3 days) measurements over 2 weeks to verify the concentrations of individual radionuclides via their half-life, and to exclude artefacts of counts from the ^{224}Ra-decay chain that may occur in the ^{219}Rn channel (Garcia-Solsona et al. 2008). All other samples were analyzed in He as carrier gas. Due to generally low absolute ^{224}Ra activities in these samples, no significant spillover of counts from the ^{224}Ra channel to the ^{223}Ra channel was expected, and no second counting for ^{223}Ra was performed in this case.

The amounts of short-lived ^{223}Ra and ^{224}Ra radionuclides were derived from the emanation of their daughter radio-

Table 1 Ra isotopes in groundwater (Sahlenburg), and waters of the southern North Sea (*NS* North Sea transect), a German Wadden Sea tidal flat at Sahlenburg and the Weser Estuary (*B* Blexen, *Bhv* Bremerhaven) at different tidal stages. Flooding and ebbing refer to the inundation stage directly after low and high tide respectively. *n.d.* Not determined, *n* sample size

Location	Sampling date	Tide	Salinity (psu)	^{228}Ra (dpm 100 kg^{-1})	^{226}Ra (dpm 100 kg^{-1})	^{228}Ra:^{226}Ra	^{224}Ra (dpm 100 kg^{-1})	^{223}Ra (dpm 100 kg^{-1})	^{224}Ra:^{223}Ra
NS5 (offshore)	20 July 05		32				5.3±0.5 (*n*=2)	0.3±0.03	17.7
NS4	20 July 05		33	23.0±2.3 (*n*=2)	8.2±0.8	2.8	2.0±0.6 (*n*=2)	0.1±0.02	20.0
NS3	20 July 05		33				4.1±1.0 (*n*=2)	0.6±0.05	6.8
NS2	20 July 05		32				3.1±1.0 (*n*=2)	0.4±0.04	7.8
NS1	20 July 05		32				10.1±0.9 (*n*=2)	0.9±0.05	11.2
NS0 (nearshore)	19 July 05	High	n.d.	28.2±2.8 (*n*=2)	11.8±1.2	2.4	9.4±3.0 (*n*=2)	0.9±0.2	10.4
NS0	19 July 05	Low	n.d.	35.1±3.5 (*n*=2)	13.8±1.4	2.6	20.3±6.1 (*n*=2)	1.2±0.1	16.9
Tidal flat (tf)	18 June 06	Flooding	28	39.3±3.8 (*n*=3)	16.5±1.7	2.3	34.3±2.2 (*n*=3)	3.6±0.5	9.5
	18 June 06	Ebbing	26	46.0±4.5 (*n*=3)	15.5±1.5	2.9	85.3±6.3 (*n*=3)	8.0±1.2	10.7
Weser Estuary (B)	21 July 05	High	18	46.3±4.6 (*n*=2)	17.1±1.7	2.6	26.1±8.2 (*n*=2)	1.8±0.1	14.5
	21 July 05	Low	12				36.5±6.1 (*n*=2)	2.5±0.2	14.6
Weser Estuary (Bhv)	3 July 02	High	15				31.6±1.1 (*n*=3)	4.0±0.4	7.9
	3 July 02	Low	6				36.1±1.0 (*n*=3)	3.0±0.5	12.0
Fresh groundwater	18 June 04	Low	0.7	42.1±4.1 (*n*=3)	21.3±2.2	2.0	5.1±0.9 (*n*=3)	2.6±1.3	2.0

nuclides ^{220}Rn and ^{219}Rn respectively. In order to limit device-specific errors, each measurement was repeated two or three times using multiple RaDeCC channels. Blank determination was performed using a manganese-oxide-impregnated fibre that had been flushed with de-ionised water. A final measurement of the samples was conducted after several weeks in order to determine the supported ^{223}Ra and ^{224}Ra. The parent of ^{223}Ra, ^{227}Ac, has been shown to be somewhat elevated in coastal areas, potentially causing a small but regionally variable amount of supported ^{223}Ra (Geibert et al. 2008).

^{222}Rn measurements

In each case, a 10 mL water sample was collected in a syringe pre-filled with 10 mL of a non-evaporating, water-immiscible scintillation cocktail (di-isopropylnaphthalene, Hidex Maxi-light) to prevent outgassing from the aqueous phase. ^{222}Rn activities were determined in the home laboratory, using a portable single tube liquid scintillation counter (Triathler® LSC). As ^{222}Rn has a much higher affinity for the organic solvent, it was extracted from the aqueous phase by short, vigorous shaking of the sample. The mixture was then allowed to stand for 3 h in order to separate the phases and to equilibrate radon with its α-emitting daughters ^{218}Po and ^{214}Po (Purkl and Eisenhauer 2004). The excess Rn concentration, $^{222}Rn_{ex}$, was determined in a second extraction step after 4 weeks, when ^{222}Rn had equilibrated with its parent radionuclide ^{226}Ra (Purkl and Eisenhauer 2004). Blank levels for this method are extremely low (a few counts per day), making the LSC particularly suitable for Rn measurements on very small volumes.

Salinity

Salinity data for the open North Sea transect were obtained from the physical oceanography group onboard the RV *Heincke*. Other salinity data are own conductivity-based measurements.

Error handling

The uncertainties for the radium isotope analyzes were determined by applying the principle of error propagation, including decay, uncertainty in the efficiency determination, and chance coincidence corrections (for the RaDeCC), following the strategy presented in Giffin et al. (1963) and Moore and Arnold (1996). The error of the blank correction, considered to be small compared to the effects of efficiency determination, was not propagated for the short-lived Ra isotopes. The detector efficiency for the long-lived Ra isotope measurements was 12 and 10% for ^{226}Ra and ^{228}Ra respectively. The efficiency of the RaDeCC varied between 27% (^{224}Ra) and 21% (^{223}Ra) in helium, and it was only ~25% (^{224}Ra) and ~17% (^{223}Ra) in air, consistent with the findings of Moore (2008). The moisture content of the fibres and, consequently, efficiency were found to be more variable when air was used as carrier gas. The uncertainties for ^{222}Rn were determined by simple counting statistics.

Results

^{228}Ra and ^{226}Ra

The offshore activities of the long-lived Ra isotopes were in general lower than in nearshore waters (see Fig. 2, Table 1). Activities of ^{228}Ra (in dpm 100 kg^{-1}) were 35.1±3.5 during low tide at nearshore site NS0 (presumably a signal from the back-barrier tidal flat), decreasing to 28.2±2.8 at high tide, and only 23.0±2.3 at the offshore site NS4 near Helgoland. ^{226}Ra activities were 13.8±1.4 dpm 100 kg^{-1} during low tide at site NS0, 11.8±1.2 during high tide at site NS0, and 8.2±0.8 at offshore site NS4.

Irrespective of the tidal phase, the values that were recorded on the tidal flat (tf) were similar to the signal originating from the nearshore site NS0 at low tide along the transect (cf. differences between ebbing and flooding tide were within the measurement uncertainties for both isotopes at tf). ^{228}Ra was found to vary from 39.3±3.8 to 46±4.5, and ^{226}Ra activity from 15.5±1.5 to 16.5± 1.7 dpm 100 kg^{-1}. Furthermore, the long-lived Ra activities in the fresh groundwater discharging on the tidal flat were quite similar, with ^{228}Ra and ^{226}Ra values of 42.1±4.1 and 21.3±2.2 dpm 100 kg^{-1} respectively. The ^{228}Ra and ^{226}Ra activities in the Weser Estuary at high tide were 46.3±4.6 and 17.1±1.7 dpm 100 kg^{-1} respectively (Table 1), again very similar to the other nearshore values, but significantly different from the offshore values.

^{224}Ra and ^{223}Ra

North Sea transect

The highest ^{224}Ra and ^{223}Ra activities along the transect were measured in the outflow of the back-barrier system (site NS0, Table 1) at low tide, with 20.3±6.1 for ^{224}Ra and 1.2±0.1 dpm 100 kg^{-1} for ^{223}Ra. Towards the open North Sea, activities decreased to 2.0±0.6 for ^{224}Ra and 0.10± 0.02 dpm 100 kg^{-1} for ^{223}Ra (Fig. 2b, c), slightly rising again near Helgoland (site NS5). The salinity increased slightly from 32 psu at site NS1 nearshore to 33 psu at site NS4 further offshore.

Tidal flat and fresh groundwater

The highest activities of the short-lived Ra isotopes were measured on water samples collected from the tidal flat near Sahlenburg (up to 85.3±6.3 for ^{224}Ra and 8.0± 1.2 dpm 100 kg^{-1} for ^{223}Ra; see Table 1). The ^{224}Ra activities from the tidal flat, even during flooding tide when only 34.3±2.2 dpm 100 kg^{-1} was recorded, were much higher than in the fresh groundwater discharging from nearby sand boils (^{224}Ra: 5.1±0.9 dpm 100 kg^{-1}). The difference was less pronounced for the ^{223}Ra activities (3.6±0.5 to 8.0±1.2 on the tidal flat vs. 2.6±1.3 in the fresh groundwater), associated with a very low ^{224}Ra/^{223}Ra ratio (Table 1). Distinctly higher ^{224}Ra and ^{223}Ra activities were detected at ebbing tide, with values rising to 85.3±6.3 and 8.0±1.2 dpm 100 kg^{-1} respectively. The salinity of seawater samples varied from 28 psu (flooding tide) to 26 psu (ebbing tide), whereas the salinity of the groundwater was found to be 0.7 psu, indicating its origin from the freshwater aquifer that extends onto the intertidal flat.

Weser Estuary

At the Bremerhaven (Bhv) and Blexen (B) sites (Fig. 1e), temporal variations of activities were found to be related to the tidal phase (Table 1, Fig. 3). The ^{224}Ra activities were 26.1±8.2 to 36.5±6.1 for B and 31.6±1.1 to 36.1± 1.0 dpm 100 kg^{-1} for Bhv. The ^{223}Ra activities ranged from 1.8±0.1 to 2.5±0.2 for B and 3.0±0.5 to 4.0± 0.4 dpm 100 kg^{-1} for Bhv. A peak in ^{224}Ra activity was observed with decreasing salinity during ebbing tide at the Bhv site (Fig. 3d). A similar trend would be expected for ^{223}Ra, but errors for low ^{223}Ra activity are too large to allow a clear statement. The salinity was in the range of 15–18 psu at high tide and 6–12 psu at low tide.

^{222}Rn

Preliminary ^{222}Rn measurements carried out on the intertidal flat revealed that the activity of ^{222}Rn in seawater was significantly lower than that in fresh groundwater (234.4±40.4 dpm kg^{-1}). This was the case at both flooding (46.9±8.8 dpm kg^{-1}) and ebbing tide (66.7±11.2 dpm kg^{-1}).

Discussion

^{226}Ra and ^{228}Ra

Extensive continental shelf areas have been reported to be an important source of ^{228}Ra to the ocean (Moore 1981), prominent examples being the Arctic and the Yellow Sea (Rutgers van der Loeff et al. 1995, 2003; Kim et al. 2005). The North Sea as a whole resembles these larger examples, while the Wadden Sea, with its extensive intertidal flats, constitutes a distinct situation within the North Sea, with exceptionally strong water and sediment dynamics. To our knowledge, we report here the first values for long-lived radium isotopes from the North Sea, the Wadden Sea and the Weser Estuary. As these are coastal environments influenced by a large shelf area, we would expect to find comparatively

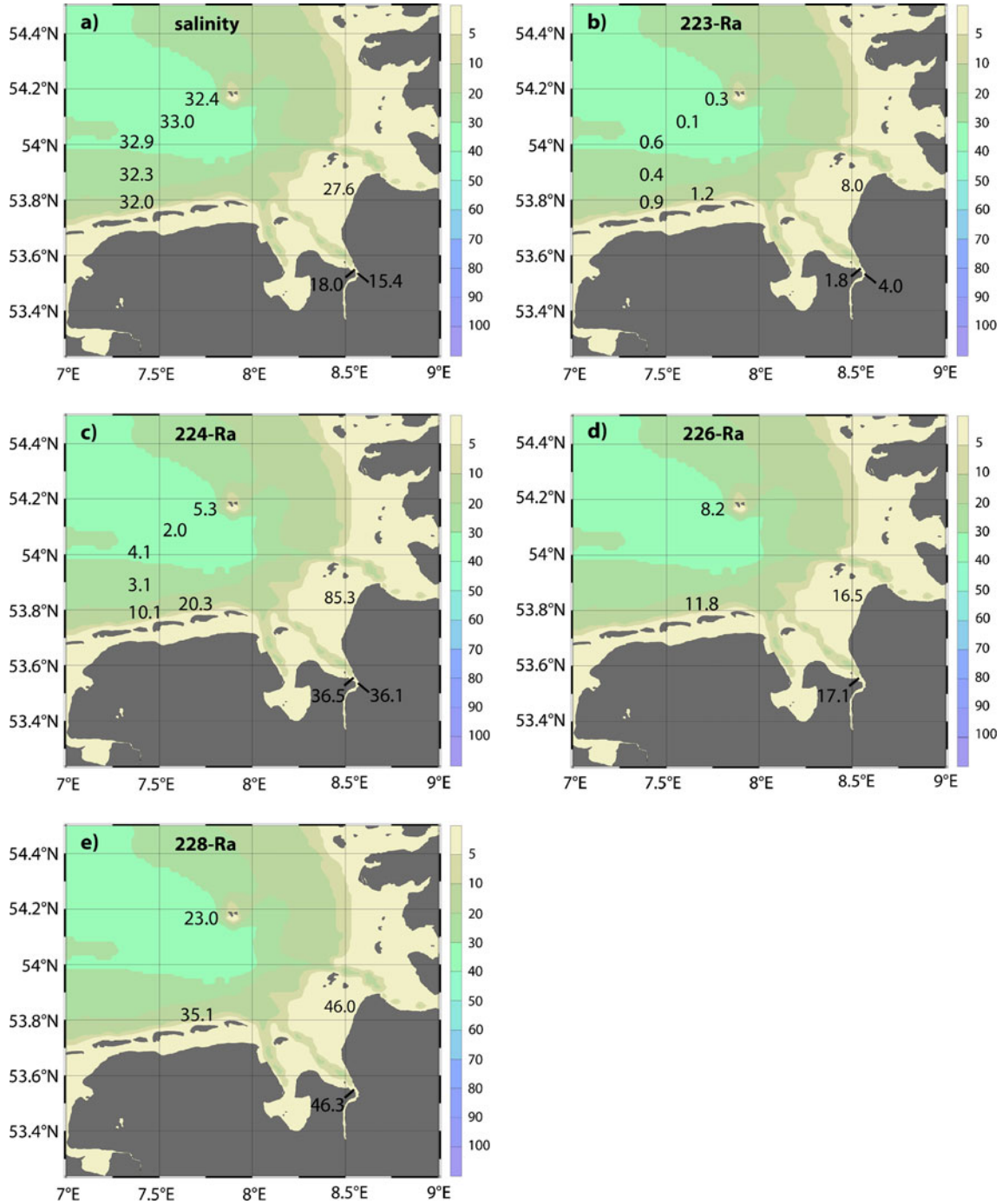

Fig. 2 Maximum activities of natural Ra isotopes (dpm 100 kg^{-1}) and corresponding salinity in the sampling area (cf. Table 1 for sampling dates). In all cases, maximum activities were recorded during ebbing or at low tide. **a** Salinity (psu), **b** ^{223}Ra, **c** ^{224}Ra, **d** ^{226}Ra, **e** ^{228}Ra. For orientation, see geographic features in Fig. 1b

high values determined largely by the residence time of Atlantic waters in this shallower North Sea sector. Indeed, open ocean ^{228}Ra concentrations are typically much lower than coastal concentrations as a consequence of decay and mixing (Sarmiento et al. 1982).

Our activities for ^{228}Ra in the open North Sea (site NS4, 23.0±2.3 dpm 100 kg^{-1}) and in the Weser Estuary (23.0± 2.3 dpm 100 kg^{-1}) are comparable to observations for the Siberian shelves incorporating the Ob, Yenisey and Lena estuaries, with values ranging from 3.3 dpm 100 kg^{-1} towards the open Arctic Ocean up to 40.9 dpm 100 kg^{-1} in the estuary of the river Ob (Rutgers van der Loeff et al. 2003). Activities reported from another large shelf region, the Yellow Sea, range from 3.4±0.8 to 68.9±1.1 dpm 100 kg^{-1},

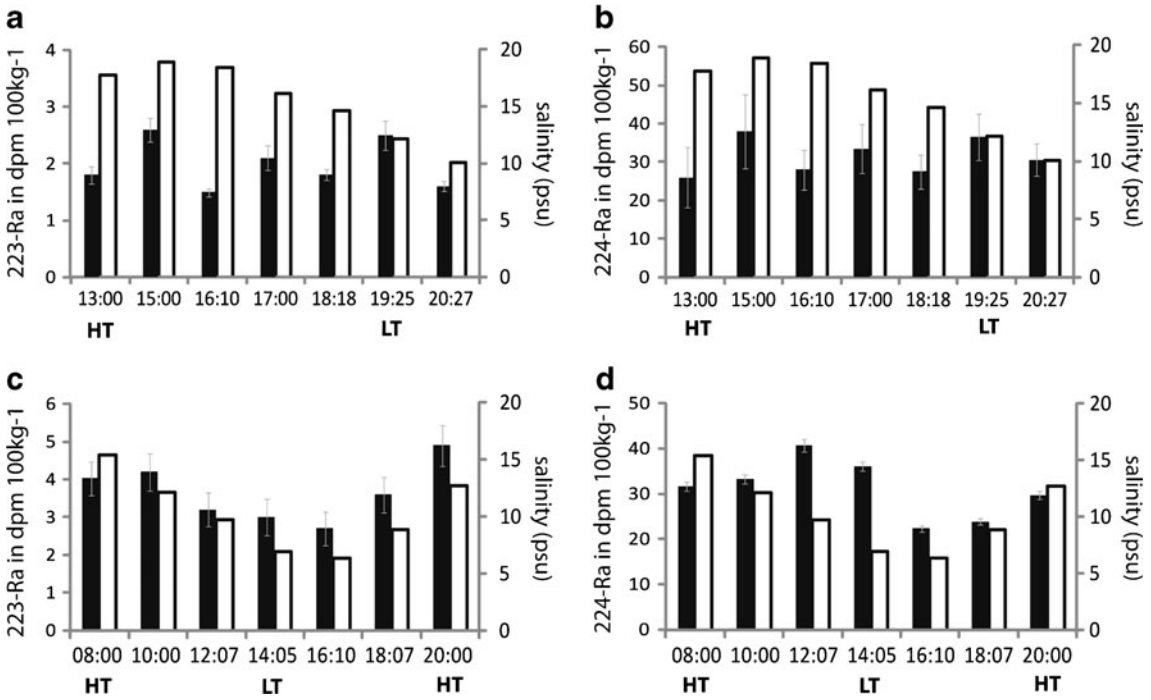

Fig. 3 Temporal variations of short-lived Ra isotopes (*black*) and salinity (*white*) in the Weser Estuary at Blexen (**a** ^{223}Ra, **b** ^{224}Ra; 21 July 2005) and Bremerhaven (**c** ^{223}Ra, **d** ^{224}Ra; 3 July 2002). *HT* High tide, *LT* low tide

with values often at the higher end of the range (Kim et al. 2005). From a slightly smaller shelf region in the northeast Gulf of Mexico, values ranging from 13.6 to 137.3 dpm 100 kg^{-1} have been reported by Moore (2003). This suggests that the North Sea is no exception to the general trend of high ^{228}Ra activities on extended continental shelves due to release from sediments. Indeed, similar activities have been reported from the South Atlantic Bight (Moore 2000b), the Amazon shelf (Moore et al. 1995), and the Mississippi and Atchafalaya rivers (Krest et al. 1999).

In contrast to ^{228}Ra, ^{226}Ra with a half-life of 1,600 years is typically less variable in surface waters, but it has previously been found to show some variation with water mass (Ku and Luo 1994, 2008). Typical values of about 7 dpm 100 kg^{-1} have been reported from the North Atlantic (Broecker et al. 1976), with relatively little variation as a result of the long half-life of the isotope. Our data for the German Bight of the North Sea (site NS4: 8.2± 0.8 dpm 100 kg^{-1}) reveal a similar concentration for ^{226}Ra, confirming the North Atlantic origin of North Sea waters, with little subsequent modification of the signal.

Summarising our findings for long-lived Ra isotopes at a larger scale, we have demonstrated that ^{226}Ra concentrations in the open North Sea are very similar to those in the North Atlantic, the former being only marginally more elevated. ^{228}Ra values indicate enrichment over the large shelf area of the North Sea, consistent with findings from other shelf regions.

Somewhat unrelated to the large-scale trends are the long-lived Ra isotope activities in our fresh groundwater, which originates from an aquifer related to a buried valley from a past glacial period (Gabriel et al. 2003). With 42.1± 4.1 and 21.3±2.2 dpm 100 kg^{-1} for ^{228}Ra and ^{226}Ra respectively, they deviate considerably from values reported for other coastal aquifers. For example, Rama and Moore (1996) found ^{228}Ra activities as high as 176 dpm 100 kg^{-1} in a seep of the North Inlet salt marsh near Georgetown, South Carolina. More recently, Breier and Edmonds (2007) measured high ^{226}Ra (95–446 dpm 100 kg^{-1}) and ^{228}Ra (74–576 dpm 100 kg^{-1}) activities in the freshwater end-member of a spring discharging in the Corpus Christi Bay groundwater system of Texas. We explain the low radium activity in our groundwater by the very low salinity (0.7 psu), leading to a stronger adsorption onto particles. The lack of pronounced enrichment of long-lived Ra isotopes in fresh groundwater discharging in the intertidal zone limits the use of ^{228}Ra and ^{226}Ra isotope signals as tracers of fresh localised groundwater inputs to the German Bight. However, recirculated saline pore water or groundwater would contribute to radium enrichment in the Wadden Sea and, eventually, the open North Sea.

^{223}Ra and ^{224}Ra

The decrease in short-lived Ra isotopes observed along the North Sea transect is consistent with the release from a

main source of short-lived radium in the Wadden Sea and its estuaries, and subsequent decay towards the open North Sea. Although the decrease of ^{224}Ra and ^{223}Ra with distance from the coastline resembles the results of studies done elsewhere (e.g. the Gulf of Mexico, Moore and Krest 2004; the Amazon shelf, Moore et al. 1995), the absolute magnitude of Ra activities in the open North Sea is distinctly smaller. At a distance of 60 km offshore, only a negligible activity of short-lived Ra was measured, whereas in the Amazon shelf and the Gulf of Mexico, the decrease of the coastal Ra signal could be followed over tens to hundreds of kilometres. As a consequence of the fast decay of short-lived Ra isotopes, and the strong dilution of Ra derived from adjacent nearshore sources (i.e. the Weser Estuary, tidal flats, and submarine groundwater), short-lived Ra isotopes may be in the range of the detection limit beyond Helgoland. In principle, the decrease of short-lived Ra with distance from shore would allow constraining horizontal mixing according to previous studies (Moore 2000b). However, the potential importance of Ra diffusing from sediments in the offshore area would need to be assessed in order to understand the overall Ra budget in the German Bight of the North Sea, and the limited amount of data on the offshore transect of the present study is not sufficient to derive a robust mixing estimate.

On the tidal flat, distinct variations in ^{224}Ra and ^{223}Ra activity were measured as a function of the tidal stage. The peak activities might be related to the turbulent flushing of the sediment bed due to tidal disturbance, and possibly due to bioirrigation. As the vast tidal flats are exposed to air during low tide, which temporarily prevents a loss of newly produced short-lived Ra, the inundation during flooding tide causes an extensive flushing of the upper sediment layers. We hypothesise that this flushing is assisted by bioirrigation due to burrowing benthic organisms, causing a stripping of radionuclides from particles after ebb tide. Also, pore water from tidal flats lost to seawater during ebbing tide (Billerbeck et al. 2006a, b) is likely to represent an important source of Ra to the Wadden Sea.

In the Weser Estuary, the increasing Ra activities observed during ebbing tide most probably result from the radionuclide fraction that is adsorbed to particles under low salinity conditions, and stripped off when brought in contact with the tidal river water of higher ionic strength. Li et al. (1977) showed that Ra is released in estuaries during the mixing between freshwater and seawater. High loads of suspended particles in the Weser Estuary, especially at low tide (Schrottke et al. 2006), may cause a release of Ra within the water column, as a consequence of both increasing salinity and decreasing particle concentrations, whereas hydraulic action of the tides can deliver short-lived Ra from pore water and groundwater further upstream, in combination leading to a delayed and more complex response of Ra isotopes. Our results can be seen only as a first indication of possible processes, and more detailed sampling campaigns would be required to establish a Ra budget for the Weser Estuary.

^{222}Rn

During both flooding and ebbing tide, the ^{222}Rn signal was clearly lower in seawater than in fresh groundwater. Turbulent mixing during inundation would support the mixing of ^{222}Rn in the overlying water and, consequently, outgassing at the water–atmosphere interface. We expect that the overlying water body of the intertidal flat would be too shallow to develop a vertical ^{222}Rn activity gradient, especially as the intertidal flat is partially exposed to air during low tide. Our small dataset provides at least a preliminary indication of activity levels that should prove useful in the future design of more detailed studies. A particularly promising application is the linking of the noble gas ^{222}Rn to investigations of methane (Grunwald et al. 2009), as this could help to constrain regional budgets of gas release.

Conclusions

This paper presents a first dataset on four radium radioisotopes (the radium quartet) in the German Bight of the North Sea. On a regional scale, the isotope distributions were found to track primarily the mixing between nearshore and offshore water masses. It was shown that localised fresh groundwater discharge is most probably not an important source of the short-lived ^{223}Ra and ^{224}Ra isotopes in this environment. Rather, ^{223}Ra and ^{224}Ra are released from the vast tidal flats during inundation, with a potential contribution of diffuse fluxes from saline or brackish groundwater. We found very similar activities of both short- and long-lived Ra isotopes in all potential water mass end-members, except for the waters of the open German Bight. The Weser Estuary, the tidal flats near Sahlenburg, and discharge originating from the back-barrier tidal flats near Spiekeroog all have virtually identical activities of ^{228}Ra and ^{226}Ra. These activities decrease towards the open German Bight, revealing a potential for constraining offshore fluxes of material originating in the tidal zone on a scale of tens of km, but limiting the potential discrimination of signals from sources like the Weser Estuary, as well as back-barrier and unprotected tidal flats. For the establishment of a Ra budget for the region, the signatures from nearby the Elbe River and from possible Ra fluxes from the sea floor in the open North Sea would be required, especially as the Elbe has been shown to be the main contributor of fresh water to our study area in historical times (Scheurle and Hebbeln 2003).

As an additional finding, we demonstrate for the first time that ^{228}Ra in the open German Bight is elevated, comparable to the situation in other regions with extended submerged shelf areas.

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