Natural Radioactivity in Produced Water from the Norwegian Oil and Gas Industry in 2003

Statens strålevern

Abstract:
This report presents results of a survey of natural radioactivity (^{226}Ra, ^{228}Ra and ^{210}Pb) in produced water from all 41 Norwegian platforms in the North Sea discharging produced water. The sampling campaign took place from September 2003 to January 2004. Based on the data presented the average activity concentrations of ^{226}Ra and ^{228}Ra in produced water from the Norwegian oil and gas industry have been estimated to 3.3 Bq l^{-1} and 2.8 Bq l^{-1}, respectively. With one exception, all results obtained for ^{210}Pb were below the detection limit of about 1 Bq l^{-1}. The estimated total activities of ^{226}Ra and ^{228}Ra discharged in 2003 are 440 GBq (range 310-590 GBq) and 380 GBq (range 270-490 GBq), respectively.

Resymé:
Rapporten viser resultater fra en undersøkelse av naturlig radioaktivitet (^{226}Ra, ^{228}Ra and ^{210}Pb) i produsert vann fra samtlige 41 norske plattformer i Nordsjøen med slike utslipp. Prøvene ble samlet inn fra september 2003 til januar 2004. Dataene anslår gjennomsnittelig aktivitetskonsentrasjon av ^{226}Ra og ^{228}Ra i produsert vann fra norsk olje- og gassvirksomhet til henholdsvis 3,3 Bq l^{-1} og 2,8 Bq l^{-1}. For 210Pb var alle resultatene, med ett unntak under deteksjonsgrensen på rundt 1 Bq-1. De totale utslippene av ^{226}Ra og ^{228}Ra i 2003 er estimert til henholdsvis 440 GBq (fra 310 GBq til 590 GBq) og 380 GBq (fra 270 GBq til 490 GBq).

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Contents

Summary

The oil and gas industry represents by far the largest industry in Norway in terms of economical importance. Altogether, more than 40 offshore platforms operate in the North Sea and the Norwegian Sea. The largest waste stream by volume, from this industry is water co-produced with the oil and gas (referred to as produced water, formation water or oilfield brines). In 2003 about 135 million m^3 of produced water was discharged to the marine environment from the Norwegian oil and gas industry. One problem with produced water is that it may contain elevated levels of naturally occurring radium isotopes, of which ^{226}Ra and ^{228}Ra are the most long-lived. Previously reported results show that the activity concentrations of ^{226}Ra and ^{228}Ra are about three orders of magnitude higher than what is normally encountered in seawater. Produced water from the oil and gas industry was also identified by the MARINA II study, published by the European Commission in 2003, as a significant contributor of alpha emitting radionuclides in northern European waters. In order to obtain an up to date estimate of the discharge of natural radioactivity from the Norwegian oil and gas industry for 2003, the industry was asked to report the activity concentrations of ^{226}Ra, ^{228}Ra and ^{210}Pb in produced water. The sampling campaign took place from September 2003 to January 2004 and included all 41 Norwegian platforms discharging produced water. The aim was to collect one sample per month for 5 consecutive months for each Norwegian production platform discharging produced water in the North Sea or the Norwegian Sea. The reason for sampling monthly during a five-month period was to measure the variation that may occur during this period in order to determine a suitable sampling frequency for future surveys.

Results obtained in this study show that the activity concentration of ^{226}Ra in the produced water samples ranged from below the detection limit (about 1 Bq l^{-1}) up to 16 Bq l^{-1}, while the activity concentration of ^{228}Ra ranged from below the detection limit (about 1 Bq l^{-1}) up to 21 Bq l^{-1}. For ^{210}Pb, almost all results were below the detection limit. The total discharged activities of ^{226}Ra and ^{228}Ra in 2003 were estimated to be 440 GBq (range 310 to 590 GBq) and 380 GBq (range 270 to 490 GBq), respectively. Dividing the total discharged activity by the total volume of produced water discharged gives average activity concentrations of ^{226}Ra and ^{228}Ra of 3.3 and 2.8 Bq l^{-1}, respectively. The discharged activity of ^{226}Ra in 2003 for most platforms was below a few tens of GBq, while a higher discharge was observed for the Troll B and C platforms. Together these platforms discharged about 193 GBq of ^{226}Ra in 2003, corresponding to about 40 % of the total activity discharged from the Norwegian continental shelf installations. A similar pattern was also observed for ^{228}Ra. This estimate is in good agreement with an estimate for ^{226}Ra made for the Norwegian oil and gas industry in 2002, also based on platform-specific data (Varskog, 2003). The results from this study also show that the total activity of ^{226}Ra and ^{228}Ra discharged to the North Sea by the Norwegian oil and gas industry, as postulated and presented in the MARINA II study, was overestimated with about a factor of 10.

The report also includes results from dispersion modelling of the discharges of radium, where data from this study have been used. In most areas the contribution of ^{226}Ra from produced water was well below 1 mBq l^{-1}. Natural background levels of radium in the North Sea are uncertain, but probably range from about 1.5 to 5 mBq l^{-1} for ^{226}Ra. For a continuous discharge over one year the model showed that levels up to 1 mBq l^{-1} in the seawater may occasionally be found for ^{226}Ra and ^{228}Ra, each, in limited areas in the northern North Sea, assuming all radium is in soluble form (higher activity concentrations may be found close to the discharge points). Discharge of radium from the British sector of the North Sea was not included in these calculations

Sammendrag

Olje- og gassvirksomheten er Norges største næring målt i verdiskapning. Mer enn 40 felt er i produksjon i Nordsjøen og Norskehavet. Det største utslippet til sjø fra denne industrien er vann, som sammen med olje og gass strømmer opp fra brønnen (kalt produsert vann eller formasjonsvann). I 2003 ble det sluppet ut 135 millioner m^3 produsert vann til havmiljøet fra norsk petroleumsvirksomhet. Produsert vann inneholder blant annet forhøyede nivåer av naturlig forekommende radiumisotoper. Av disse har ^{226}Ra og ^{228}Ra lengst levetid. Tidligere målinger har anslått at aktivitets- konsentrasjonene av ^{226}Ra og ^{228}Ra i produsert vann er tusen ganger innholdet av de samme isotopene i sjøvann. MARINA II-studien publisert av Europakommisjonen i 2003, fastslo også at olje- og gassvirksomheten bidrar med en betydelig andel alfa-emitterende radionuklider til nordeuropeiske havområder. For å etablere sikre utslippstall for naturlig radioaktivitet fra norsk petroleumsindustri, ble operatør- selskapene i 2003 bedt om å rapportere aktivitetskonsentrasjonen i produsert vann av ^{226}Ra, ^{228}Ra og ^{210}Pb. I perioden september 2003 til januar 2004 ble det samlet inn månedlige prøver fra de 41 plattformene som slipper ut produsert vann. Hensikten med å ta prøver hver fjerde uke i fem måneder var å studere variasjonsbredde og finne optimal prøvetakningsfrekvens for fremtidige under- søkelser.

Resultatene fra denne studien viser at aktivitetskonsentrasjonen av ^{226}Ra i produsert vann varierte fra under deteksjonsgrensen (cirka 1 Bq l^{-1}) til 16 Bq l^{-1}. Aktivitetskonsentrasjonen av ^{228}Ra varierte fra under deteksjonsgrensen til 21 Bq l^{-1}. For ^{210}Pb lå nesten samtlige resultater under deteksjonsgrensen. De totale utslippene i 2003 av ^{226}Ra og ^{228}Ra ble estimert til henholdsvis 440 GBq (mellom 310 GBq og 590 GBq) og 380 GBq (mellom 270 GBq og 490 GBq). Når samlet radioaktivitet sluppet ut fra alle plattformer divideres med totalt utslippsvolum, blir gjennomsnittlig aktivitets- konsentrasjon av ^{226}Ra 3,3 Bq l^{-1}. Tilsvarende tall for ^{228}Ra er 2,8 Bq l^{-1}. Fra de fleste plattformene ble det sluppet ut i underkant av noen titalls GBq av ^{226}Ra. Imidlertid var utslippene fra Troll B- og Troll C-plattformene av denne isotopen høyere, omtrent 193 GBq. Det utgjør omtrent 40 % av total aktivitet sluppet ut på norsk sektor. Et lignende mønster ble funnet for ^{228}Ra. Estimatene ovenfor for ^{226}Ra stemmer overens med plattform- spesifikke resultater for norsk olje- og gassvirksomhet i 2002 (Varskog, 2003). Denne studien viser dessuten at MARINA II- undersøkelsen overestimerte total aktivitet av ^{226}Ra and ^{228}Ra sluppet ut til Nordsjøen fra norsk petroleumsvirksomhet med en faktor på 10.

Resultater fra spredningsmodellering av radium i vannmassene er også inkludert i rapporten. Data fra denne studien ble brukt i modelleringen. I de fleste havområder vil bidraget av ^{226}Ra fra produsert vann ligge langt under 1 mBq l^{-1}. Modellberegningene viser imidlertid at nivåene av ^{226}Ra og ^{228}Ra enkelte steder i nordlige deler av Nordsjøen kan komme opp i 1 mBq l^{-1} sjøvann for hvert av stoffene (nær utslippspunktet kan verdiene for tilført radium være høyere). Naturlig bakgrunnsnivå av radium i Nordsjøen er usikkert, men ligger antagelig mellom 1,5 mBq l^{-1} og 5,0 mBq l^{-1} for ^{226}Ra. Beregningene forutsatte at produsert vann ble sluppet ut kontinuerlig i ett år. Det ble også antatt at utslippsvannet kun inneholdt radiumisotoper i løst form. Utslippet av radium fra plattformer på britisk sektor var ikke inkludert i beregningene.

1   Introduction

In recent years the focus on discharges of natural radioactivity from non-nuclear industries has increased. The MARINA II study published in 2003 by the European Commission estimated that non-nuclear industries, especially the phosphate and the oil and gas industries, were responsible for a large fraction of the total discharged alpha activity in Northern European marine waters. Since the discharges of phosphogypsum have largely stopped since 2000, the discharge of produced water from the oil and gas industry has become relatively more important. One major problem when assessing the discharges from non-nuclear industries has, however, been the lack of data, which has led to uncertainties in these assessments.

The oil and gas industry represents by far the largest non-nuclear industry in Norway in terms of economical importance. Altogether, more than 40 offshore platforms operate in the North Sea and the Norwegian Sea. The largest waste stream by volume, from this industry is water co-produced with the oil and gas (referred to as produced water, formation water or oilfield brines). In 2003 about 135 million m^3 of produced water was discharged to the marine environment from the Norwegian oil and gas industry. Concerning radioactivity, produced water can contain elevated levels of especially radium, a naturally occurring radioactive element leached to the formation water from the surrounding bedrock. Taking the large volumes discharged into consideration, relatively little data has been published on the activity concentration in produced water from the Norwegian oil and gas industry. In order to obtain an overview and improve the estimate of discharged activity, the industry was asked in 2003 to participate in a study initiated by the NRPA, where produced water from each Norwegian production platform was analysed for ^{226}Ra, ^{228}Ra and ^{210}Pb monthly over a five-month period. The primary objective of this report is to present the results of this study. Together with reported discharge volumes for 2003, the results have also been used to model the dispersion of radium in the North Sea from produced water discharge. In 2002, seawater collected around the Gullfaks A, B and C platforms and the Sleipner A and T platforms was analysed for ^{226}Ra. The results of this study are also presented in the report.

2   Natural radioactivity

2.1   Introduction

Since the creation of earth, radioactive elements have been part of the natural environment. Naturally occurring radioactive elements are present in the atmosphere and in the aquatic and terrestrial environments in varying concentrations. Natural radioactivity can be divided into two types depending on its origin: cosmogenic and primordial radionuclides. The first category is constantly produced mainly in the atmosphere in reactions between cosmic radiation and air molecules (some reactions also occur in the outermost layer of the earth's crust). The second category of natural radionuclides is the primordials which have been present since the creation of the earth. The primordials can be further divided into single and serial primordials, depending on whether the decay product is radioactive or not. Characteristic for these elements are their long half-lives, which are at least of the order of the age of the earth. Primordials with shorter half-lives exist only as decay products which can be traced to a parent nuclide with a long half-life.

2.1.1   Natural decay series and geochemistry

Three primordial decay series are present in nature: the uranium series, the thorium series and the actinium series (after its fourth member, ^{227}Ac); the parent nuclides for these series are ^{238}U, ^{232}Th and ^{235}U, respectively. The most abundant of these three nuclides are ^{238}U and ^{232}Th (see Figures 2.1 and 2.2) (the natural ^{235}U/^{238}U ratio is constant with a mass ratio of 0.00727 and an activity ratio of 0.0462). Both ^{238}U and ^{232}Th decays via several radioactive nuclides to stable lead isotopes, ^{206}Pb and ^{208}Pb, respectively. In an undisturbed system, secular radioactive equilibrium, meaning that the activity concentrations of all nuclides in a decay chain with a long-lived parent-nuclide are equal, will be established after a certain amount of time. In nature, many systems are far from undisturbed, which can result in significant disequilibria in the decay series. One example is ground water/formation water/brines, where fractionation occurs at the rock/water interface. Generally, the natural radionuclides most often encountered in ground water are uranium, radium and radon. Thorium and protactinium are the least soluble, while lead, polonium, bismuth and actinium may be found under certain conditions (Osmond and Cowart, 1992). Mobilisation, transport and redeposition are complex processes and depend on both physical and chemical parameters. The decay process of alpha-emitting elements may itself facilitate leaching by direct alpha recoil into the water or facilitated leaching of dislocated atoms. Solubility is also related to parameters such as pH, redox potential (closely related to the dissolved oxygen content), temperature, salinity and organic and inorganic complexing. Due to the different chemical properties and half-lives of the nuclides in the decay series, chemical leaching from the rock material will occur at different rates.
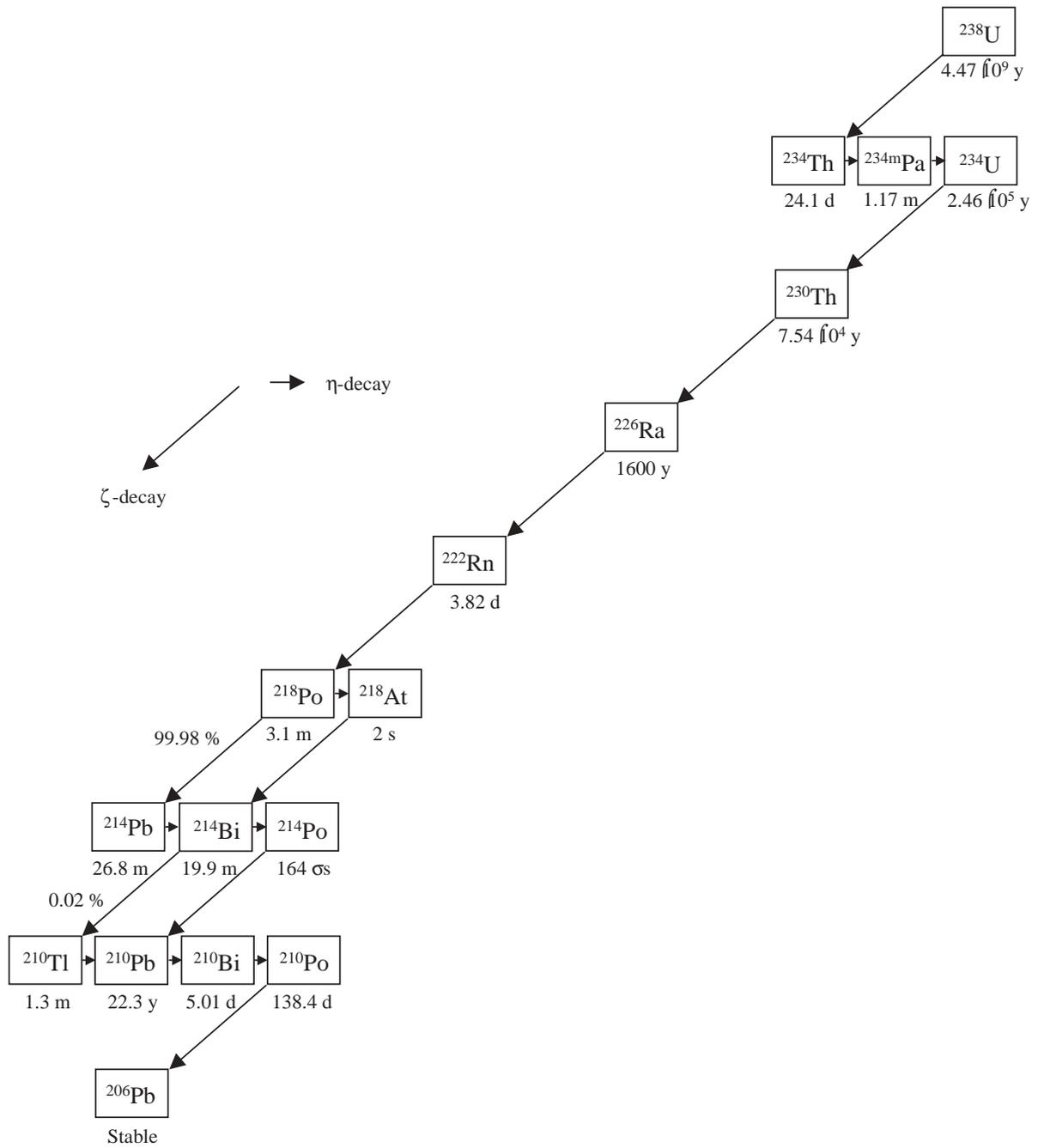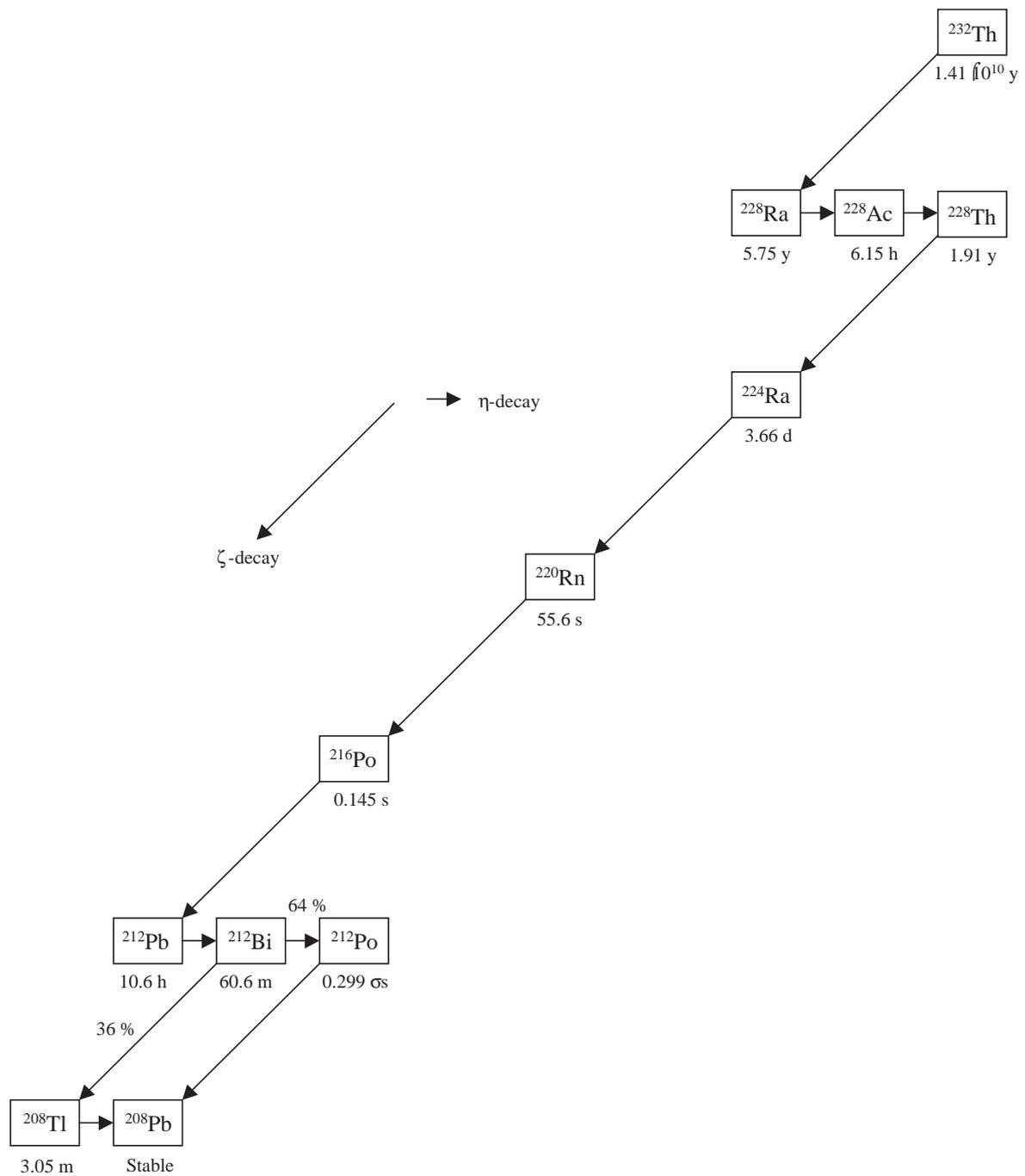
Figure 2.1. The uranium decay series

Figure 2.2. *The thorium decay series*

2.1.2 Uranium isotopes

Three uranium isotopes from the natural decay series can be found in nature: ^{238}U and ^{234}U from the uranium series and ^{235}U from the actinium series (Table 2.1). The most stable oxidation states for uranium are +4 and +6, where +4 occurs in reducing environments and is almost immobile. In oxidizing environments the +6 oxidation state dominates, which is far more soluble. In the presence of carbonate ions, the very mobile $UO_2(CO_3)_2^{2-}$ complex can be formed.

Table 2.1. *Naturally occurring uranium isotopes.*

Nuclide	Half-life	Decay mode
^{238}U	$4.47 \cdot 10^9$ y	ζ, ν
^{234}U	$2.46 \cdot 10^5$ y	ζ, ν
^{235}U	$703.8 \cdot 10^6$ y	ζ, ν

Typical activity concentrations in Nordic groundwater range from 0.002 to 0.1 Bq l^{-1}, but significantly higher concentrations, up to 100 Bq l^{-1}, can be found in uranium-rich areas (TRPA, 2000). Due to the alpha recoil effect, the $^{234}U/^{238}U$ ratio encountered in natural waters is normally above 1. In deeply buried ground water/formation water, the environment is reducing which means that uranium is mainly present in the +4 oxidation state with low solubility as a consequence. Activity concentrations of U in brines, reported by Osmond and Cowart (1992), range from 0.04 to 7.4 mBq l^{-1}.

2.1.3 Thorium isotopes

Six naturally occurring Th isotopes can be found in the environment (see Table 2.2): ^{232}Th and ^{228}Th from the thorium series, ^{234}Th and ^{230}Th from the uranium series, and ^{231}Th and ^{227}Th from the actinium series. Thorium exists only in oxidation state +4 and is generally considered to be insoluble in natural waters. Zukin *et al.* (1987) reported low ^{232}Th, ^{230}Th

and ^{234}Th activity concentrations in brines, but relatively high levels of ^{228}Th (up to 1 Bq kg^{-1}). This was explained by leaching and subsequent decay of ^{228}Ra, and reversible exchange of ^{228}Th between the solid phase and brine. Relatively high activity concentrations of ^{228}Th have also been reported by Lagera *et al.* (1999) in oil-field brines from the US Gulf Coast. The activity concentration in samples of produced water from 8 offshore platforms was found to be in the range from 0.4 to 4.5 Bq l^{-1}.

Table 2.2. *Naturally occurring thorium isotopes.*

Nuclide	Half-life	Decay mode
^{232}Th	$1.4 \cdot 10^{10}$ y	ζ, ν
^{228}Th	1.9 y	ζ, ν
^{234}Th	24.1 d	η, ν
^{230}Th	$7.53 \cdot 10^4$ y	ζ, ν
^{231}Th	25.6 d	η, ν
^{227}Th	18.2 d	ζ, ν

2.1.4 Radium isotopes

Four radium isotopes can be found in nature: ^{226}Ra from the uranium series, ^{228}Ra and ^{224}Ra from the thorium series, and ^{223}Ra from the actinium series (Table 2.3).

Table 2.3. *Naturally occurring radium isotopes.*

Nuclide	Half-life	Decay mode
^{226}Ra	1,600 y	ζ, ν
^{228}Ra	5.75 y	η, ν
^{224}Ra	3.66 d	ζ, ν
^{223}Ra	11.1 d	ζ, ν

Radium belongs to the alkaline earth elements and has similar chemical behaviour to, for example, barium, strontium and calcium. As an alkaline earth element it forms insoluble salts with especially sulphate, but also carbonate.

Radium only exists in the +2 oxidation state and is thus not affected by redox processes in the same way as uranium.

Since radium isotopes are radioactive and decay, and the levels of mother nuclides are too low to support the observed activities in especially saline, deep groundwater, radium must be constantly supplied from the surrounding rock material. Processes responsible for this are believed to be chemical leaching and alpha particle recoil (Kraemer and Reid, 1984). Alpha recoil may either be direct recoil into the water phase or facilitated leaching from intercrystalline damage caused by the recoil energy (Fisher, 1998).

At high sulphate concentrations, the low solubility product of $BaSO_4$ results in decreasing radium concentrations in the water due to co-precipitation of Ra with $BaSO_4$, if barium ions are present. An explanation of high radium concentrations in oilfield brines has been proposed, namely that the low redox potential ensures low sulphate concentrations which in turn permits higher radium concentrations in the water (Bloch and Key, 1981; Zukin, 1987). Also, the reducing environment ensures the absence of manganese and iron hydroxides, which can both effectively absorb radium (Bloch and Key, 1981).

The salinity of the water is also a parameter that is correlated with the radium concentration. Kraemer & Reid (1984) and Wiegland & Feige (2002) found a positive correlation between radium activity and salinity in brines from the Gulf Coast (USA) and in Germany. Correlation between radium and salinity has also been observed by Fisher (1998) in produced water from the USA, Poland and Austria. In the presence of other cations, these ions will compete with the Ra ions for adsorption sites on surrounding clay minerals and keep radium in solution. In contrast, in low-ionic-strength water, multivalent ions such as radium would be preferentially adsorbed over univalent ions (Kraemer and Reid, 1984). Other parameters

that have been reported to affect the levels of radium in brines are temperature, grain size (and total surface area) of the host material and the U and Th contents of these grains.

As for uranium, radium levels in groundwater and brines vary over a wide range. Typical activity concentrations of ^{226}Ra in ground water from wells drilled in normal bedrock in the Nordic countries range from 0.01 to 0.25 Bq l^{-1}. Levels up to 7.5 Bq l^{-1} have been observed in areas with uranium-rich granites (TRPA, 2000). Activity concentrations encountered in deeply buried ground-water[1]/oilfield brines can be much higher, but this will be discussed in Chapter 3.

2.1.5 Lead isotopes

Four radioactive lead isotopes occur naturally in the environment: ^{210}Pb and ^{214}Pb from the uranium series, ^{212}Pb from the thorium series, and ^{211}Pb from the actinium series (Table 2.4).

Table 2.4. *Naturally occurring radioactive lead isotopes.*

Nuclide	Half-life	Decay mode
^{210}Pb	22.3 y	η, ν
^{214}Pb	26.8 min	η, ν
^{212}Pb	10.6 h	η, ν
^{211}Pb	36.1 min	η, ν

The most long-lived of these isotopes is ^{210}Pb, with a half-life of 22.3 years. An important feature of ^{210}Pb is that it decays via ^{210}Bi to ^{210}Po, one of the radiologically most important nuclides in both the marine and terrestrial environments.

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[1] One important difference between shallow groundwater and deeply buried brines is that groundwater is generally influenced by more rapid hydrological circulation than brines at great depth. This slow circulation may in turn allow chemical equilibrium between the water and the surrounding rock (Osmond and Cowart, 1992).

At some locations, elevated activity concentrations of ^{210}Pb have been reported in brines. Zukin *et al.* (1987) explained high levels (up to 97 Bq l^{-1}), comparable to those ^{226}Ra, in brines from a geothermal well in California, as being the result of the formation of soluble chloride complexes, high reservoir temperatures and high ^{222}Rn concentrations (^{222}Rn decays to ^{210}Pb via 4 short-lived Rn daughters). Worden *et al.* (2002) reported high ^{210}Pb levels but low ^{226}Ra levels in a Triassic fluvial reservoir in the UK. The explanation of this was also proposed to be the formation of chloride complexes. Since the water was relatively oxidized and high concentration of sulphate was present, Ra could coprecipitate as barite (BaSO$_4$). The low sulphide concentrations in the water prevented the formation of insoluble galena (PbS).

2.2 Natural radioactivity in the marine environment

Natural radionuclides can be supplied to marine waters in several ways. The most important ones are described below (Cochran, 1992).

1. The supply of dissolved uranium and radium from river water. These elements and their daughter products, as well as particle-reactive elements, such as thorium, are carried on particulate matter to estuarine areas. In the mixing zone of fresh and saline water some of the elements may be desorbed and released to the seawater.

2. Production of elements such as ^{226}Ra, ^{228}Ra and ^{222}Rn in marine sediments by longer-lived parents. The nuclides can be mobilized to sediment pore water by alpha recoil and subsequently reach the seawater.

3. Decay of the relatively soluble isotopes of uranium, radium and radon leading to the *in situ* production of their daughter nuclides in seawater, for example ^{210}Pb and ^{210}Po.

4. Deposition from the atmosphere, especially ^{210}Pb. This is due to the emanation of the noble gas ^{222}Rn from land, which can then be transported over the seas and decay to ^{210}Pb, which is scavenged from the atmosphere by precipitation.

The concentration of natural radionuclides in the oceans can vary with location and depth. Typical natural background levels of natural radionuclides in the North Sea have been reviewed by van der Heijde *et al.* (1990) and are presented in Table 2.5.

Table 2.5. Typical background levels of natural radionuclides in the North Sea (van der Heijde et al.*, 1990).*

Radionuclide	Activity concentration in seawater (Bq m^{-3})
^{238}U	41
^{234}U	47
^{230}Th	0.05
^{226}Ra	1.5
^{210}Pb	1
^{210}Po	1
^{235}U	1.9
^{231}Pa	0.001
^{227}Ac	0.001
^{232}Th	0.1
^{228}Ra	1
^{228}Th	1

The activity concentration of ^{226}Ra in the surface water of the world's oceans is relatively uniform. For the Atlantic Ocean the average activity concentration has been measured and found to be 1.3 Bq m^{-3} (Broecker *et al.*, 1976). In comparison with open seawater, coastal and shelf water may have higher concentrations of ^{226}Ra (IAEA, 1990). Köster *et al.* (1992) reported an activity concentration of ^{226}Ra 30 km off the coast of the Netherlands to be about 5 Bq m^{-3}, while Plater *et al.* (1995) reported an

average activity concentration of 2.8 Bq m^{-3} in the Wash estuary on the eastern cost of the UK. Even more pronounced is the non-uniformity of ^{228}Ra. One of the major sources of ^{226}Ra and ^{228}Ra is marine sediments and, due to different half-lives, ^{228}Ra can reach high concentrations in shallow waters with low water exchange rates. As a result the ^{228}Ra/^{226}Ra ratio is higher in shallow coastal regions than in the surface of open seawater. Typical activity concentrations of ^{228}Ra in the surface of open seawater are in the range 0.2 to 0.7 Bq m^{-3} (IAEA, 1990).

For ^{210}Pb the two major sources in the oceans are atmospheric fallout from the decay of ^{222}Rn in the atmosphere, and *in situ* production from the decay of ^{226}Ra via ^{222}Rn in the water. In the surface water atmospheric input is the most important, while in the total water column *in situ* production is the most important. For ^{210}Po the atmospheric input is negligible and the dominating source is *in situ* production from the decay of ^{210}Pb via ^{210}Bi (Cherry and Heyraud, 1988). Average activity concentrations of ^{210}Pb and ^{210}Po in the North Sea have been reported to be 0.72 ± 0.42 and 0.80 ± 0.23 Bq m^{-3}, respectively (Spencer *et al.*, 1980 cited by Cherry and Heyraud, 1988).

3 Radioactivity in produced water

3.1 Produced water

During oil exploitation large amounts of water follow the production stream. This water is usually referred to as produced water, formation water or oilfield brine (Neff, 2002). This water may be formation water trapped within the reservoir for millions of years, or a mixture of seawater and formation water, when seawater has been injected in order to maintain pressure in the reservoir during oil and gas production. Alternatives to seawater injections are to reinject the produced water or inject water from nearby formations.

The composition of produced water can show large variations, depending on geological characteristics, the type of hydrocarbons produced and operating conditions (van Hattum *et al.*, 1992). The age of a field is also an important factor. At the end of production the composition of the produced water will more or less resemble that of seawater, if seawater injection has been practiced (Neff, 2002; van Hattum *et al.*, 1992; Stephenson *et al.*, 1994). So even if the discharged volumes of produced water increases with time, the total mass of different discharged elements may not increase, due to dilution (Neff, 2002).

The major natural components consist of inorganic salts and metals, and a wide variety of organic chemicals (Neff, 2002). Among the organic chemicals, the polycyclic aromatic hydrocarbons (PAHs) and alkylated phenols are of the greatest environmental concern (Røe, 1998; Neff, 2002). The salinity in produced water can range from below that of seawater up to that of saturated brine (corresponding to about 300 ‰). In North Sea production water the salinity normally ranges from fresh water to about 10 times that of seawater (Stephenson *et al.*, 1994). As in seawater the salinity is mainly caused by dissolved sodium and chloride ions. The concentration of sulphate ions in the water is of great importance for the solubility of Ra and Ba. High levels of sulphate ions in the produced water can be the result of breakthrough of seawater that has previously been injected into another zone of the reservoir to enhance production. The reduction of Ra in the produced water after seawater injection can thus be the result of both dilution and co-precipitation of Ra together with $BaSO_4$. The variation of Ba and seawater fraction (calculated from the concentration of sulphate ions in the water) in the produced water from a production well at Statfjord Nord is presented in Figure 3.1. This gives an illustration of how Ba, and probably Ra, levels can decrease during breakthrough of seawater containing sulphate ions. Breakthrough occurred in the autumn 2000, as shown by the increased fraction of seawater. Simultaneously, Ba levels declined. One year later, at the end of 2001, the seawater fraction fell because production at Statfjord Nord was changed to a zone in the reservoir where breakthrough had not yet occurred.

In addition to the natural components, a variety of production chemicals, such as scale inhibitors and scale dissolvers, are injected into the reservoirs. Similar chemicals and in addition corrosion inhibitors, biocides, demulsifiers and antifoaming agents are also added to the production stream on the platform. Most chemicals are soluble in oil, and therefore follow the oil. However, a water-soluble fraction of the chemicals is discharged together with produced water (Neff, 2002). In connection with Ra, scale inhibitors are of importance. Scale is a mineral salt deposit (mainly carbonate and sulphate salts of Ca, Ba and Sr), which may occur on the rock in an oil well or inside production equipment (see Figure 3.2). The deposit restricts flow and may even plug a tube or valve. In the North Sea this is recognized as a major problem in production, since the whole region is prone to scaling (Crabtree *et al.,* 1999). In order to prevent, for example, barium sulphate from precipitating in the production system, certain chemicals blocking the active sites of crystal growth, such
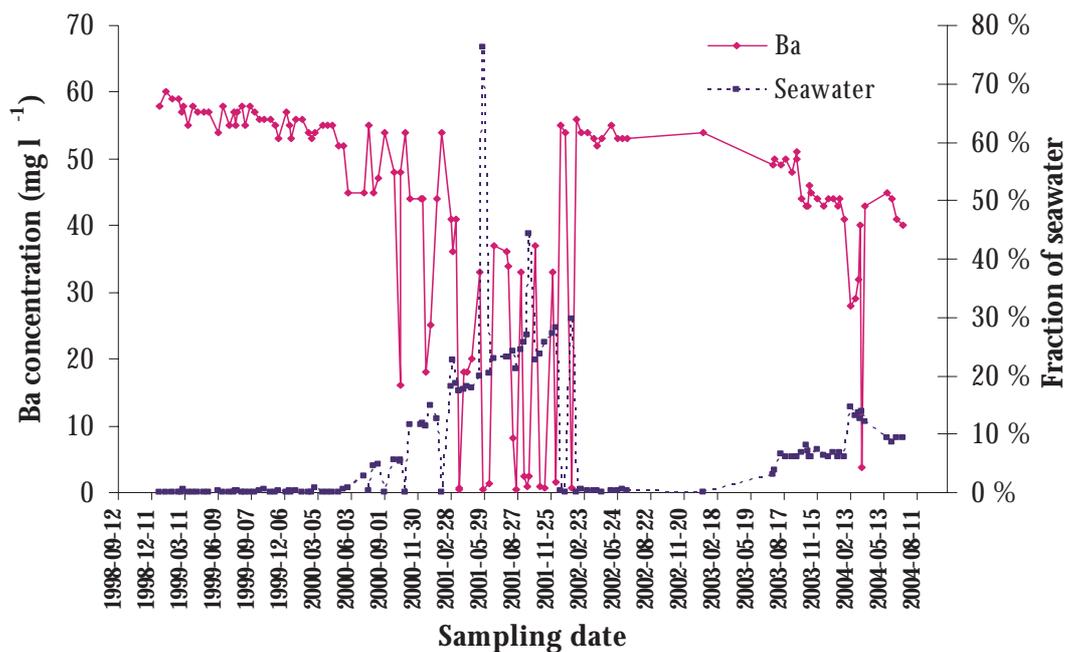
Figure 3.1. Concentration of Ba and seawater fraction in produced water at Statfjord Nord (unpublished data from Thingvoll, Statoil, 2004).

as organic phosphonates, organic phosphate esters, polycarboxylates or other compounds, can be added (Bosbach *et al.,* 1998; Crabtree *et al.,* 1999).

Removal of scale in cases where deposits have already blocked the production requires the use of chemical scale dissolvers. These dissolvers consist of strong chelating agents, such as EDTA or similar molecules, forming strong complexes with barium and other metals (Crabtree *et al.*, 1999). Since EDTA also forms complexes with radium, this type of chemical scale dissolver may also increase the mobility of Ra in the environment. The use of EDTA has, for example, been suggested to be the reason for increased mobility of radium and other radionuclides in water and soil around a disposal site at Oak Ridge National Laboratory, USA (Means *et al.*, 1978).

Figure 3.2. Hard scale deposits about one cm thick inside a production pipe. (Photo: Norwegian Radiation Protection Authority).

3.2   Radioactivity in produced water – A review

Levels of natural radioactivity in produced water/formation water, especially the most abundant, long-lived Ra isotopes, [226]Ra and [228]Ra, have been reported by several authors. Less data have been reported for ^{210}Pb and other nuclides in the natural decay chains. Reviews of radioactivity in produced water, with emphasis on Ra, have been presented by, for example, Fisher (1998), Strålberg *et al.* (2002) and Neff (2002). A more complete review, including

natural radionuclides other than radium have been presented by Jonkers *et al.,* 1997 (Table 3.1). Some published activity concentrations of [226]Ra and [228]Ra in produced water are presented in Table 3.2. The activity concentrations range from below detection limits up to several hundred Bq l[-1]. The majority of the results seem to be in the lower range, up to a few tens of Bq l[-1]. In the 215 samples presented by Fisher (1998), for example, about 75 % of the samples had activity concentrations below 11.1 Bq l[-1].

There is not much information available on [210]Po or [228]Th in produced water. Both nuclides are generally found in low concentrations in natural waters. However, activity concentrations of [228]Th in the range from 0.4 to 4.5 Bq l[-1] were reported by Lagera *et al.* (1999)

in produced water from the US Gulf Coast. Polonium-210 levels in the same samples ranged from 22 to 85 mBq l[-1].

Table 3.1. Natural radioactivity in produced water (from *Jonkers* et al., *1997).*

Radionuclide	Reported range (Bq l[-1])
[238]U	0.0003 - 0.1
[226]Ra	0.002 - 1,200
[210]Pb	0.05 - 190
[232]Th	0.0003 - 0.001
[228]Ra	0.3 - 180
[224]Ra	0.5 - 40

Table 3.2. Published datasets on radium concentration in produced water.

[226]Ra (Bq l[-1])		[228]Ra (Bq l[-1])		No. of samples	Location	Reference
Range	Average	Range	Average			
<0.002 - 58	11.7	0.02 - 59	15.5	41	US Gulf Coast	Kraemer and Reid, 1984
<2 - 302		<1 - 20		10[a]	The Netherlands	Van Hattum *et al.*, 1992
0.04 - 15	2.5[b]			41[c]	Norway	Varskog, 2003
< DL - 10.4	4.1	<DL - 10.0	2.1	11[d]	Norway	Strand *et al.*, 1997
< 0.01 - 6.0		< 0.05 - 12.0		18	Brazil	Jeres Vegueira *et al.*, 2002
0.05 - 191				215	USA, Poland and Austria	Fisher, 1998
6 - 9		< 2 - 17		4[e]	Norway	Røe, 1998
< DL - 34.4	5.9	< DL - 34.3	6.1	405[f]	Louisiana, USA	Hamilton *et al.*, 1991
0.1 - 21.6	9.7	0.7 - 21.7	10.2	42[g]	USA	Hamilton *et al.*, 1991
2 - 55		2.6 - 22		24[h]	US Gulf Coast	Lagera *et al.*, 1999
< DL - 11.1				4	Denmark	Varskog, *2003*

[a]Samples from 7 gas platforms and 3 oil platforms on the Dutch Continental Shelf.

[b] Average activity conc. of [226]Ra for produced water from 41 Norwegian platforms in 2002.

[c]Samples from each Norwegian production platform in the North Sea in 2002.

[d]Samples from 11 platforms.

[e]Samples from 4 fields (Brage, Oseberg F, Oseberg C and Troll).

[f]Radium data from 405 stations included in the State of Louisiana database.

[g]Radium data from 42 offshore outfalls included in the Offshore Operator's Committee Database.

[h]24 samples from 8 offshore platforms. The highest [226]Ra activity concentration is probably caused by contamination of scale.

In 2003, the MARINA II study was published by the EU, in which exposure to discharges from non-nuclear industries in north European marine waters was investigated. To estimate the activity concentration of ^{226}Ra, ^{226}Ra and ^{210}Pb in produced water from North Sea operators, an unpublished and confidential dataset from the Netherlands was used. According to these data the average activity concentration in produced water over the lifetime of an oil-producing platform is 10 Bq l^{-1}, for ^{226}Ra and ^{228}Ra, each. For gas production the corresponding activity concentration was quoted as being 10 Bq l^{-1}, for ^{226}Ra, 5 Bq l^{-1} for ^{210}Pb and 3 Bq l^{-1} for ^{228}Ra. Another assumption in this study is that over the lifetime of a well 3 m^3 of water are produced for each m^3 of oil. For gas the corresponding proportion is 50 m^3 of produced water for each million m^3 of gas (MARINA II, 2003).

3.2.1 Radium in Norwegian produced water

Until recently, not much information had been published on radium levels in produced water from the Norwegian oil and gas industry. The first data, published by Strand *et al.* (1997), were obtained from produced water samples collected in 1996 from 11 platforms in the North Sea. Radium-226 and ^{228}Ra ranged from below detection limit up to 10.4 Bq l^{-1}, and up to 10.0 Bq l^{-1}, respectively. The average activity concentration was reported to be 4.1 for ^{226}Ra and 2.1 Bq l^{-1} for ^{228}Ra.

Radium levels in produced water samples from four North Sea fields (Brage, Oseberg F, Oseberg C and Troll have been presented by Røe (1998) (Table 3.3). The samples were collected in the period Oct. 1995 to Aug. 1996.

Table 3.3. *Radium levels in produced water from four Norwegian oil fields (Røe, 1998).*

Field	^{226}Ra (Bq l^{-1})	^{228}Ra (Bq l^{-1})
Brage	9	17
Oseberg F	6	11
Oseberg C	7	<2
Troll	6	7

Samples from Brage were also collected once a day on five consecutive days (Table 3.4).

Table 3.4. *Activity concentration of radium in produced water collected from Brage on 5 consecutive days.*

Day	^{226}Ra (Bq l^{-1})	^{228}Ra (Bq l^{-1})
1	10	17
2	10	16
3	10	<1[*]
4	11	16
5	9	17

[*]The reason for the lower activity concentration of ^{228}Ra on day 3 was not explained.

Strålberg *et al.* (2002) published 60 results (22 analysed by gamma spectrometry and 38 by the ^{222}Rn-emanation method) from the analysis of produced water at a Norwegian laboratory (Institute for Energy Technology, Kjeller) during the period 1997 to 2002. There is no detailed information on where the samples included in this dataset were collected. The activity concentration of ^{226}Ra in 57 of the samples was in the range from below the detection limit up to 7.2 Bq l^{-1}, and for ^{228}Ra, 21 of 22 samples were in the range from below the detection limit up to 5.4 Bq l^{-1}. One sample had a slightly higher activity concentration of ^{226}Ra and ^{228}Ra, 21 and 19 Bq l^{-1}, respectively. The remaining two samples had much higher ^{226}Ra activity concentrations, 160 and 165 Bq l^{-1}. These two activity concentrations do not seem to be representative for produced water from the Norwegian

continental shelf, and due to the lack of information, this is not easy to explain.

Data on 41 produced water samples published by Varskog (2003) represent samples from each Norwegian production platform in the North Sea in 2002. Some samples from 2000 and 2001 were also included. Due to the analytical technique used (the ^{222}Rn-emanation method), results were only obtained for ^{226}Ra. The activity concentration of ^{226}Ra in these samples ranged from 0.04 to 15 Bq l^{-1}. The total discharged activity of ^{226}Ra from Norwegian production platforms in 2002 was estimated to be 306 GBq. The average activity concentration, 2.5 Bq l^{-1}, was calculated by dividing the total ^{226}Ra activity discharged from the Norwegian continental shelf by the total volume of produced water in 2002.

In summary, based on previously published results on radium in produced water from the Norwegian oil and gas industry, one can conclude that majority of the published results are below 10 Bq l^{-1} for both ^{226}Ra and ^{228}Ra (see Fig. 3.3). Two significantly higher results have been reported, but there is no information available on where, and under what circumstances, these samples were collected. The most complete dataset, in which both platform-specific activity concentrations of ^{226}Ra and discharge volumes for all Norwegian production platforms are available, is for 2002. Based on the total activity of ^{226}Ra discharged and the total discharged volume gives an average activity concentration of ^{226}Ra in produced water from the Norwegian continental shelf of 2.5 Bq l^{-1} in 2002.
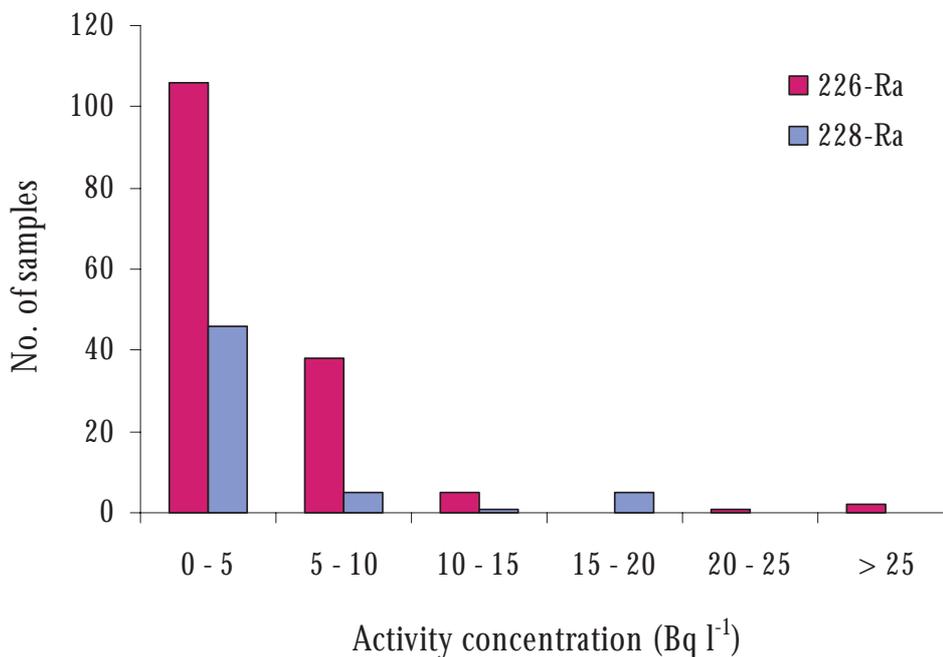

Figure 3.3. Overview of published radium levels in produced water from the Norwegian continental shelf in the period 1995 to 2002 (Strand et al., 1997; Røe, 1998; Strålberg et al., 2002 and Varskog, 2003).

3.3 Volume of produced water discharged into the North Sea

3.3.1 The Norwegian petroleum industry

Oil and gas production is the main industry in Norway in terms of value added. At the turn of 2004, 42 oil fields in the North Sea and 6 in the Norwegian Sea were operating. The four largest fields are Ekofisk, Statfjord, Gullfaks and Troll. A map of the major fields in the Norwegian sector of the North Sea is shown in Appendix B.

Oil and gas production in Norway has increased continuously since output began in 1971. While oil exploitation reached a peak in 2000/2001, it has now declined slightly. However, a rise in gas output contributes to further growth in total production. The Norwegian continental shelf contains a large number of small and medium-sized fields which have yet to be developed. The Ministry of Petroleum and Energy (2004a) has estimated that 39 % of the total resources have been exploited to date. In total, the production in 2003 reached 189 million Sm^3 o.e. oil[ii] and condensate, and 119 million Sm^3 o.e. gas[iii] (OLF, 2004).

3.3.2 Discharges from Norwegian oil and gas fields

Produced water is the largest waste stream arising from offshore oil and gas production. When the production stream enters the platform, it is directed into several large, cylindrical vessels. The solids are allowed to settle and the water, oil and gas are separated into different streams. The water stream, or

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[ii] For oil 1 m^3 is equivalent to 1 Sm^3 o.e. (o.e. = oil equivalents).

[iii] For gas 1000 Sm^3 (standard cubic metres) is equivalent to 1 Sm^3 o.e. (OLF, 2004).

produced water, is then subjected to further treatment to remove oil and other chemical compounds. Waste water treatment is based on the use of hydrocyclones, centrifugation, skimming, filtration and adsorption. Radionuclides present in the produced water are probably only removed to a limited extent by these techniques. Finally, the water is discharged to the sea or reinjected under the sea floor. The discharge outlet point is always below the water surface to facilitate dilution. At some minor fields, production is tied back to a nearby platform. Therefore, not all platforms discharge produced water.

The discharge of produced water was 135 million m^3 water on the Norwegian continental shelf in 2003 (OLF, 2004). Three major oil fields in the northern North Sea, Statfjord, Gullfaks and Troll, contributed to about 70 % to these discharges.

Generally, smaller volumes of water are produced early in the lifetime of a reservoir. As production continues, the volume of water increases. For an old field, the production stream can consist of 5 % oil and 95 % water. Major Norwegian oil fields such as Statfjord and Gullfaks, are now reaching the last phase of production. The average water-to-oil ratio for all fields has therefore increased from 0.19 in 1993 to 0.88 in 2003 (OLF, 2004), and is expected to increase in the years to come (see Fig. 3.2). This trend is expected to continue for several years, before it turns down around 2015 due to closing down of old platforms or the implementation of measures (reinjection, plugging of water zones and side-tracking of wells) on existing platforms. The discharge does not increase to the same extent as the water production. The reason for this is that technology to reinject water is being used on an increasing number of production platforms. In 2003, 14 % of the produced water was reinjected, an increase from 7 % in 1997 (OLF, 2004).
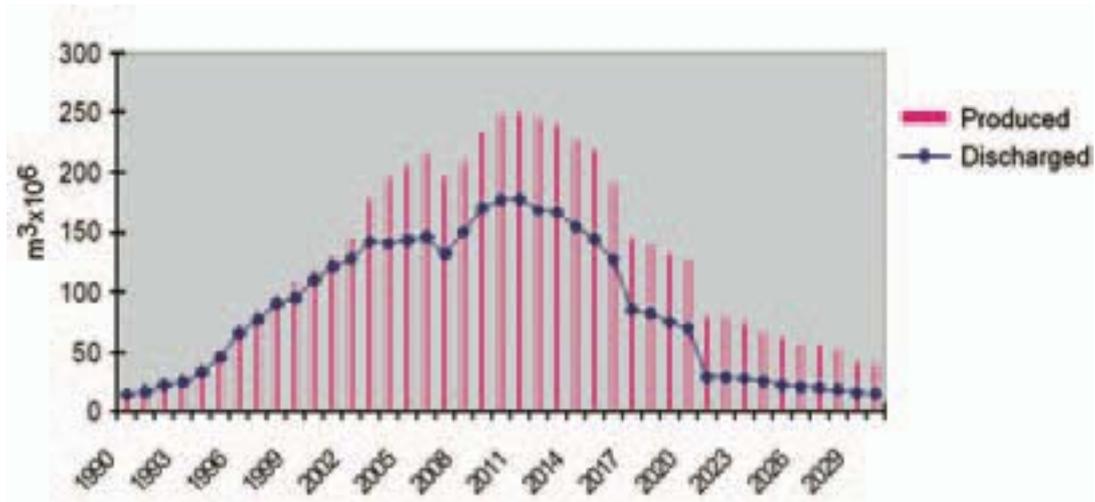
Figure 3.2. *Historical and predicted figures regarding water production and discharges on the Norwegian continental shelf from 1990 to 2030 (Ministry of Petroleum and Energy, 2004b).*

3.3.3 Discharges from other countries

The discharge of water into the British sector of the North Sea was 266 million m^3 in 2003 (DTI, 2004). Despite the fact that this amount includes other waste streams than produced water, the volume is nearly doubled that of the Norwegian sector. The total volume of produced water discharged to the North Sea was about 400 million m^3 in 2002 (OSPAR, 2004). As can be seen in Table 3.5, the contribution from the minor producers, Denmark, Germany and the Netherlands, was less than 10 %.

Table 3.5. *Annual quantity of produced water discharged to the North Sea in 2002 (OSPAR, 2004).*

Country	Discharged volume (m^3)	Fraction of total (%)
Denmark	12,437,142	3.1
Germany	7,011	0.002
The Netherlands	8,856,073	32.2
Norway	118,932,536	29.2
The UK	266,745,198[*]	65.5
Total	397,340,203	

[*]Figures from the UK include other waste water such as drainage water and displacement water.

4 Dilution and fate of radium after discharge

Produced water discharged to the sea will be rapidly diluted in well-mixed waters (Neff, 2002). The dilution upon discharge can be divided into two phases: a near-field phase, describing the discharge plume during the first few minutes after discharge, and a far-field phase. The dilution in the near field is due to, for example, turbulence caused by discharge momentum and plume buoyancy (Till and Meyer, 1983). Upon reaching neutral buoyancy subsequent dilution is caused only by ambient forces. This far-field mixing occurs at a slower rate than in the near-field phase. In the North Sea, thermal stratification occurs during the summer (thermocline at about 50 m), while the water column is well mixed during the winter (Ducrotoy *et al.*, 2000). This can lead to a lower dilution of the discharge plume during the summer. Dispersion modelling carried out on the Gullfaks and Statfjord oil fields in the North Sea showed a 20- to 100-fold dilution within 100 m of the discharge point, and a 500- to 10,000-fold dilution within 1,000 m (Ynnesdal and Furuhold, 1994). Dilution of discharged produced water in the North Sea has also been modelled by Stephenson *et al.* (1994). Two simulations were performed, one with a stratified water column and one with a mixed water column. The discharge rate was assumed to be 6,340 m^3 per day, the discharge depth 30.5 m, the salt concentration 70,000 mg l^{-1}, and the temperature of the produced water 75 °C. The results are shown in Figure 4.1.
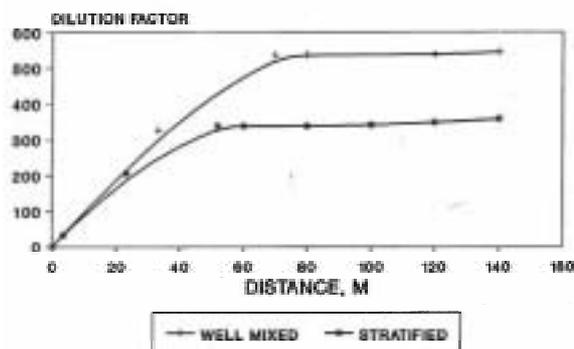
Figure 4.1. Modelled dilution of produced water discharge into the North Sea (from Stephenson et al., 1994).

Chemical reactions between ions in the seawater and in the discharged produced water may also occur, leading to the formation of insoluble compounds. The formation of $BaSO_4$ from Ba^{2+} ions in the produced water and SO_4^{2-} ions in the seawater is of importance for radium. If $BaSO_4$ is formed near the discharge point, some of the Ra^{2+} ions may coprecipitate and be removed from solution and transferred to the sediments (Hamilton *et al.*, 1992). For produced water with a high Ba^{2+} concentration, the fraction of radium that coprecipitates with $BaSO_4$, may be significant. However, no studies investigating this could be found in the literature. Jerez Vegueria *et al.* (2001) investigated sediments and seawater close to two offshore platforms (discharging about 30 MBq day[-1] and 41 MBq day[-1]) at the Bacia de Campos oilfield (Brazil) and concluded that both sediments and seawater showed normal background levels, even at the closest sampling distance of 250 m from the platforms.

4.1 Dispersion modelling by the NRPA for 2003

The dispersion of radium in the North Sea for continuous discharge of produced water from Norwegian platforms during 2003 has been modelled, using the DREAM model developed by SINTEF in Norway. Two scenarios were simulated: a continuous discharge over one year of produced water from all Norwegian production platforms in the North Sea, and

another scenario including only the Troll B and C platforms. The DREAM model is a three-dimensional model that simulates dispersion caused by vertical and horizontal diffusion and advection due to the sea currents. The spreading algorithm used in the model has been verified against field measurements on the Oseberg oil field in the North Sea (Rye *et al.*, 1996). Details about the model can be found in Reed *et al.* (1995) and Reed *et al.*, (2001). Activity concentrations of ^{226}Ra and ^{228}Ra in the produced water are taken from the results of the monitoring presented in this report, and the discharge volumes are those reported for 2003 by the OLF. It is assumed that all discharged radium is in a soluble form after discharge. The results of this simulation are presented in Appendix A.

The results of dispersion modelling show that on a large scale, the highest activity concentrations of ^{226}Ra and ^{228}Ra are found in the Tampen area and downstream of the Troll B and C platforms. Assuming no sedimentation, levels may occasionally reach about 1 mBq l^{-1} in limited areas within the Tampen and Troll areas for continuous discharge over 1 year. The somewhat higher activity concentrations in the seawater during the summer can be explained by the formation of a thermocline, leading to lower mixing of the water column. Higher levels can, however, be expected locally, in the close vicinity of the discharge points. The major part of the discharged activity is transported towards the Norwegian coast, into the Norwegian Coastal Current, where it is transported northwards out of the area covered by the model (the North Sea). For ^{226}Ra about 90 % of the total discharged activity has been transported out of the North Sea in after 12 months of continuous discharge. An additional source not accounted for in this simulation is the contribution of radium from UK platforms, which is expected to enhance the levels further. The naturally occurring levels are assumed to be in the range from about 1.5 mBq l^{-1} in the open sea to about 5 mBq l^{-1} closer to the coastline. For most of the area the contribution of radium from the produced water is well below 1 mBq l^{-1}. This would mean that a

doubling of radium levels may be observed in the most affected areas.

4.2 Monitoring of ^{226}Ra in seawater in 2002

During 2002, depth profiles of seawater were sampled around the oil platforms Sleipner A and T, and Gullfaks A, B and C, and in two reference areas (Egersundsbanken 1 and 2) and analysed for ^{226}Ra. The locations of the sampling points are shown in Figure 4.2.
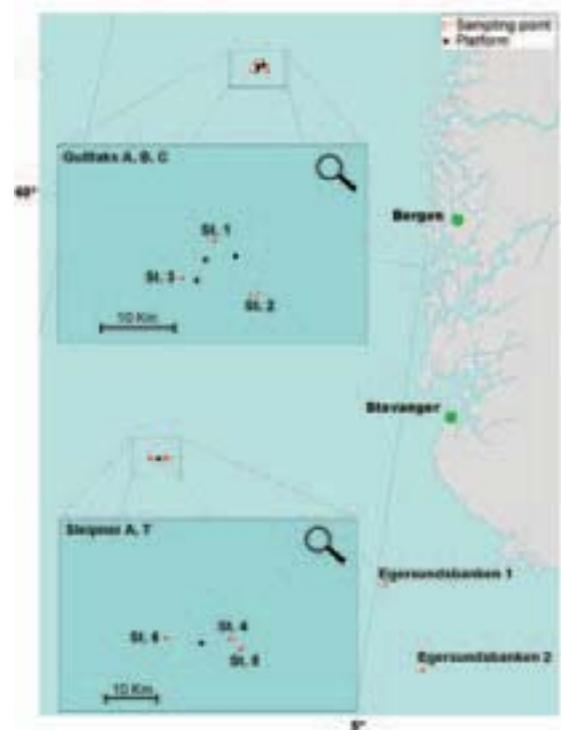

Figure 4.2. Sampling sites (St.) were depth profiles of ^{226}Ra in seawater have been obtained.

Gullfaks A, B and C discharged large volumes of produced water with relatively low levels (< 1 Bq l^{-1}) of ^{226}Ra in 2002. According to data from the Norwegian Oil Industry Association (the OLF) the total discharge from these platforms was around 13 GBq in 2002. Sleipner A and T discharged relatively low volumes of produced water with a higher activity concentration of ^{226}Ra (average 3.6 Bq l^{-1} for both platforms). The total discharged activity of ^{226}Ra from Sleipner A and T in 2002 has been estimated to be 0.7 GBq. The seawater samples were

collected in order to investigate if generally increased levels of ^{226}Ra can be detected in the area around a platform and to obtain information on the levels of ^{226}Ra in areas not significantly affected by the discharge of produced water.

The results of the analyses are presented in Figures 4.3, 4.4 and 4.5. The levels encountered in this study are similar to those in Atlantic water and it is thus probable that the sampled water is inflowing Atlantic water. Only one sample (Sleipner, St. 4, depth 4 m) had a slightly higher activity concentration of ^{226}Ra than the levels encountered in the reference area which indicates that the levels of ^{226}Ra around these platforms, at the distances where these samples were collected, are not affected to any significant extent by the discharge of produced water. At the time of the sampling there was no information available on the exact direction on the discharge plume, and thus these samples may not represent the highest activity concentration that can be found around these platforms.
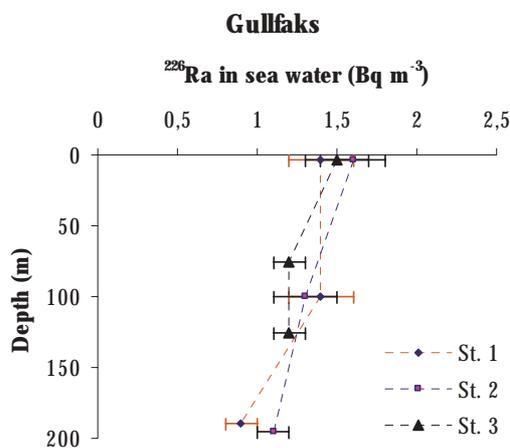
Figure 4.3. *Activity concentration (Bq m^{-3}) of ^{226}Ra around the Gullfaks A, B and C platforms.*
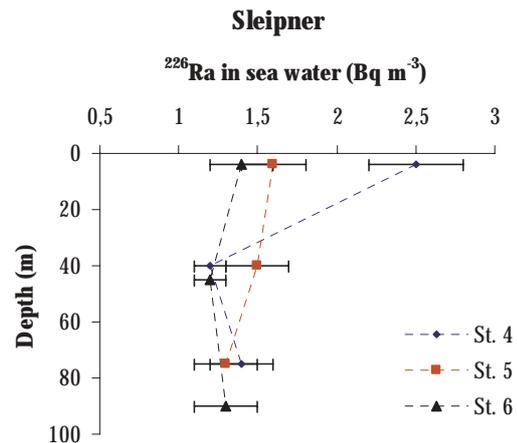
Figure *4.4. Activity concentration (Bq m^{-3}) of ^{226}Ra around the Sleipner A and T platforms.*
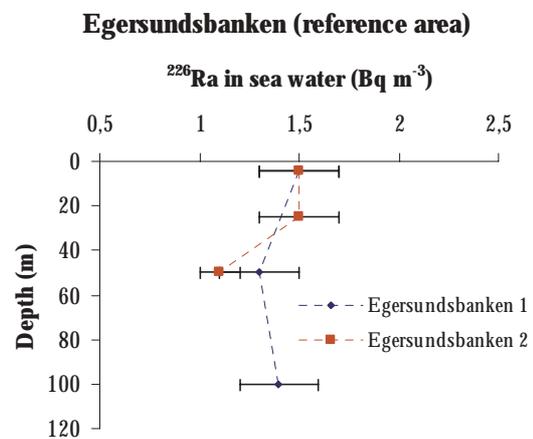
Figure 4.5. *Activity concentration (Bq m^{-3}) of ^{226}Ra in the reference areas.*

5 Monitoring of radioactivity in produced water – Results for 2003/2004

In order to obtain an up to date estimate of the discharge of natural radioactivity from the Norwegian oil and gas industry for 2003, the industry was asked to report the activity concentrations of ^{226}Ra, ^{228}Ra and ^{210}Pb in produced water. The sampling campaign took place from September 2003 to January 2004. The aim was to collect one sample per month for 5 consecutive months for each Norwegian production platform discharging produced water in the North Sea or Norwegian Sea. The reason for sampling monthly during a five-month period was to measure the variation that may occur during this period in order to determine a suitable sampling frequency for future surveys.

Overall, the response to the request to monitor produced water with respect to ^{226}Ra, ^{228}Ra and ^{210}Pb was good, and results were obtained from all 41 production platforms that discharge produced water. For various reasons, some platforms did not report results for all five months, and in total 185 results were reported for ^{226}Ra, ^{228}Ra and ^{210}Pb each.

Data on total discharge volumes during 2003 for all 41 production platforms was provided by the OLF. Together with the results from the radioactivity analyses, these data were used to estimate the total discharged activity of ^{226}Ra and ^{228}Ra in 2003 from each production platform on the Norwegian continental shelf.

In addition parallel samples from 12 production platforms were analysed with regard to ^{210}Po at the NRPA.

5.1 Sampling

All samples were collected after the treatment processes used at the platforms to separate solids, oil and gas from the produced water. Each sample consisted of about two litres. In order to investigate the total discharge the samples were not filtered. Neither were the samples acidified in connection with sampling, but the bottles were carefully washed with diluted nitric acid later at the laboratory to remove radium and lead that may have been absorbed on the walls of the bottles.

5.2 Analytical methods

5.2.1 Analysis of ^{226,228}Ra and ^{210}Pb

All samples of produced water were analysed by gamma spectrometry at the Institute for Energy Technology (IFE) at Kjeller (Norway). In order to lower the detection limit, radium and lead were coprecipitated with MnO_2 or a combination of $Pb(Ba)SO_4$ and MnO_2. The method used has been developed and tested at IFE. It was slightly modified during the project, and the original and modified versions are described briefly below (Sidhu R, IFE, personal communication, 2004).

Original method

A 2-litre sample to which ^{133}Ba had been added as a yield determinant was first treated with permanganate under acidic conditions. After raising the pH, MnO_2 was precipitated and filtered off from the solution. After the precipitate had been dried it was mixed with Al_2O_3 and placed in a vial for gamma spectrometric analysis using lead-shielded HPGe detectors.

The method was tested by adding known activities of ^{226}Ra and ^{210}Pb to produced water

samples with good results for both [226]Ra and [210]Pb. Most of the samples showed a chemical yield above 80 %. For unknown reasons, some samples showed a chemical yield below 60-70 %. These samples were also evaporated and the activities of the residue and the precipitate were analysed separately and added. One suggested reason for the lower yield is that complexing agents, such as scale dissolvers or inhibitors, could be present in the samples, preventing Ra from precipitating. Since many complexing agents are effective at elevated pH, the method was modified and MnO_2 precipitated at a low pH together with $Pb(Ba)SO_4$.

Modified method

After a 2-litre sample of produced water had been acidified, Pb and Ba carriers were added together with [133]Ba, which was used as a radiochemical yield determinant. Potassium permanganate and sodium sulphate were then added and Ba, Pb and Ra were precipitated as sulphates. Part of the manganate is reduced to MnO_2 in this initial step and the remaining manganate was reduced by the addition of sodium sulphite. Both precipitates were then filtered from the solution, dried and homogenised together with Al_2O_3, in order to fill one of the calibrated vials used at the laboratory. All samples analysed with this method had chemical yields above 90 %. Also this method was tested by adding known amounts of [226]Ra and ^{210}Pb to produced water samples with good results.

After the radiochemical separation, the samples were stored for a sufficient period of time to ensure secular equilibrium between [228]Ra and [228]Ac. The samples were then analysed using lead-shielded HPGe detectors. Radium-228 was determined from the gamma radiation from [228]Ac. Radium-226 and ^{210}Pb were determined from their 186 keV and 46.5 keV gamma photons, respectively. All samples were corrected for self-absorption as described by Cutshall *et al.* (1983). This method has previously been tested at the IFE laboratory, and the results have been presented by Sidhu

and Strålberg (2003). For most of the samples the detection limit was below 1 Bq l^{-1} for each nuclide and the typical uncertainty (± 2 SD) about 20 %. Efficiency calibration of the HPGe detectors has been performed using a multi-nuclide solution traceable to a national standard (LMRI). Quality assurance concerning the performance of detector equipment is in accordance with ANSI (American National Standards Institute) N13.30 and N42.14. The laboratory frequently participates in intercomparison tests arranged, for example, by the IAEA and Nordic Nuclear Safety Research (NKS) with satisfactory results (due to the less common intercomparison tests for radium, the results were for gamma-emitting nuclides other than radium isotopes).

5.2.2 Analysis of [210]Po

Samples from 12 production platforms were also analysed for [210]Po at the NRPA. Between 0.5 and 1 litre of produced water was acidified with HNO_3 to pH 1-2. Polonium-209 was then added to the sample as a yield determinant. Polonium was coprecipitated with MnO_2 at pH 8-9, after the addition of $KMnO_4$ and $MnCl_2$. After the precipitate had been separated from the solution it was dissolved in diluted HCl and a few ml of H_2O_2. Finally, polonium was spontaneously deposited onto a silver disc from a hot, diluted hydrochloride solution in which 1 g of hydroxylamine hydrochloride had been added. The activity was later determined by alpha spectrometry. The radiochemical yield in the analyses varied from 28 to 71 %.

5.3   Results

In Figure 5.1 all results from the analyses of [226]Ra and [228]Ra in the produced water are presented.
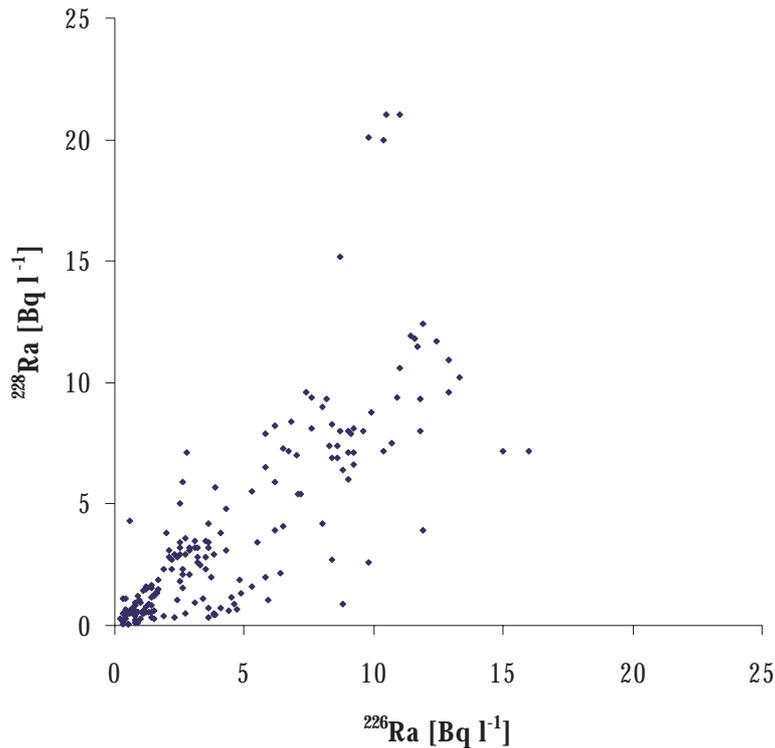
Figure 5.1. Overview of all results obtained for ^{226}Ra and ^{228}Ra in the period September 2003 to January 2004.

The average activity concentration of ^{226}Ra in all analysed samples was 4.5 Bq l^{-1} and values ranged from below the detection limit up to 16 Bq l^{-1}. Most of the results, 65 %, were below 5 Bq l^{-1}. For ^{228}Ra, the average activity concentration of the samples was 3.9 Bq l^{-1} and ranged from below the detection limit up to 21 Bq l^{-1}. As for ^{226}Ra, most of the results, 69 %, were below 5 Bq l^{-1}. A relatively good correlation ($R^2 = 0.63$) was observed between the activity concentrations of both radionuclides.

In Figures 5.2 and 5.3 the average activity concentrations (and range) of ^{226}Ra and ^{228}Ra in the produced water from each platform during the monitoring period are presented. In both Figures the platforms have been arranged by increasing level of ^{226}Ra.

Figure 5.4 shows the discharged volume of produced water from each Norwegian platform. The total discharged volume for all platforms in 2003 was about $135 \cdot 10^6$ m^3. The platforms are arranged as in Figure 5.2, with

increasing activity concentration of ^{226}Ra from left to right.

The estimated total discharge of ^{226}Ra and ^{228}Ra for each platform during 2003 is shown in Figures 5.5 and 5.6. The total discharged activities of ^{226}Ra and ^{228}Ra in 2003 were estimated to be 440 GBq (range 310 to 590 GBq) and 380 GBq (range 270 to 490 GBq), respectively. Dividing the total discharged activity by the total volume of produced water discharged gives average activity concentrations of ^{226}Ra and ^{228}Ra of 3.3 and 2.8 Bq l^{-1}, respectively.

For ^{210}Pb, all samples except one showed activity concentrations below the detection limit (between 0.2 and 1.5 Bq l^{-1}, depending on parameters such as measurement time and detector efficiency). The one sample above the detection limit was found to have an activity concentration of 0.4 ± 0.1 Bq l^{-1}. The total discharged activity of ^{210}Pb in 2003 was estimated to be < 92 GBq.

The results of the ^{210}Po analysis are presented in Table 5.1. All 12 samples had levels below 10 mBq l^{-1}.

Table 5.1. *Activity concentration of ^{210}Po in produced water from 12 Norwegian platforms in 2003.*

Platform	^{210}Po (mBq l^{-1})
Snorre B	6.1 ± 0.5
Ula	2.1 ± 0.3
Heidrun	1.3 ± 0.2
Gullfaks A	0.5 ± 0.3
Åsgard B	1.3 ± 0.1
Visund	0.2 ± 0.1
Vigdis	2.6 ± 0.2
Gullfaks B	1.0 ± 0.1
Åsgard A	1.1 ± 0.1
Snorre B	1.9 ± 0.2
Gullfaks C	1.1 ± 0.2
Heidrun TLP	2.8 ± 0.2
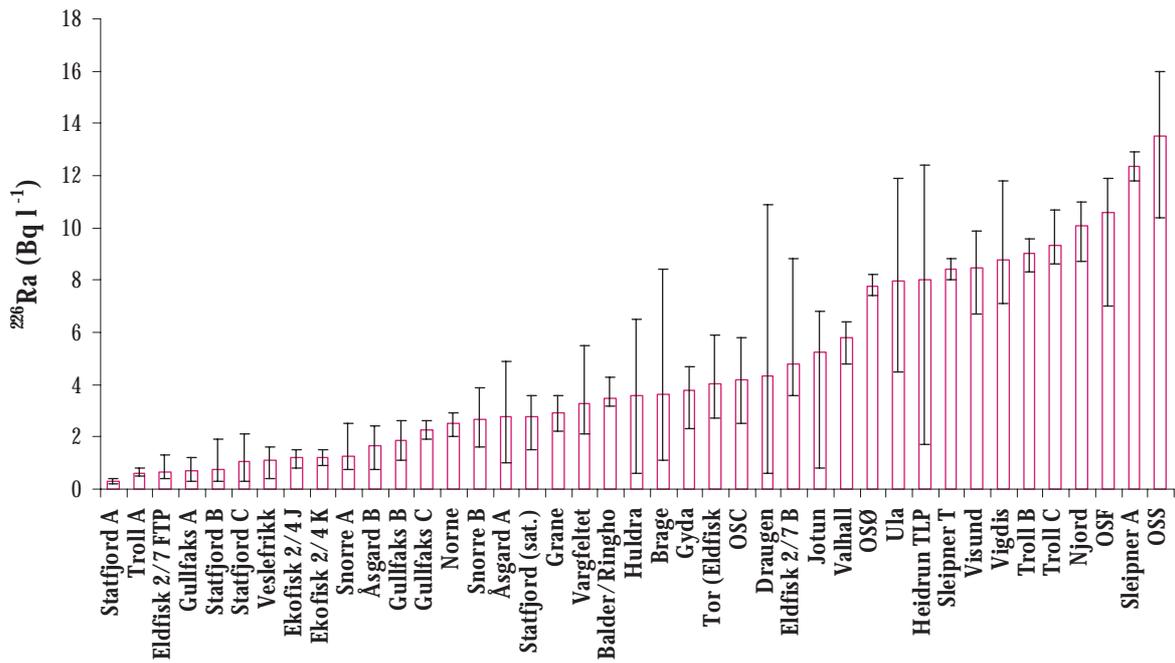
Figure 5.2. *Average activity concentration (and range) of* ^{226}*Ra in produced water samples from Norwegian platforms collected in the period September 2003 to January 2004.*
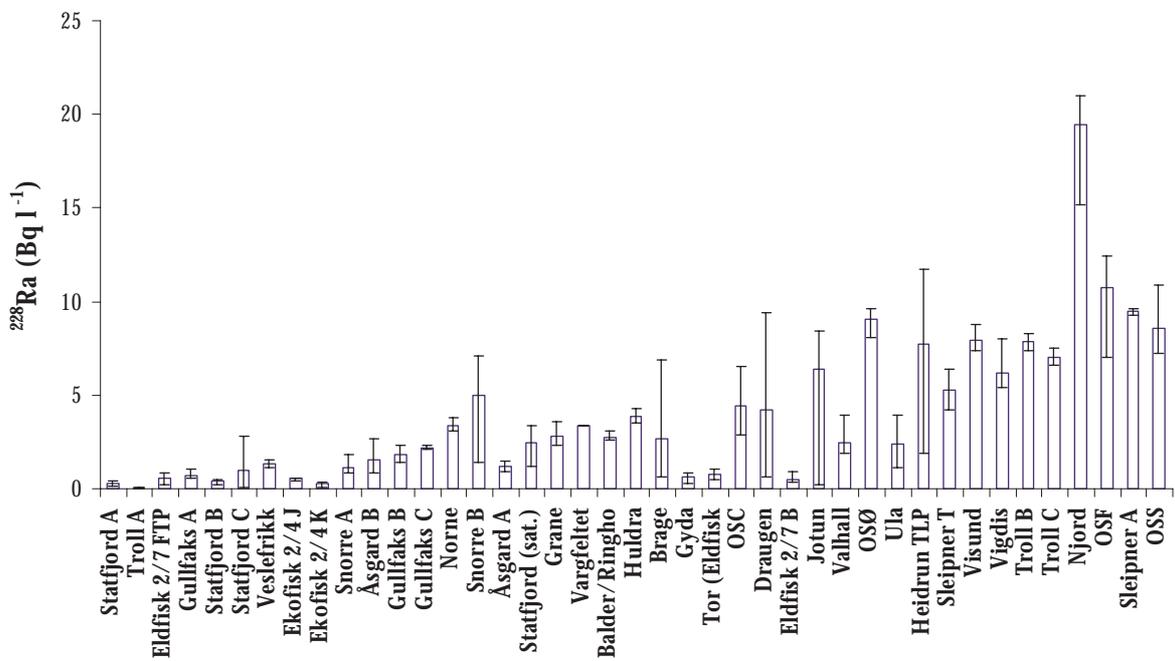
Figure 5.3. *Average activity concentration (and range) of* ^{228}*Ra in produced water samples from Norwegian platforms in the period September 2003 to January 2004.*
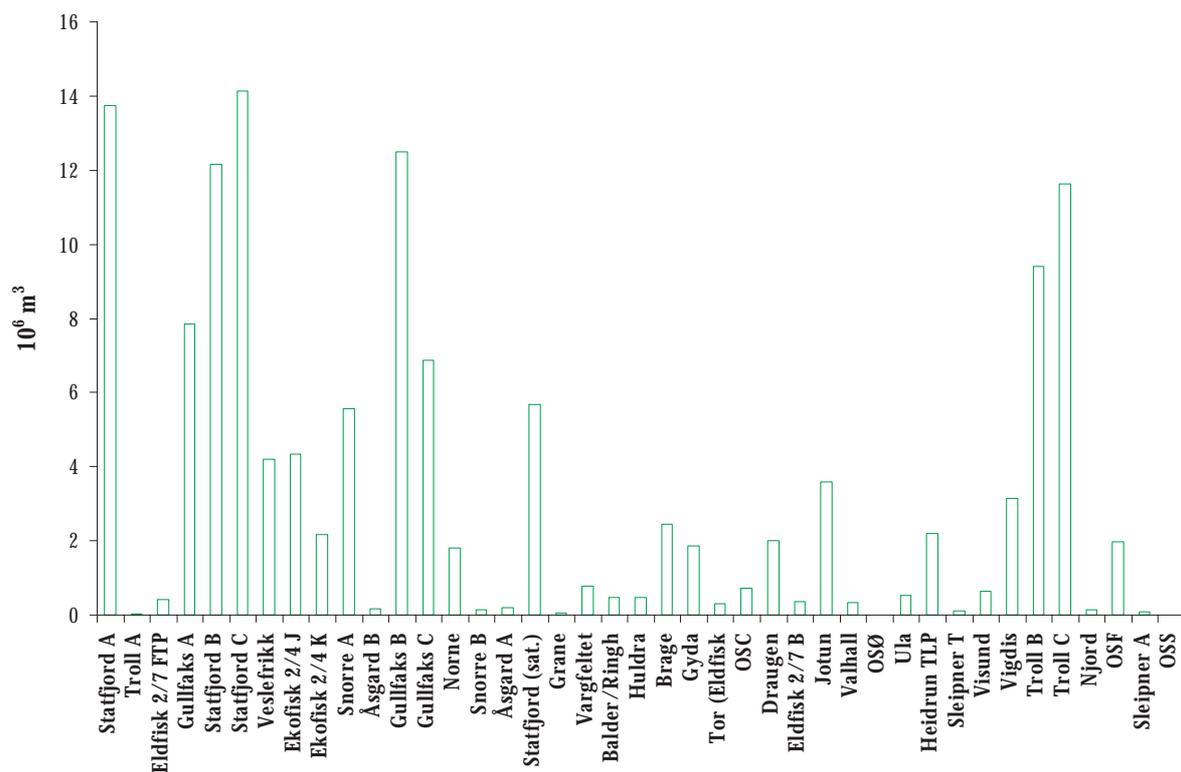
Figure 5.4. *Volume of produced water discharged from each platform during 2003.*
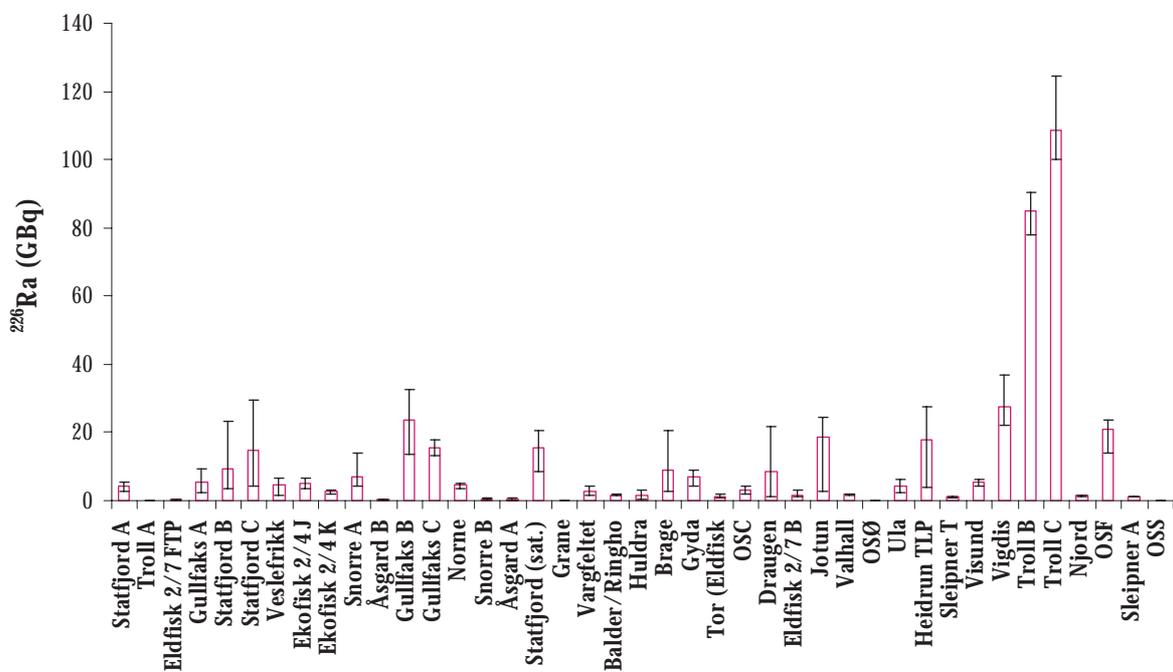
Figure 5.5. *Estimated total discharged activity of ^{226}Ra for each platform during 2003.*
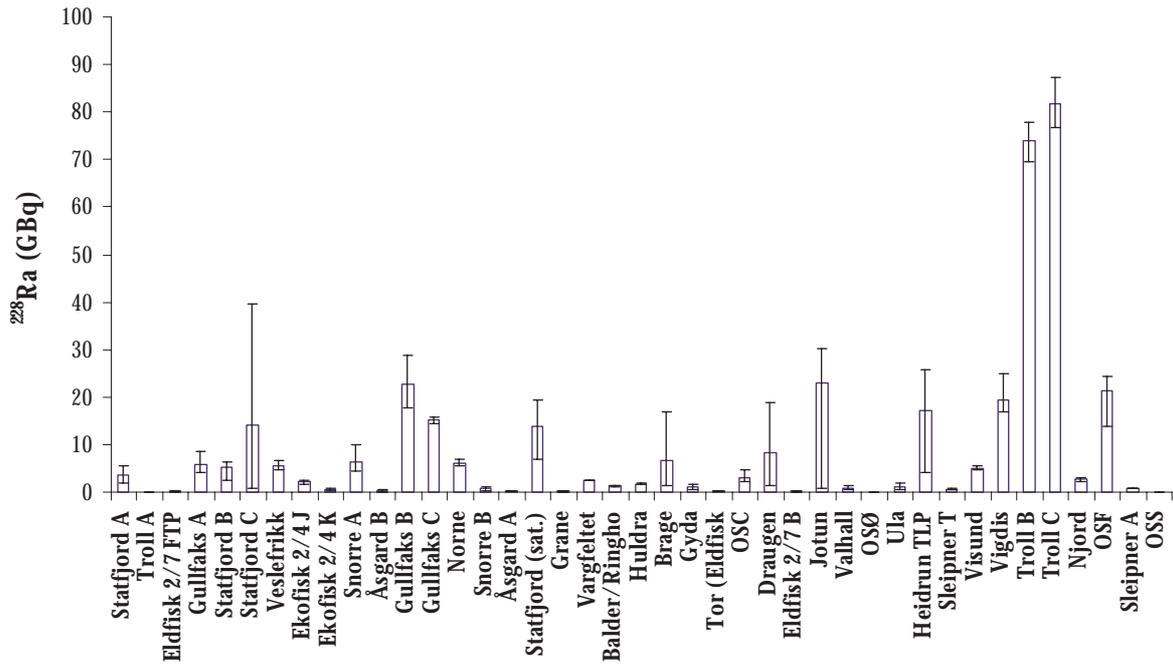
Figure 5.6. *Estimated total discharge of ^{228}Ra for each platform during 2003.*

5.3.1 Monthly variation

The activity concentration of radium in the produced water from some of the platforms showed a relatively large variation between the monthly samples during the sampling period (see Figures 5.2 and 5.3). For about 25 % of the platforms the variation was greater than 4 Bq l^{-1} for ^{226}Ra. Figures 5.8 to 5.11 show the activity concentration of ^{226}Ra on the different sampling dates for these platforms.
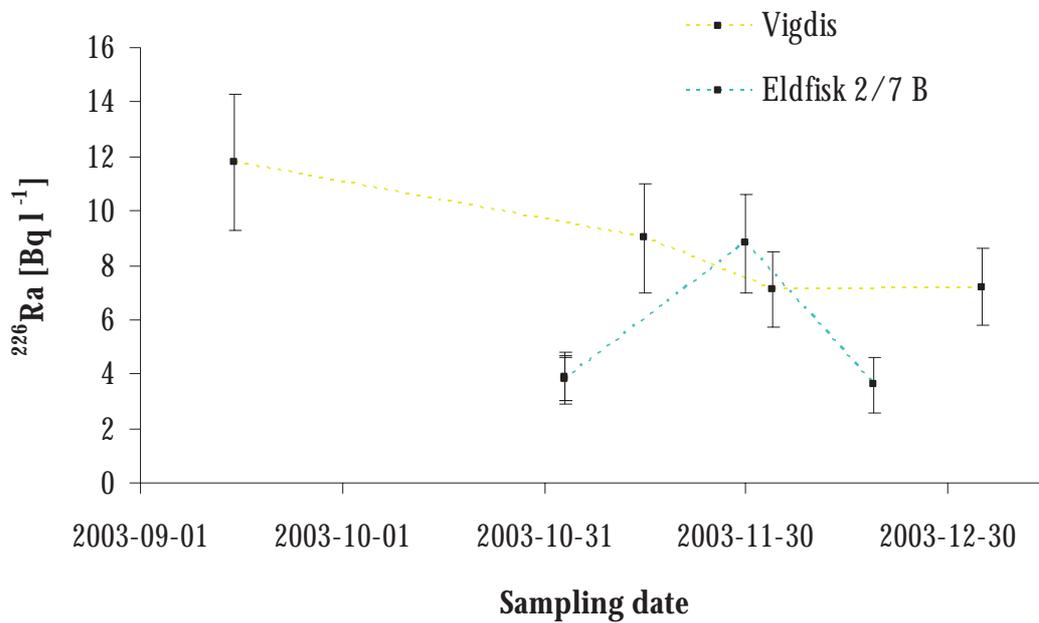
Figure 5.8. *Activity concentration (± 2 SD) of* ²²⁶*Ra in produced water on different sampling dates for 2 of the platforms where a large variation was observed.*
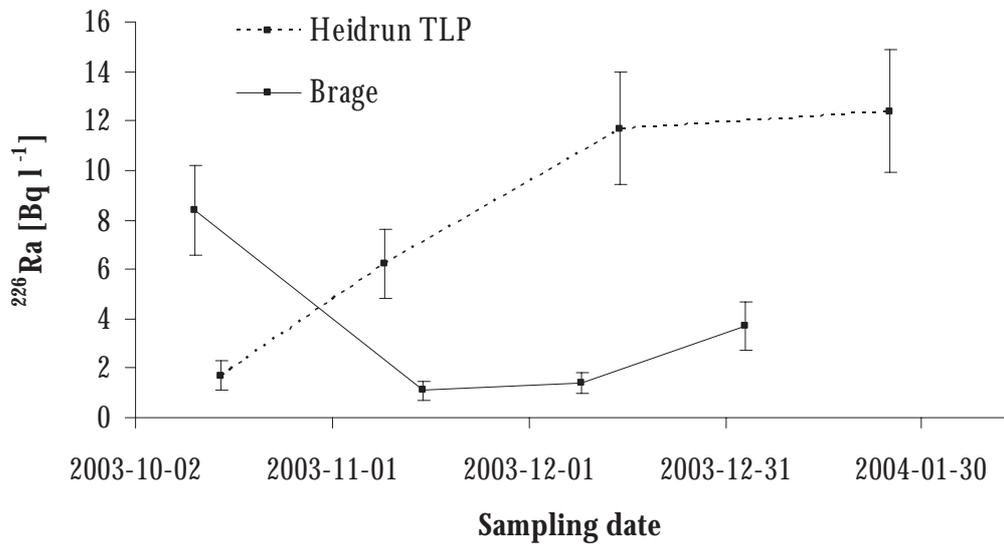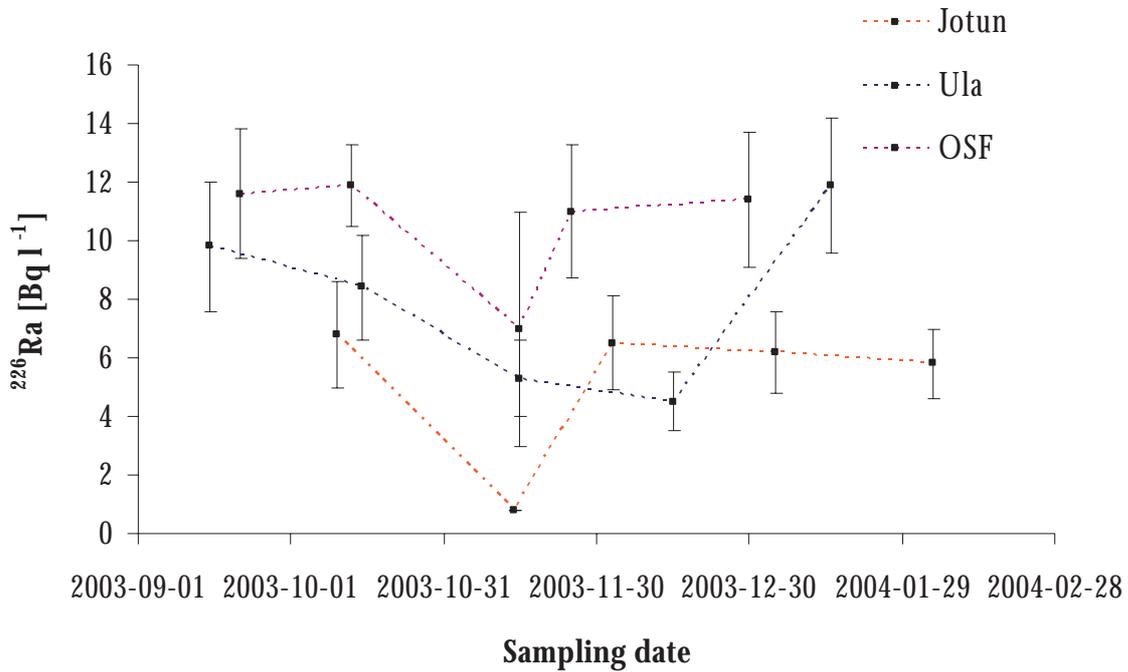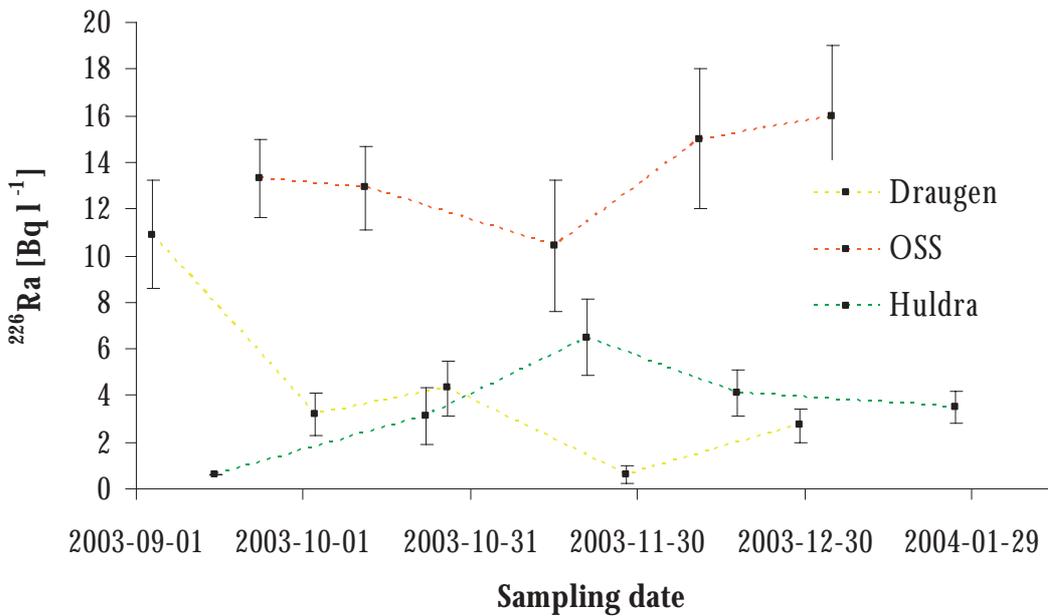

Figure 5.9. *Activity concentration (± 2 SD) of* ²²⁶*Ra in produced water on different sampling dates for 2 of the platforms where a large variation was observed.*

Figure 5.10. *Activity concentration (± 2 SD) of* ^{226}*Ra in produced water on different sampling dates for 3 of the platforms where a large variation was observed.*

Figure 5.11. *Activity concentration (± 2 SD) of* ^{226}*Ra in produced water on different sampling dates for 3 of the platforms where a large variation was observed.*

6   Discussion

The range in activity concentrations of ^{226}Ra and ^{228}Ra found in produced water in the period September 2003 to January 2004 agrees well with what has been reported earlier. Based on the data presented the average activity concentrations of ^{226}Ra and ^{228}Ra in produced water from the Norwegian oil and gas industry for 2003 have been estimated to be 3.3 and 2.8 Bq l^{-1}, respectively. For ^{226}Ra this agrees well with the estimate for 2002 presented by Varskog (2003). In Figure 6.3, ^{226}Ra levels in produced water in 2002 from 35 of the 41 platforms (provided by the OLF) are compared with the results for 2003. For most platforms the result for 2002 and 2003 show good agreement. An explanation of the somewhat higher levels in 2003 for platforms with lower activity concentrations of ^{226}Ra is that the analytical method (gamma spectrometry) was less sensitive than the method used in 2002 (^{222}Rn-emanation). The lowest activity concentrations for 2003 thus represent the detection limit for the method used in 2003.

By comparing Figures 5.2 and 5.4 it can be seen that most platforms with a high annual discharge of produced water also tend to have a lower activity concentration of radium in the water. Many of these fields produce large volumes of oil, for example, Statfjord, Gullfaks and Ekofisk, but have also been in production since the mid 1980s or earlier and large volumes of seawater have previously been injected into the reservoirs. For Statfjord A, B and C, for example, it has been estimated that about 62 % of the produced water in 2003 consisted of seawater that had previously been injected in the reservoirs (Thingvoll J. T., Statoil, personal communication, 2004). The lower radium levels in the produced water is thus probably the result of both dilution and precipitation of Ba(Ra)SO$_4$ within the reservoirs. One obvious exception is the Troll oilfield (Troll B and C platforms), which produces large amounts of produced water and also has a relatively high activity concentration of radium in the produced water.
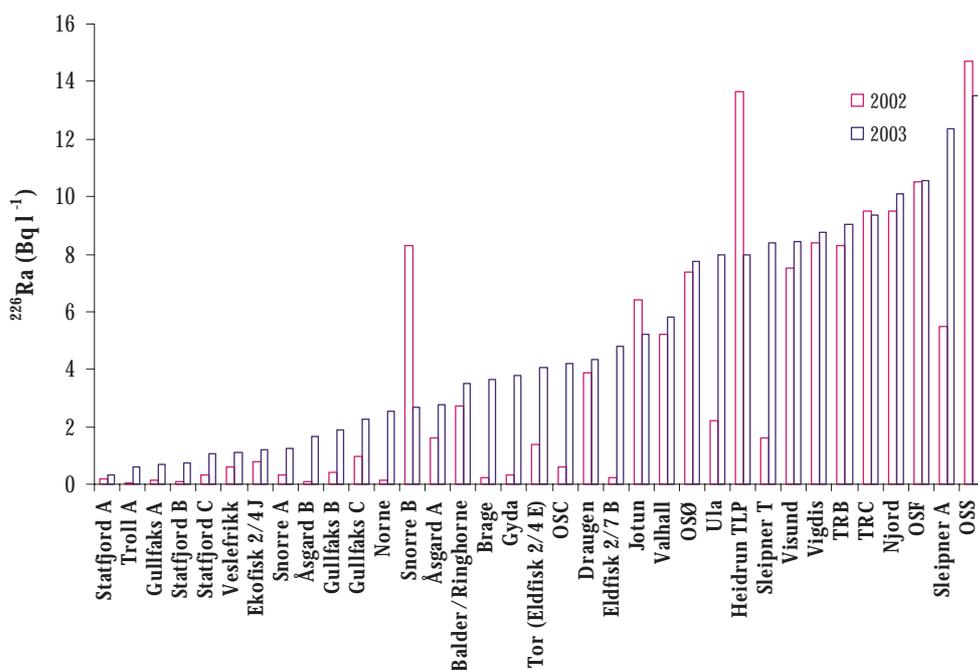

Figure 6.1. Comparison between average ^{226}Ra levels observed in produced water from 35 Norwegian production platforms in 2002 and 2003 (data for 2002 provided by the OLF).

The Troll field is located in the northern North Sea, 60 to 80 kilometres off the coast of Hordaland County. The field is situated adjacent to other major fields like Oseberg, Statfjord and Gullfaks. Oil from the Troll field is produced by two platforms, Troll B (Figure 6.2) and Troll C, while Troll A is a gas-producing platform. Production from Troll B started in 1995 and from Troll C in 1999. Troll Oil is now among the largest oil producing fields on the Norwegian continental shelf with a production of about 21 million m^3 of oil in 2003 (Norsk Hydro, 2004). One reason for the large volumes of produced water is that the field contains naturally large volumes of formation water. The oil is produced from horizontally drilled wells with thin oil-containing layers (thickness between 12 to 26 meters). This special procedure leads to the production of large volumes of produced water compared with other fields. Since no seawater is injected into the field (Røe Utvik T. I., Norsk Hydro, personal communication, 2004), the water quality is relatively stable, and radium levels may not decrease over time due to, for example, dilution or coprecipitation with $BaSO_4$.

The estimated total discharged activities of [226]Ra and [228]Ra for 2003 is 440 GBq (range 310 to 590 GBq) and 380 GBq (range 270 to 490 GBq), respectively. Varskog (2003) estimated for [226]Ra a total discharge of 306 GBq for 2002 for all Norwegian production platforms in the North Sea. The combination of relatively high activity concentration in the produced water and the large discharge volumes of produced water make Troll B and C the major contributors of radium from the oil and gas industry to the North Sea on the Norwegian continental shelf in 2003. The total discharged activity of [226]Ra and [228]Ra from these platforms has been estimated to be 193 GBq and 156 GBq, respectively, corresponding to 44 % of the total discharged activity of [226]Ra and 41 % of the total discharged activity of [228]Ra. The remaining platforms have an annual discharge of [226]Ra in the range < 1 GBq to about 30 GBq. For [228]Ra the corresponding range is from < 1 GBq to slightly below 25 GBq.
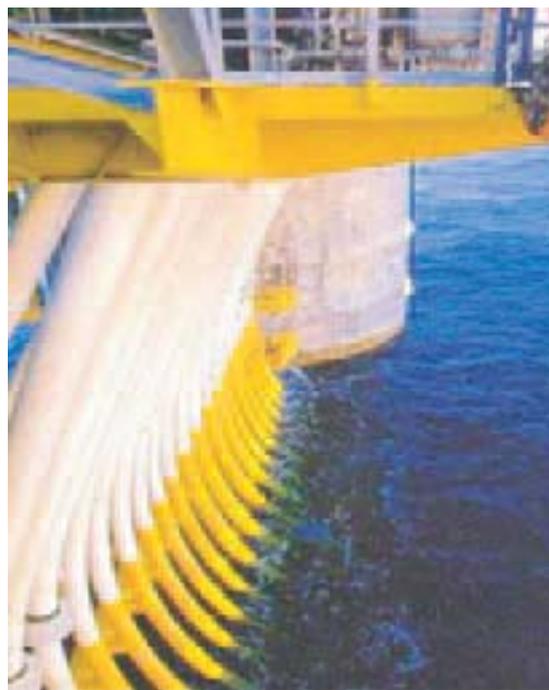

Figure 6.2. *Detail from the Troll B platform which together with Troll C, discharges nearly half of the radium arising from the oil industry on the Norwegian continental shelf. (Photo: Norsk Hydro).*

The estimated total discharged activity in 2003 of [226]Ra agrees well with the estimate for 2002 presented by Varskog (2003), which was also based on platform-specific data. The slightly higher levels for 2003 are a combined result of both a slightly higher average activity concentration in the produced water and a larger discharged volume for 2003 compared with 2002. Another estimate of discharged activity of [226]Ra and [228]Ra, for the Norwegian oil and gas industry, was presented in the MARINA II study (MARINA II, 2003). In this assessment it was assumed that the average activity concentration of [226]Ra and [228]Ra, over the lifetime of an oil-producing reservoir was 10 Bq l^{-1}. The discharged volumes of produced water were assumed to equal 3 times the volume of the oil produced. A small contribution was also assumed from gas production. With these assumptions it was estimated that 5.5 TBq of [226]Ra and [228]Ra, each, were discharged in 1997. Since the production of oil and gas from the Norwegian continental shelf has increased slightly since 1997 (OLF, 2004) the discharged activity should be slightly higher in 2003. According to the data presented

in this study, it seems that both the activity concentration in the produced water and the discharged volumes were overestimated with the methodology used in the MARINA II study.

The total annual discharge of ^{210}Pb is lower than for radium. Since almost all analysed samples were below the detection limit, it can only be concluded that the total discharged activity in 2003 is less than 92 GBq. Since only 12 samples were analysed for ^{210}Po it is not possible to reliably calculate the total discharged activity. However, the low activity concentration (about 1000 times lower than radium) in all analysed samples indicates that the total discharged activity could be about 1000 times lower than for radium. Since ^{226}Ra decays via several short-lived daughters and ^{210}Pb ($t_{1/2}$ = 22 y), to ^{210}Po, there will eventually be a contribution of ^{210}Po from the decay of ^{226}Ra. Due to the half-life of ^{210}Pb, the time required to establish secular equilibrium between ^{226}Ra and ^{210}Po is relatively long. The build-up of ^{210}Po activity from ^{226}Ra as a function of time is shown in Figure 6.3. Since both ^{210}Pb and ^{210}Po are more particle reactive than ^{226}Ra a large fraction will probably be absorbed onto particles and finally reach the sediments.

Ten of the 41 production platforms showed a difference between maximum and minimum in the activity concentration greater than 4 Bq l^{-1} for ^{226}Ra during the monitoring period. In Figures 3.8 to 3.11 the results for each sampling date are presented. Taking the uncertainty in the analysis into consideration, 3 of the platforms did not show a significant difference between individual samples collected on different dates. However, for the other 7 platforms it is obvious that short-term variation in the activity concentration of radium occurred. Suggested explanations for this are given below.

1) Many of the platforms usually produce oil and gas from several wells in the area. If production rates change between the wells connected to the platform and the water chemistry is different between the wells, due to, for example, local geological variations, one can expect a variation in the activity concentration of radium in the produced water.

2) Another factor is breakthrough of seawater in the wells. As shown in Figure 3.1, barium levels can change rapidly when sulphate-rich seawater is mixed with the formation water. Due to the similar chemical behaviour of barium and radium a similar variation can also be expected for radium due to dilution and coprecipitation with $BaSO_4$.
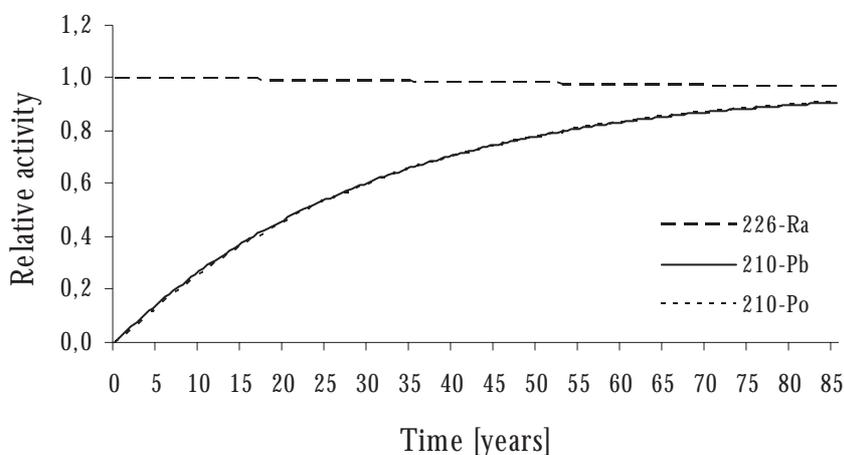

Figure 6.3. Build-up of ^{210}Pb and ^{210}Po from the decay of ^{226}Ra

3) In this study the total fraction of radium in the produced water was analysed. If radium is present in suspended particulate material and colloids, short term variations in the particulate load in the produced water can be responsible for a variation of radium concentration in the samples. Once or twice per week the separators used to separate oil, gas and water are cleaned with high-pressure water (water-jetting) to remove solid particles (such as sand and scale particles); this may temporarily increase the load of radium-rich scale particles in the produced water.

4) Occasionally, scale removal operations take place at the platforms, in order to remove scale in fixed equipment, by dissolving the scale with acids or chelating agents. The liquid waste from these operations is discharged together with the produced water. If a sample is collected during such an operation, elevated levels of radium can be expected. At some platforms scale dissolvers are also occasionally injected into wells when scale formation has slowed down the production in the well. If a sample is collected in connection with such treatment elevated levels of radium may also be observed. In order to prevent scale formation, scale inhibitors are usually added to the reservoirs or to the production stream on the platform. An inhomogeneous concentration of scale inhibitor in the produced water may also result in varying radium levels in the produced water.

The purpose of initially collecting monthly samples for five consecutive months in this study was to observe possible variations, and to use this information to determine a suitable sampling frequency for future sampling. Due to the relatively large number of platforms with a high variation it is desirable to continue sampling at a high frequency in order to be able to estimate of the discharged activity. Collecting samples only once per year can, for certain platforms, lead to large over or underestimates concerning the total annual discharged activity. For practical reasons the number of samples from each production platform will be reduced to 4 per year in 2005. A possible future strategy is to further reduce the samples collected from platforms showing low variation and activity concentration of radium in the produced water, while keeping the sampling frequency high for platforms with elevated levels of radium in the produced water, and where variations can be expected. For some platforms where the radium levels have been relatively low, but where the discharged volumes are very large, the sampling frequency will also continue to be high, since a small change in the radium activity concentration can lead to a significant change in the total discharged activity of radium.

7   Conclusions

Samples collected in 2003 (and early 2004) from all 41 production platforms that discharge produced water, show an average activity concentration in Norwegian produced water of 3.3 Bq l^{-1} for ^{226}Ra and 2.8 Bq l^{-1} for ^{228}Ra. Almost all analysed samples showed an activity concentration of ^{210}Pb below the detection limit (about 1 Bq l^{-1}).

An estimate of the total discharged activity of ^{226}Ra and ^{228}Ra, based on platform-specific data on activity concentrations of radium in produced water, and discharged volumes of produced water has been made. About 440 GBq (range 310 to 590 GBq) and 380 GBq (range 270 to 490 GBq) of ^{226}Ra and ^{228}Ra, respectively, was discharged from the Norwegian oil and gas industry in 2003.

Dispersion modelling has been performed with the DREAM model developed by SINTEF. A scenario of continuous discharge of radium (with the data presented in this report for 2003) during 1 year, from all 41 Norwegian platforms discharging produced water, shows in most areas, that the contribution of ^{226}Ra from produced water is well below 1 mBq l^{-1}. Background levels of radium in the North Sea are uncertain, but probably range from about 1.5 to 5 mBq l^{-1} for ^{226}Ra. Occasionally, an additional activity concentration of about 1 mBq l^{-1} can be encountered in the Tampen/Troll area. This means that in limited areas in the northern North Sea, a doubling of the activity concentration of ^{226}Ra could be encountered. The major part of the discharged activity is transported towards the Norwegian coast, into the Norwegian Coastal Current, where it is transported further northwards. Taking discharges from UK platforms into account, the levels will be further enhanced.

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Appendix A

The data on radium in produced water obtained for 2003/2004 in this study, together with discharge volumes for 2003 have been used to model the dispersion of radium in the North Sea. The model used is the DREAM model developed by SINTEF in Norway. The DREAM model is a three-dimensional model based on vertical and horizontal diffusion and advection due to sea currents. Detailed information on the model can be found in Reed *et al.* (1995) and Reed *et al.* (2001). One simplification assumed in the calculation is that the produced water discharged has the same temperature and salinity as the surrounding seawater. It is also assumed that all discharged radium is in soluble form. The ocean current data used were generated from the ECOM-3D model developed by the Norwegian Meteorological Institute (DNMI). The data used are from a simulation carried out for the North Sea in 1990. The currents are depth and time variable throughout the whole year, and the horizontal resolution is 20 km.

Two scenarios have been modelled:

1) One year of continuous discharge of produced water from all Norwegian production platforms in the North Sea. Results presented show the levels of ^{226}Ra and ^{228}Ra in the seawater in January, July and December.

2) One year of continuous discharge of produced water from the Troll B and C platforms. Results presented show the levels of ^{226}Ra and ^{228}Ra in January, July and December.

Figures A.1 to A.12 show the concentration field for radium at the depth with the highest radium concentration in Bq m^{-3}. A vertical cross section is also included. In the maps of the North Sea area a cross section from the Ekofisk area through the Troll area is shown. In the maps of the Troll area a cross section to the Troll area and northwards is shown. The mass balance shows the percent of the total annual discharged activity that has been dispersed. The column marked "outside" shows the percentage that is dispersed outside the area shown in the map.
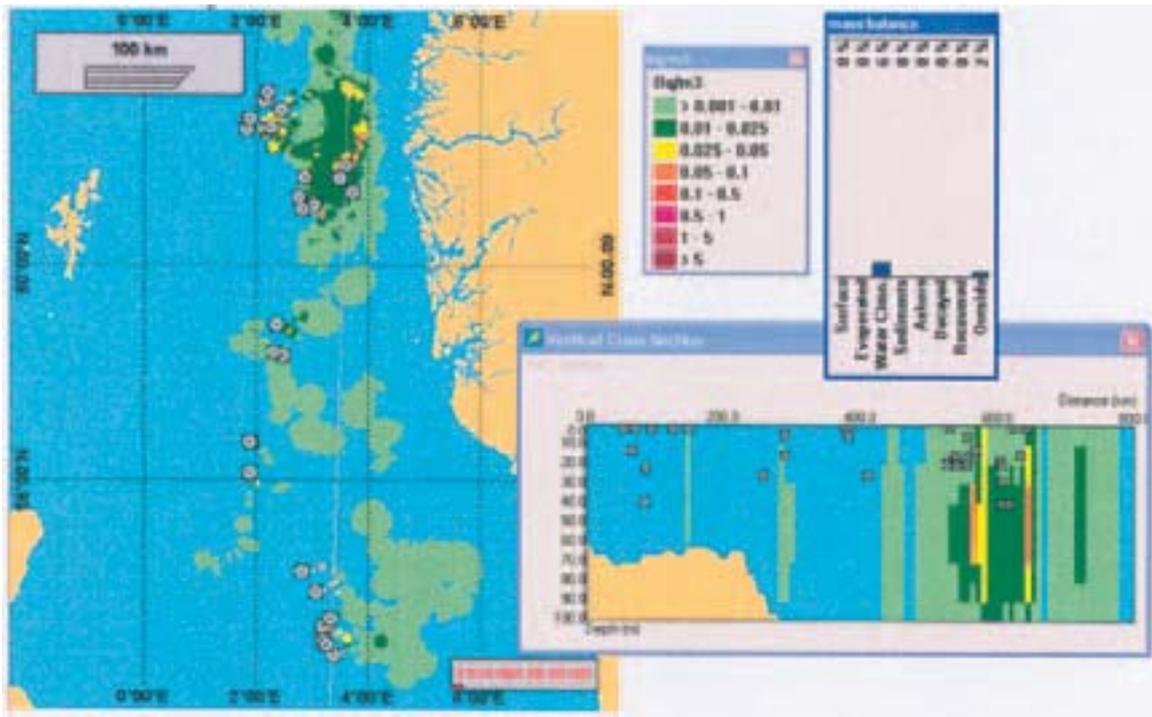
Figure A.1. Concentration field for ^{226}Ra in the North Sea for January.
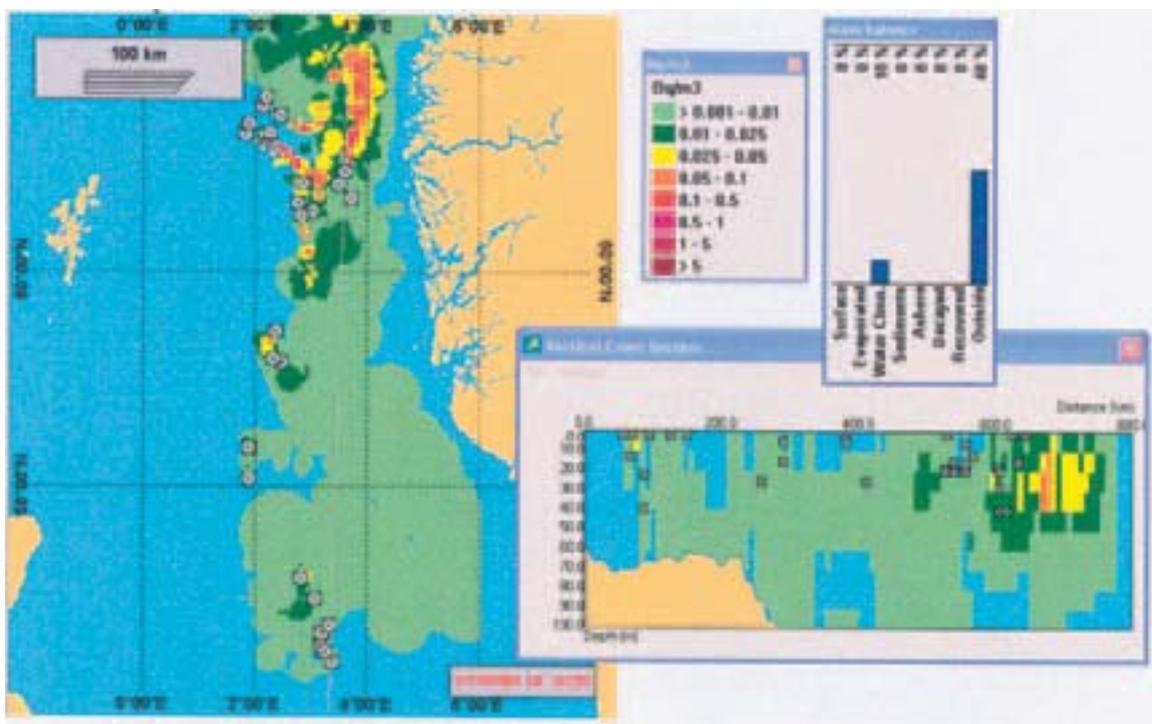

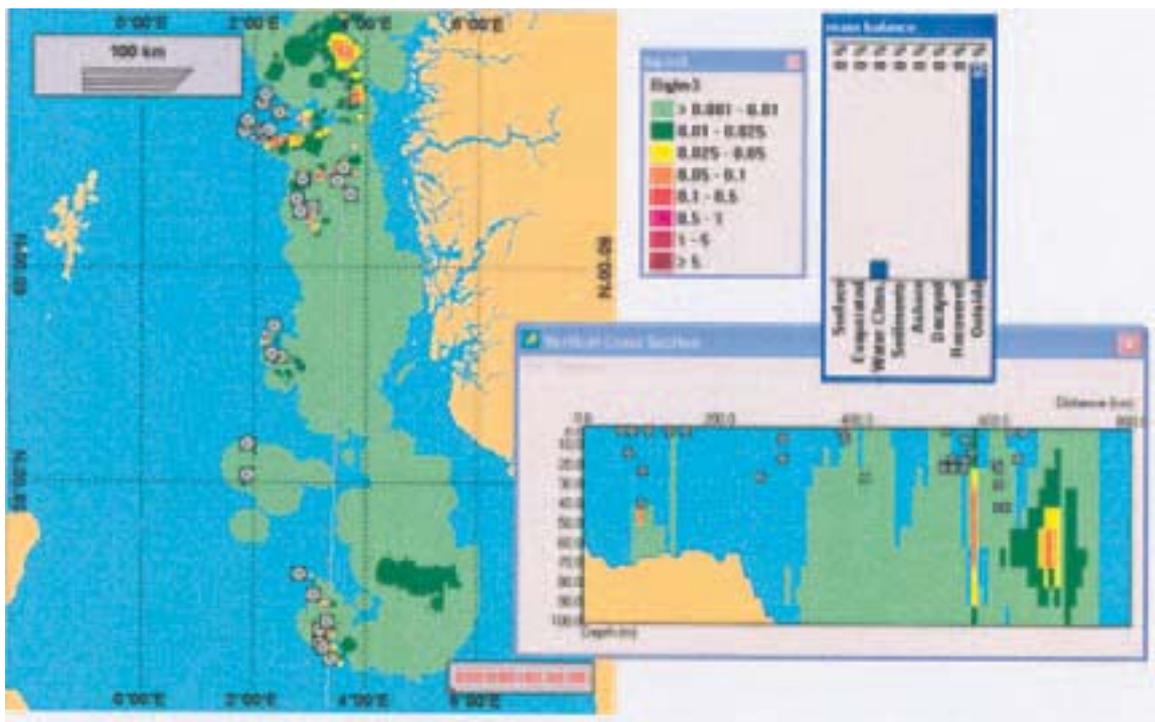*Figure A.2.* Concentration field for ^{226}Ra in the North Sea for July.

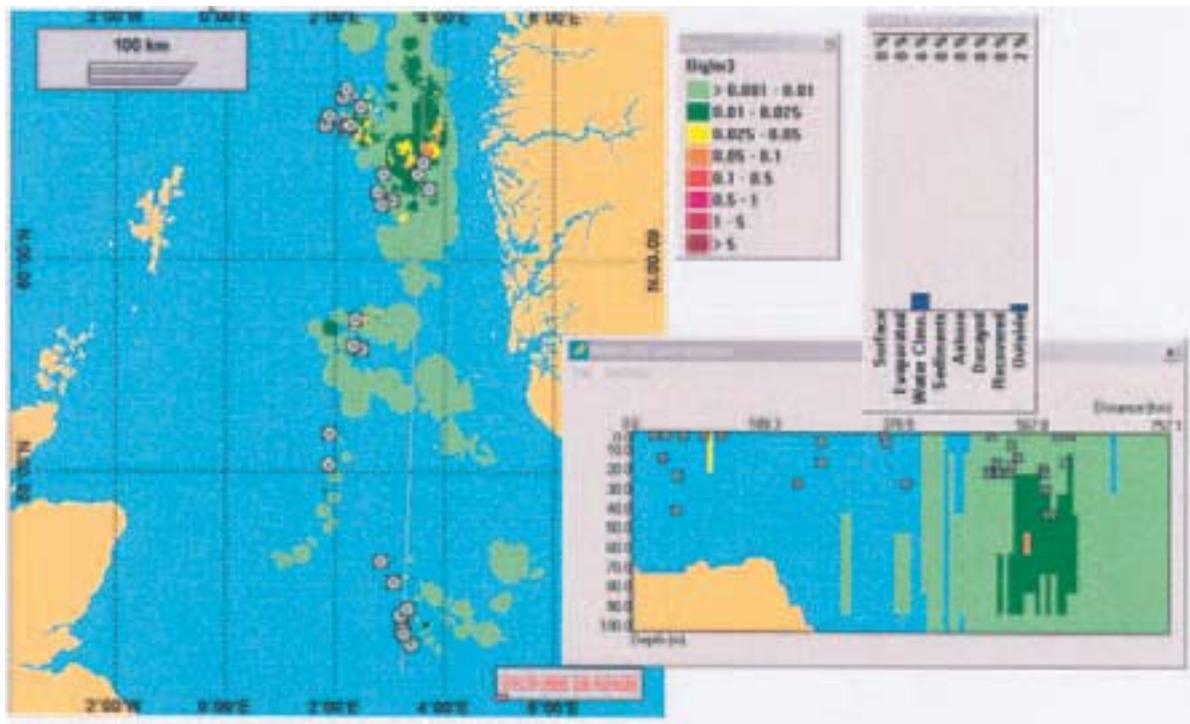**Figure A.3.** *Concentration field for ^{226}Ra in the North Sea for December.*

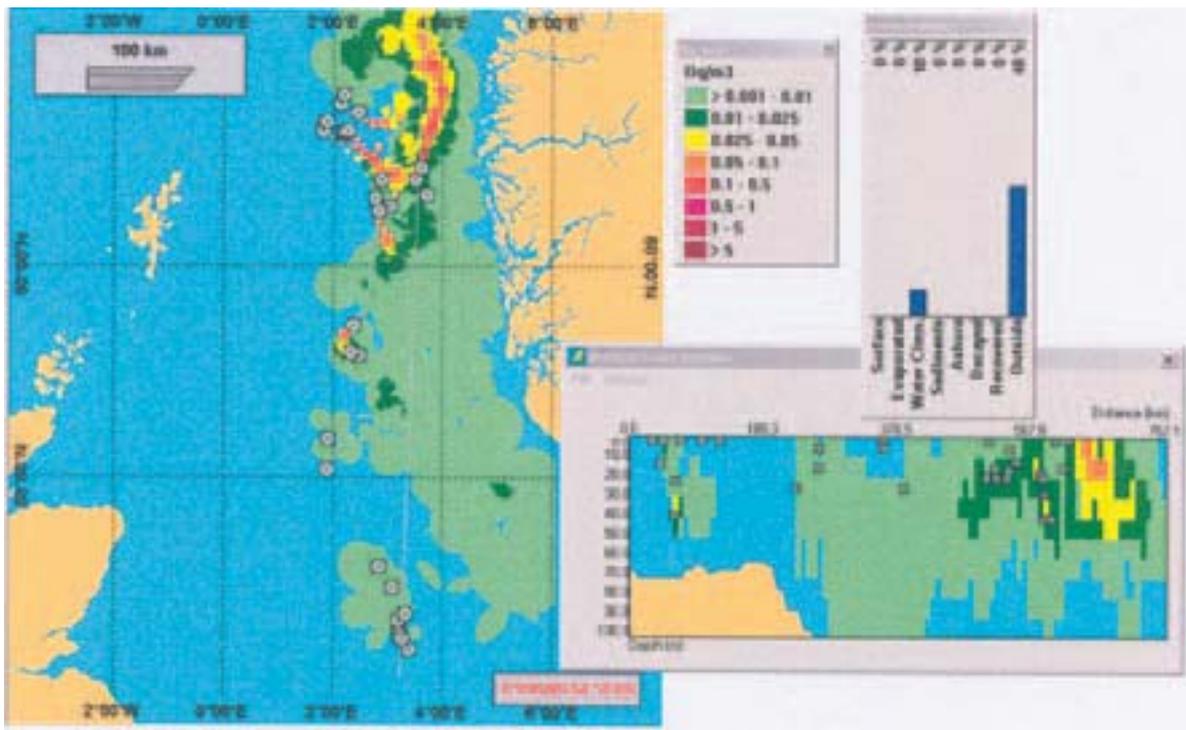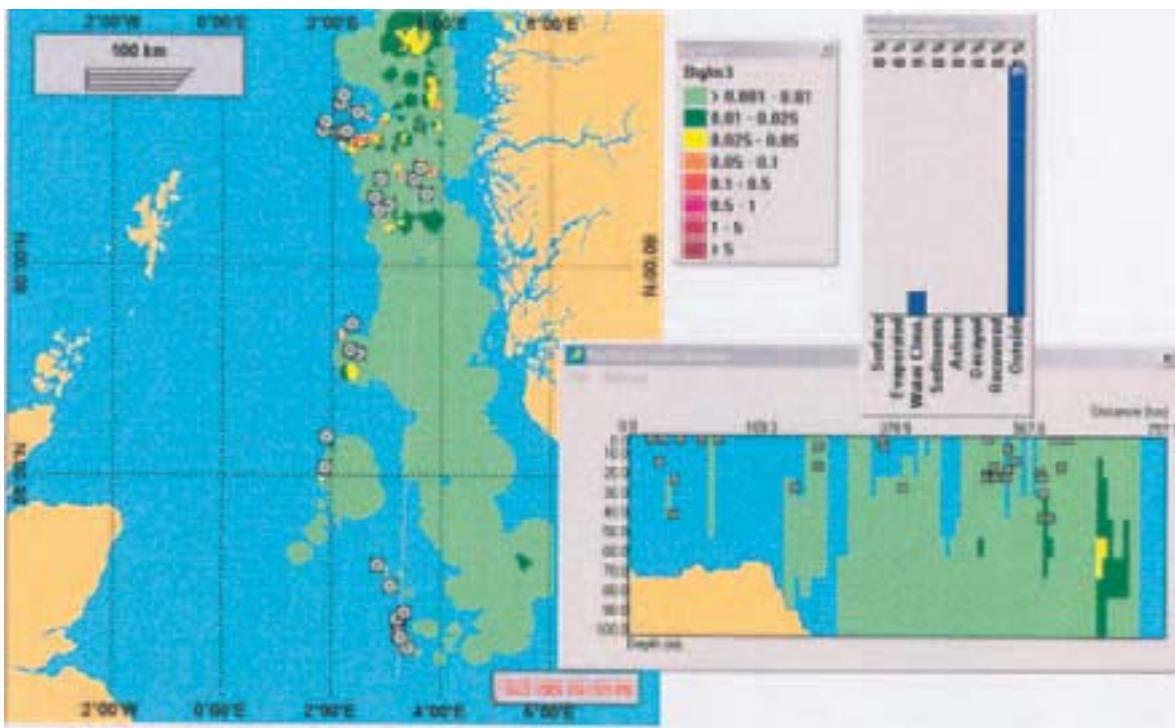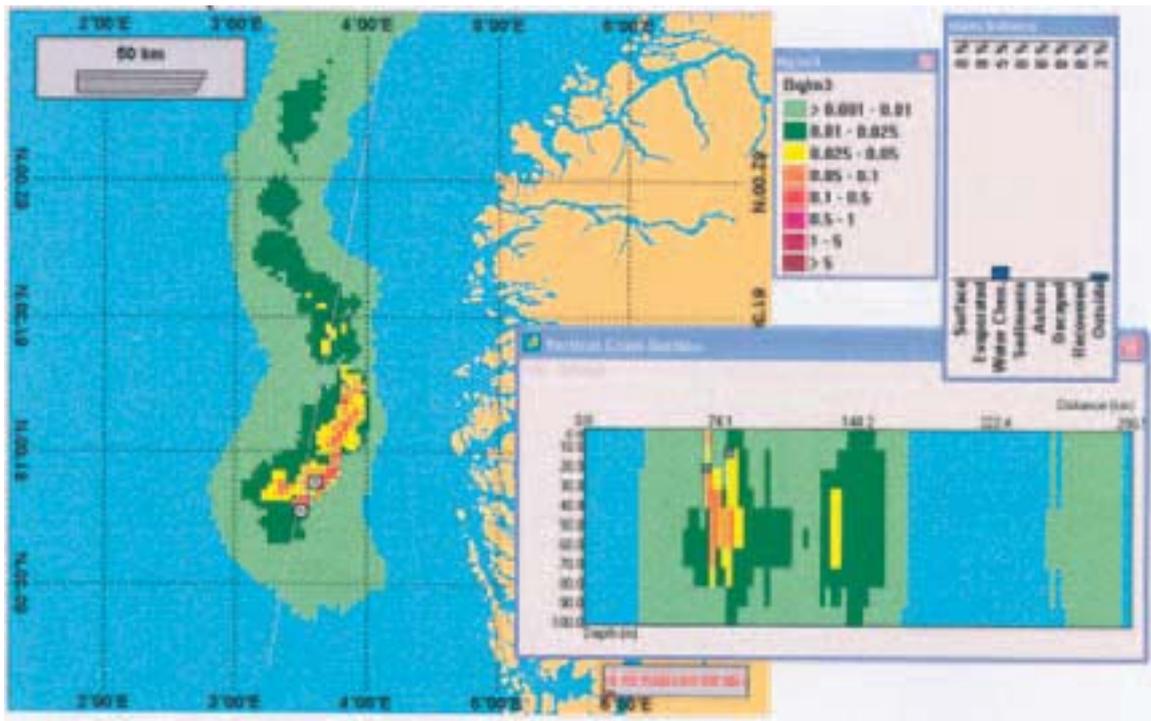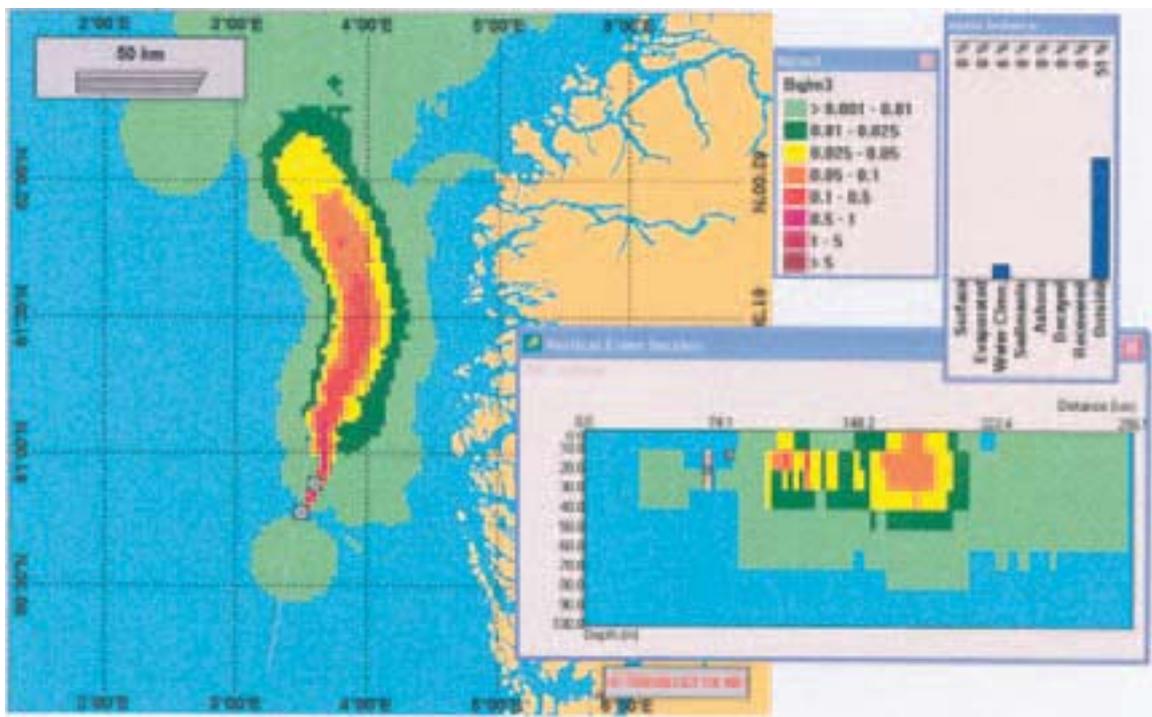**Figure A.4.** *Concentration field for ^{228}Ra in the North Sea for January.*

Figure A.5. Concentration field for ^{228}Ra in the North Sea for July.
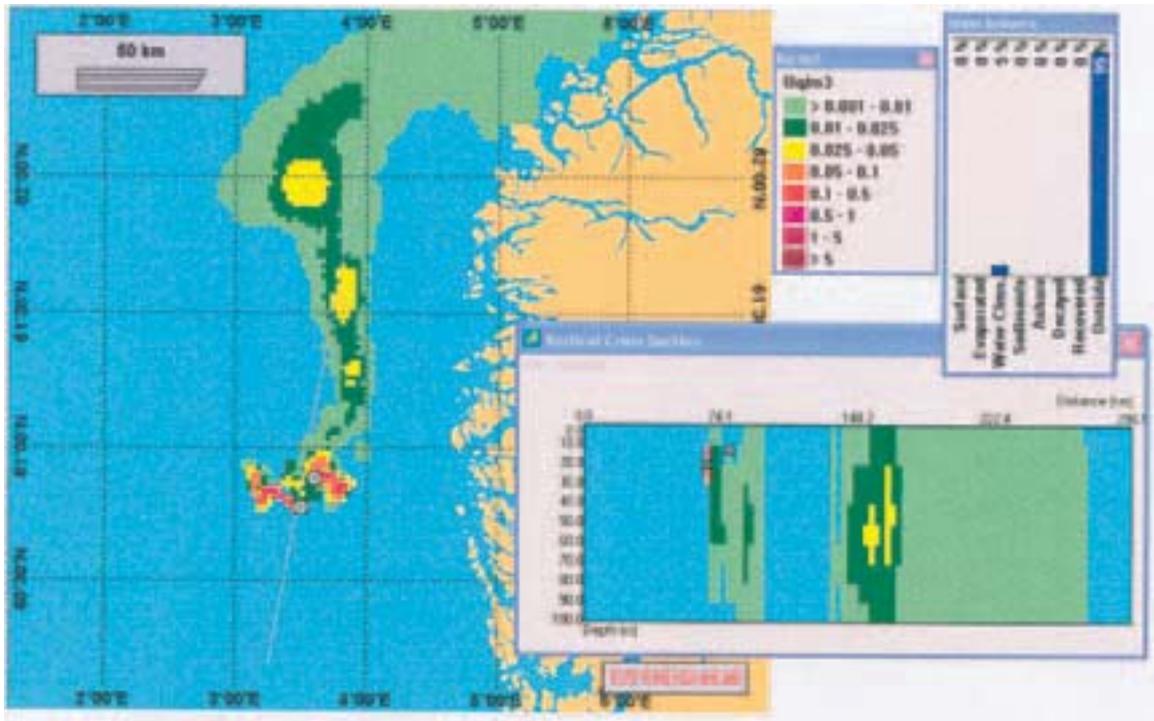

Figure A.6. Concentration field for ^{228}Ra in the North Sea for December.

Figure A.7. Concentration field for ^{226}Ra in the Troll field for January.

Figure A.8. Concentration field for ^{226}Ra in the Troll field for July.

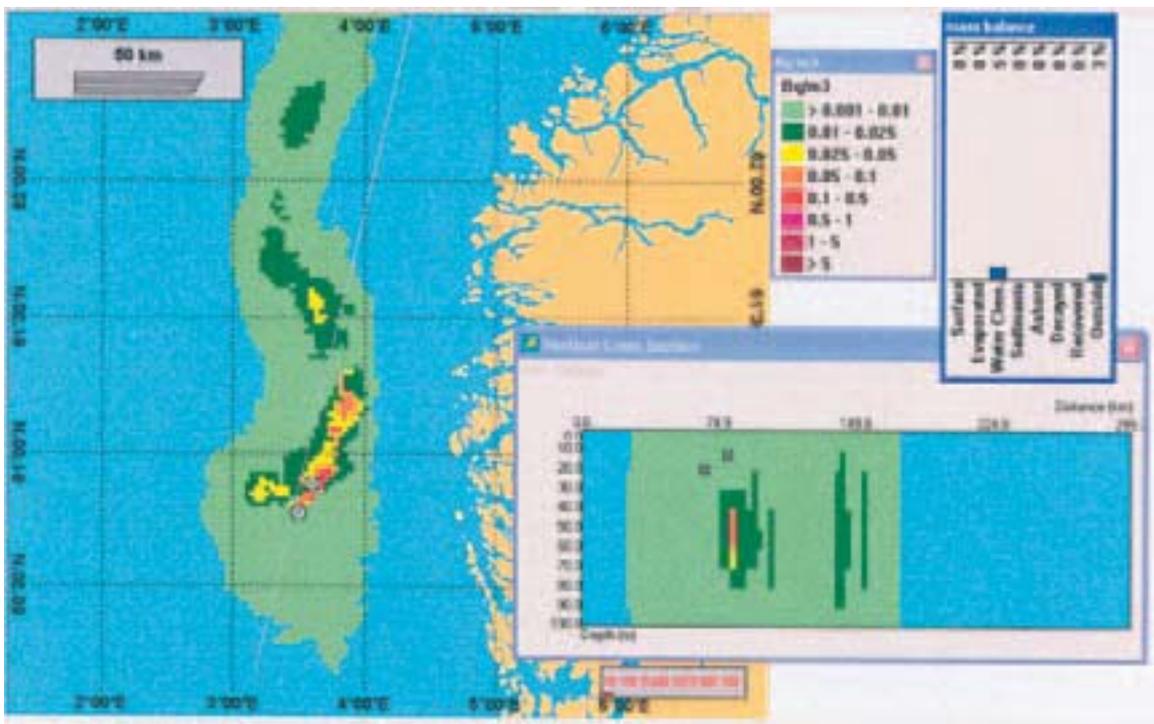**Figure A.9.** *Concentration field for ^{226}Ra in the Troll field for December.*

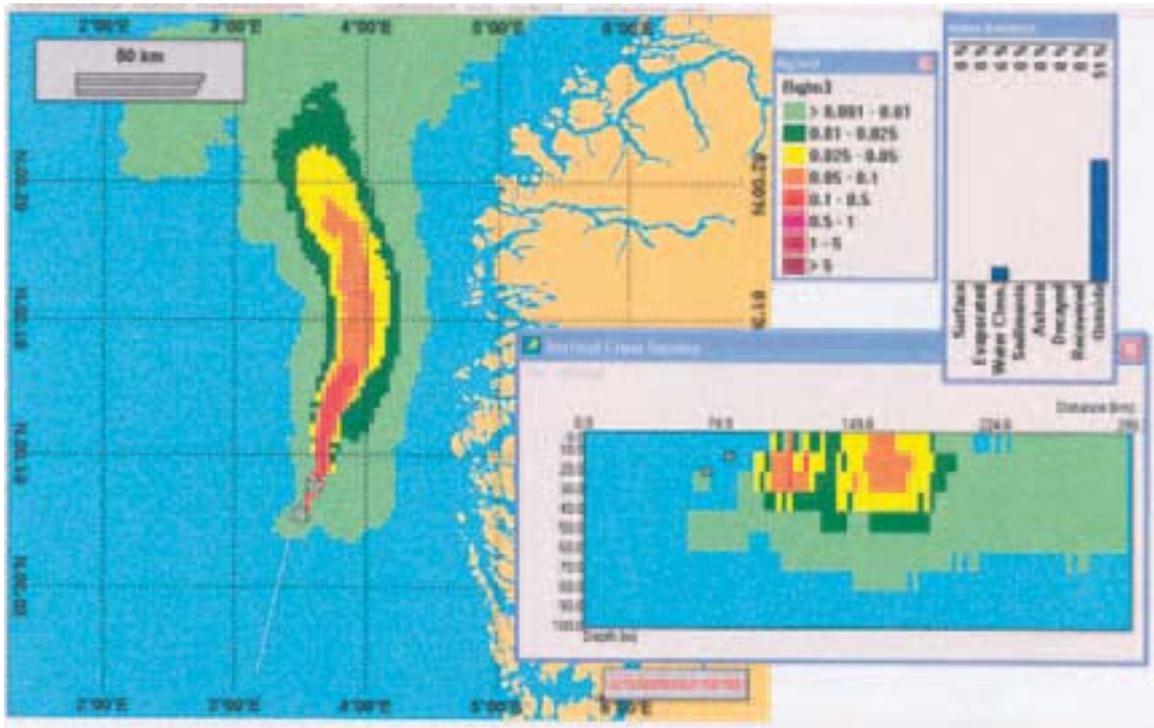**Figure A.10.** *Concentration field for ^{228}Ra in the Troll field for January.*

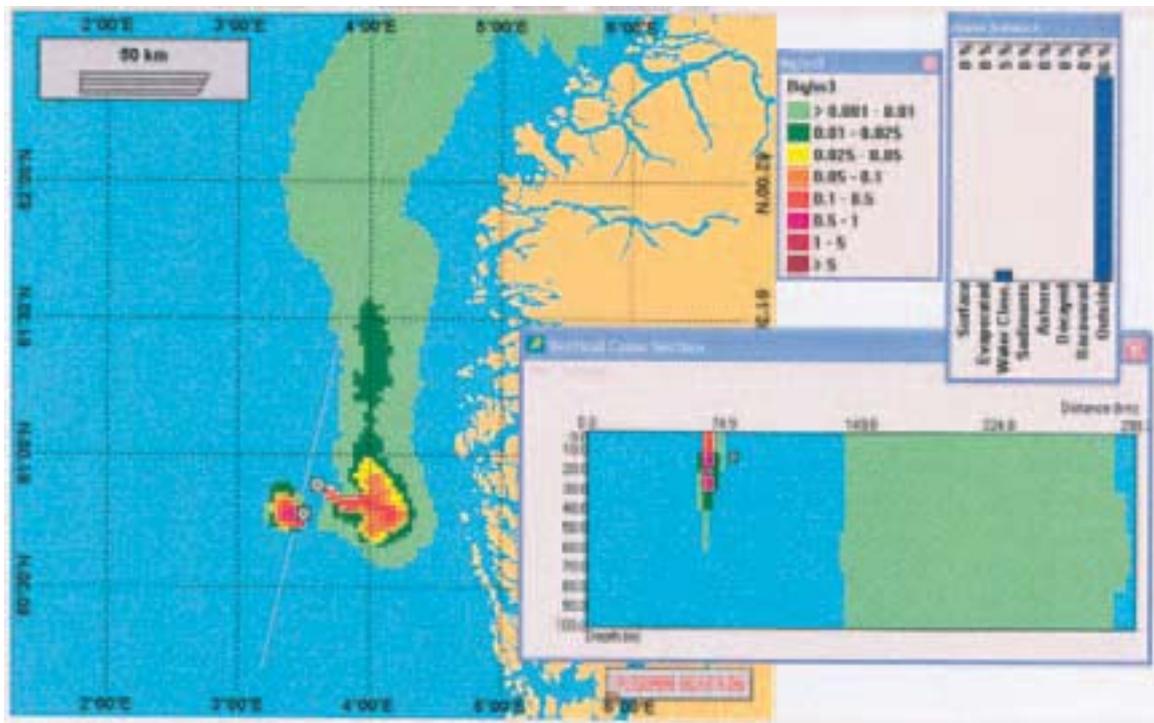*Figure A.11.* Concentration field for ^{228}Ra in the Troll field for July.

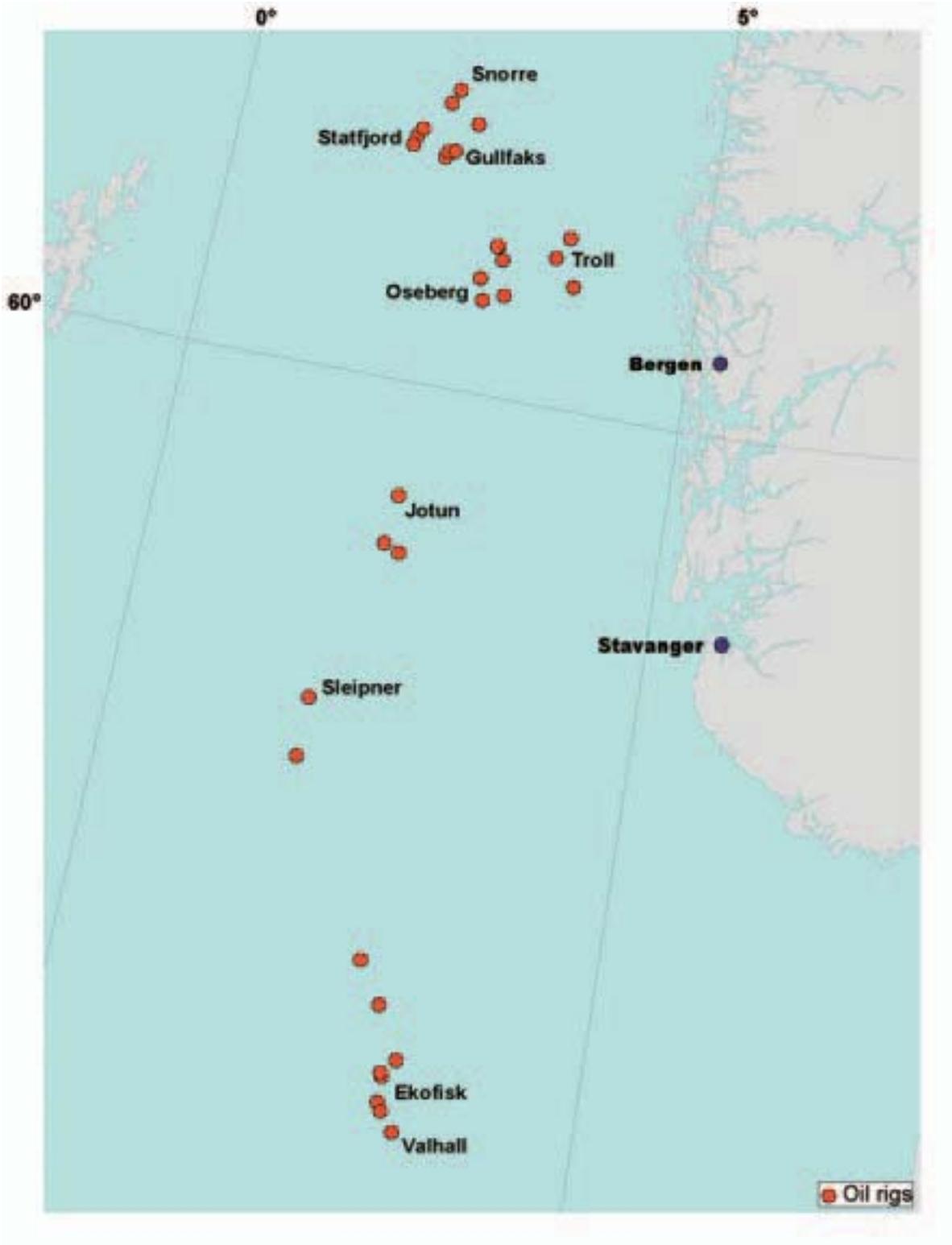*Figure A.12.* Concentration field for ^{228}Ra in the Troll field for December.

Appendix B

Figure B.1. *Overview of oilrigs and the major fields on the Norwegian sector of the North Sea.*

Glossary

Alpha recoil

When a radionuclide decays via alpha decay, a helium nucleus is emitted. If the radionuclide is located, for example, at the surface of mineral grain and the alpha particle is emitted into the body of the grain, the recoil energy can give the nuclide enough energy in to be ejected from the grain into the adjacent solution, or damage the crystal lattice.

Brines

Water with a higher dissolved salt concentration than seawater.

Formation water

Naturally occurring water within the pore spaces of the rock.

Rn-emanation method

An analytical method used to determine ^{226}Ra. Initially the sample has to be stored for 3 to 4 week to ensure secular equilibrium between ^{226}Ra and ^{222}Rn. The inert gas, ^{222}Rn, is then transferred to a ZnS-coated Lucas flask. After about 1 hour the short lived ^{222}Rn daughter nuclides have established equilibrium with ^{222}Rn and the Lucas flask is placed on a photomultiplier tube. Light pulses emitted from interactions between the ZnS and emitted alpha particles are counted and from these pulses the activity is determined.

Scale

Mineral salt deposits which may occur on the rock in an oil well, or inside production equipment. Scale is formed when changes in pressure, temperature or salinity in a solution facilitates precipitation of salts such as barium sulphate, calcium carbonate or others.

Secular equilibrium

A steady-state condition in which the activity of a short-lived daughter nuclide is equal to the activity of the parent nuclide.

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