Zpire Report 03-12

Radioactive non-equilibrium in Produced Water

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Radioactive non-equilibrium in Produced Water

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Summary:
This study comprises results from produced water samples from 10 installations representing 38.6 % of the total releases of produced water on the Norwegian Continental Shelf. The produced water samples have been analysed with respect to the relevant individual radionuclides (parent and daughter nuclei) utilizing low-level alpha- and gamma spectrometry and low level beta measurements. In addition the total alpha and total beta activities have been determined.
The results can be concluded as follows:

1. As the produced water is released, only Ra-226 and Ra-228 are present in significant amounts. All the daughter nuclei do practically play no role, since respective secular equilibrium stages are not reached.
2. Due to the apparent radioactive non-equilibrium the total activity releases as they are reported in OSPAR are almost an order of magnitude higher than the actual releases as e.g. determined by total alpha and total beta analysis.
3. The level of Pb-210 is documented to be at least an order of magnitude lower than what is usually reported.

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1 Theoretical background

1.1 Introduction

Data for the discharges from the oil/gas sub-sector was provided by Norway, Netherlands, UK, Ireland and Denmark, whereby the UK and Norway are the principal contributors. In 2007 the relative contributions, based on produced water activities, were: Norway 56%, UK 27%, Netherlands 14%, and other CPs that reported ~3% [1]. There is an unknown, but probably minor, contribution from the other three CPs with an oil/gas industry. The assessments are based on produced water discharge data. The data on scale discharges is incomplete, but the contribution of scale discharge is presumably very small compared to produced water discharge.

The total alpha and total beta discharges from produced water have been calculated using the formulae agreed at Radioactive Substances Committee (RSC) [1] to include contributions from the radioactive daughter products in the respective decay chains.

Although the formulae for calculating the total alpha and total beta discharges from the oil/gas sub-sector were derived in order that comparison could be made with the equivalent discharges from the nuclear sector, it should be remembered that for the oil/gas sector the values are the calculated upper bound of activities discharged, rather than a measured total alpha or total beta discharge. To that extent they differ from the values reported for the nuclear sector.

There are apparently no extensive data available, documenting the levels of the radium daughters presumed to be present in the produced water. Therefore, in this study, we will represent the results of the radionuclide analyses of 20 produced water samples from 10 different oil producing installations and document the levels of radionuclides as they are present in the released produced water.

This study is supported by Norsk olje og Gass and the contributing Norwegian operators (Statoil Petroleum AS, BP Norge AS, Talisman Energy Norge AS, ConocoPhillips Skandinavia AS and ExxonMobil E&P Norge AS).The project is based on a pre-study by Zpire Ltd and IAF - Radioökologie GmbH.

1.2 Natural Radionuclides

Uranium, radium and thorium occur in three natural decay series, headed by U-238, Th-232 and U-235, respectively. The decay series with half-life of the respective radionuclides and decay modes are illustrated in Figure 1. In nature, i.e. in ores or soil, the radionuclide in these three series are approximately in the state of secular equilibrium, in which the activities of all radionuclides within each single decay series are nearly equal.

Due the different solubility of radionuclides in water, secular equilibrium is not established in ordinary water samples. The radioactivity in water samples might rather be described by several smaller decay series headed by the longer-lived decay products of the original series. Each of these sub-series can be considered to represent a new, separate decay series.

Two conditions are necessary for a secular equilibrium. First, the parent radionuclide must have a half-life much longer than that of any other radionuclide in the series. Second, a sufficiently long period of time must have elapsed to allow for the ingrowth of the decay products. Under secular equilibrium the activity of the parent radionuclide undergoes no appreciable change during many half lives of its decay products.

Radionuclides that give rise to alpha and beta particles are depicted in Figure 1. Gamma radiation is not a mode of radioactive decay (such as alpha and beta decay). Rather, it is a mechanism by which excess energy is emitted from certain radionuclides.

High concentrations of these radionuclides are often found in certain geological materials, e.g. igneous rocks and ores. Human activities that exploit these resources may lead to enhanced concentrations of naturally occurring radionuclide materials and/or enhanced potential for exposure to naturally occurring radioactive materials (NORM) in products, by-products, and wastes.

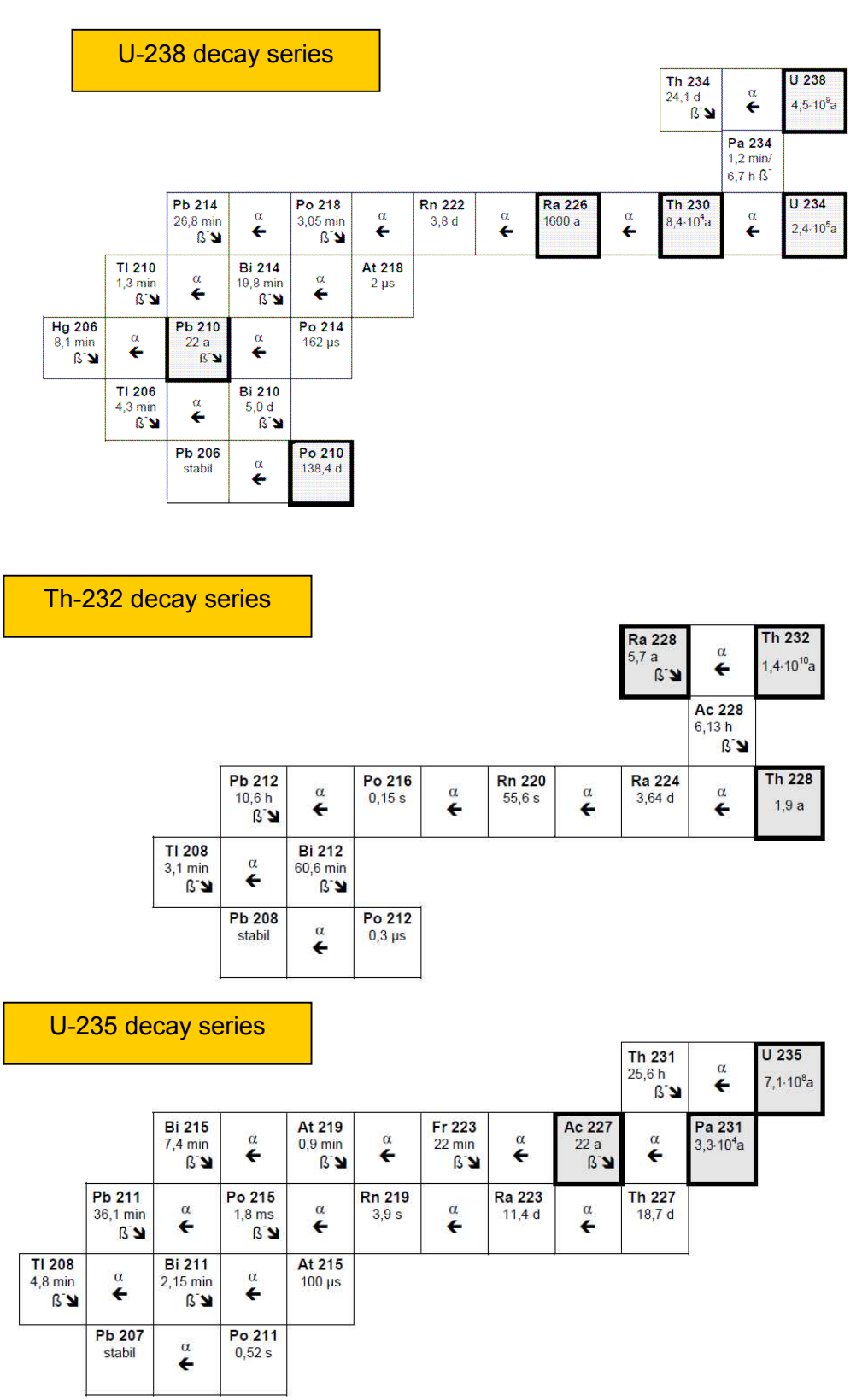


Figure 1 U-238, Th-232 and U-235 decay series

1.3 Alpha- and beta activity discharges from produced water

The formulae according to [1] estimates alpha- and beta activity discharges from produced water by assuming secular equilibrium in the respective decay chains. The total alpha and total beta activities values are calculated by considering the parent radionuclides Ra-226, Pb-210, Ra-228 for individual sub-series. In the following it will be discussed under which conditions a secular equilibrium can be provided and what are the respective boundary conditions.

1.3.1 Ra-226, Pb-210 and decay products

In Table 1 the decay modes and half lives of the Ra-226 and Pb-210 decay products belonging to the U-238 series are listed. For the formation of the secular equilibrium of Ra-226 with its short lived decay products and likewise of Pb-210 with Po-210 the elapsed time span t has to be sufficient large compared to the respective half lives of the decay products. We consider as an example the following initial conditions for the respective activity concentrations at t=0: Ra-226: 5 Bq/l, Rn-222: 0, Pb-210: 20 mBq/l, Po-210: 10 mBq/l.
At the beginning of the decay process (t=0) the total alpha activity would be equal to the Ra-226 activity (1xRa-226). For later times (0 < t < 20 days) it approaches (4xRa-226), since for the Ra-226 decay products the secular equilibrium is reached after about 20 days due to the half-life of 3,82 days of Rn-222.

Table 1: Decay modes and half lives of the Ra-226 decay

Radionuclide	decay mode	half life	decay time τ [h]	$\lambda=1/\tau$ [h^{-1}]
Ra-226	α	1600 years	2,02E+7	4,95E-8
Rn-222	α	3.82 days	132,27	7,56E-03
Po-218	α	3.05 minutes	0,07	1,36E+01
Pb-214	β	27 minutes	0,65	1,54E+00
Bi-214	β	19.7 minutes	0,47	2,11E+00
Po-214	α	1 microsecond	4,01E-10	2,50E+09
Pb-210	β	22.3 years	2,82E+05	3,55E-06
Bi-210	β	5.01 days	173,47	5,76E-03
Po-210	α	138.4 days	4792,06	2,09E-04

The secular equilibrium between Pb-210 and Po-210 is reached after about one year (half-life of Po-210 is 138,4 days). The total alpha activity is then approximately equal to (4xRa-226)+(1xPb-210). This means that the total alpha activity associated with the ingrowth of the decay products of Ra-226 and Pb-210 calculated via the formula (4xRa-226)+(1xPb-210) as recommended by [1] could in dependence of the elapsed time significantly overestimate the actual alpha activity. This holds also for the total beta activity.
The respective time evolutions of the alpha and beta activity are illustrated in Figure 2 for a time interval up to 50 days. It is seen that after 20 days an intermediate plateau is reached that is characterized approximately by (4xRa-226) for the alpha activity and (2xRa-226) for the beta activity.

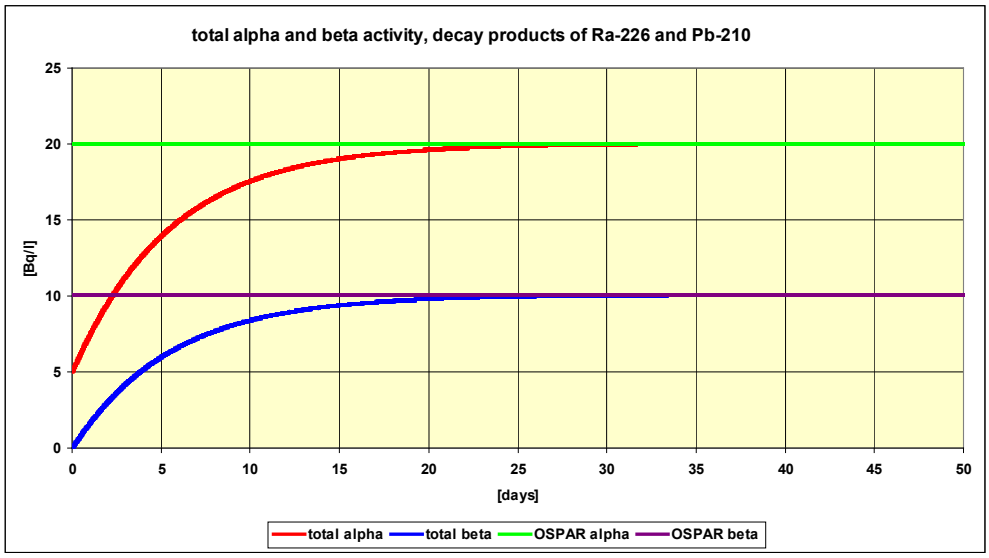


Figure 2: Time evolution of the alpha and beta activity (decay products of Ra-226 and Pb-210). Also given are the respective estimates according to OSPAR [1].
Initial concentrations are: Ra-226: 5 Bq/l, Rn-222: 0, Pb-210: 20 mBq/l, Po-210: 10 mBq/l

In Figure 3 the evolution of the alpha and beta activity is shown for time intervals up to 20 years. The total alpha and beta activities will still increase until the overall secular equilibrium is reached, i.e. the Pb-210 activity will be equal to that of Ra-226.

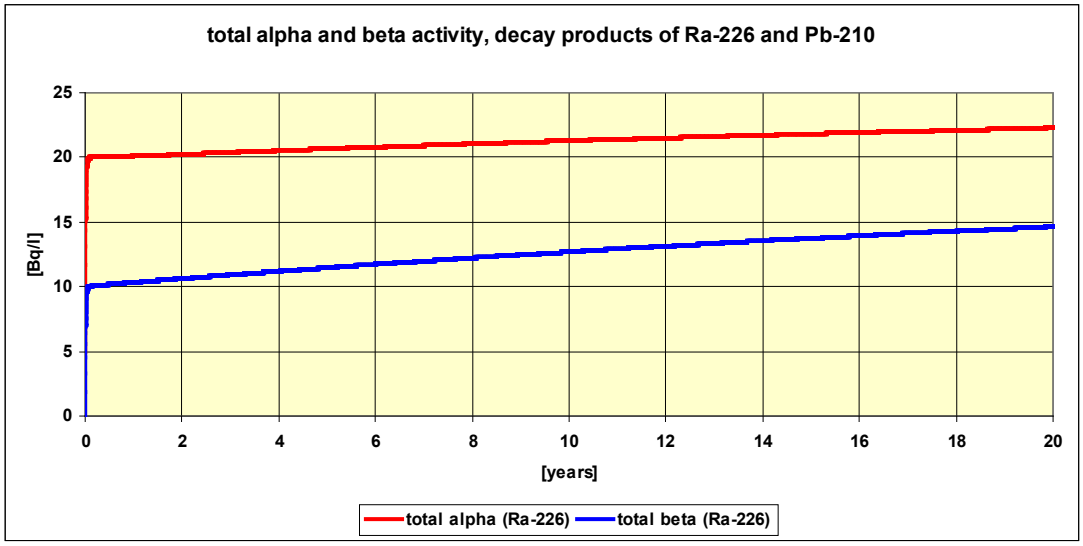


Figure 3: Same as Figure 2, but for much longer time spans

Table 1 gives an overview of the different development stages for total alpha and beta activity. At t=0 the alpha and beta activities are solely given by the initial activity of Ra-226 and Pb-210, respectively. In many cases the beta energy is negligible in comparison to the alpha activity. A maximum alpha activity could be reached being (5xRa-226) and (4xRa-226) for the beta activities, respectively. However, these are not in any case the correct alpha and beta activity concentrations associated with real situations, since it would imply to keep produced water in a tightly closed container for many decades until overall secular equilibrium is reached.

Table 2: Total alpha and beta activity as function of the elapsed time for the decay of Ra-226 and Pb-210

Total alpha activity	Total beta activity	Elapsed time
(1xRa-226)	(1xPb-210)	t=0
(4xRa-226)	(2xRa-226) + (2xPb-210)	20 days <t < 100 days
(4xRa-226) + (1xPb-210)	(2xRa-226) + (2xPb-210)	1 year
(5xRa-226)	(4xRa-226)	> 50 years

If initially, i.e. when the radon has been suddenly stripping out from the water like in the oil-water separation, the short living radon progenies could still remain to some extent. In this case, as shown in Figure 4, the total alpha and beta activities would initially quickly decrease and soon follow the curves displayed in Figure 2. The total alpha and beta activity concentration to be associated with situation at the disposal moment, would then strongly depend on the time duration of the produced water between separation and disposal and on the actual activity of the short living radon progenies.

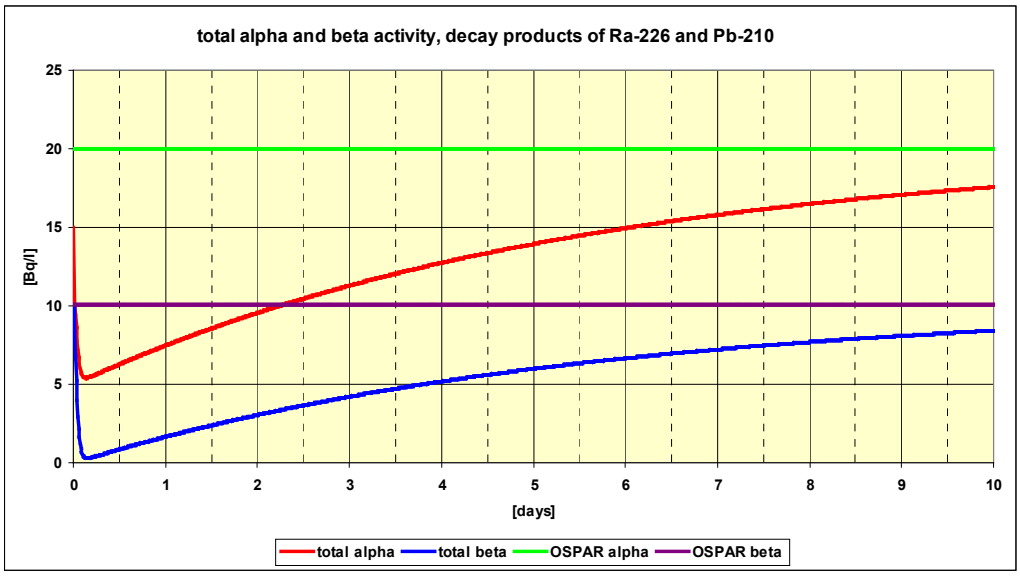


Figure 4: Same as Figure 2, but initially the short living radon decay products of 5 Bq/l are still being in the water phase.

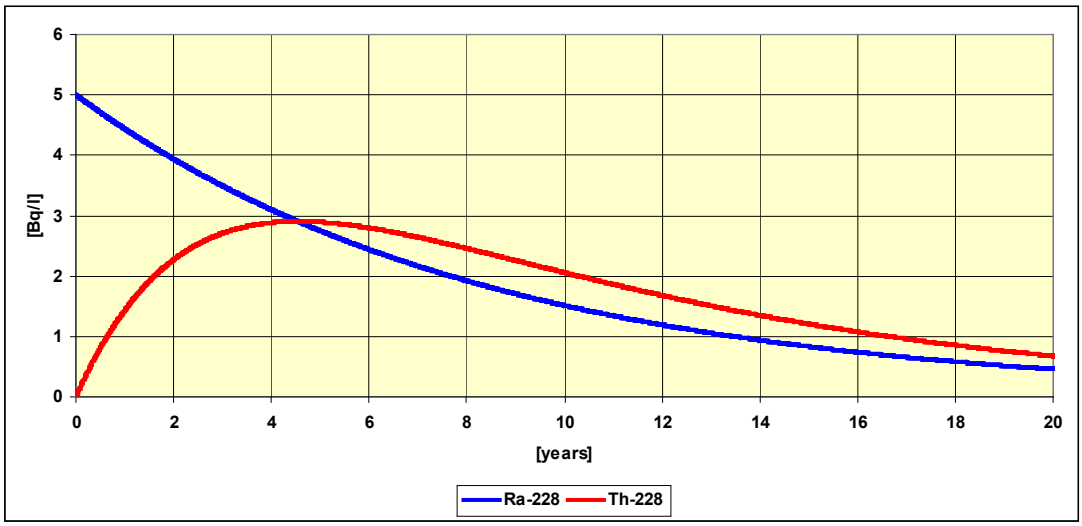
1.3.2 Ra-228 and decay products

In Table 3 the decay modes and half lives of the Ra-228 decay products originating from the Th-232 decay series are listed. It is important to note that it needs at least about 4 years to establish the secular equilibrium between Ra-228 and Th-228, since Th-228 is not abundant in the original produced water at all. However, when this time of about 4 years has been elapsed, the initial Ra-228 concentration is almost reduced by a factor of 2, since the half-life of Ra-228 is 5,8 years.
The respective results in Figure 5 show that the Th-228 activity concentration reaches only shortly after 4 years its maximum value. Afterwards the activity ratio Th-228/Ra-228 approaches quickly its asymptotic value of 1,5 given solely by the respective decay constants, whereas both activity concentration decay exponentially.

Table 3: Decay modes and half lives of Ra-228 decay

Radionuclide	decay mode	half life	decay time τ [y]	$\lambda=1/\tau$ [y^{-1}]
Ra-228	β	5,8 years	8,37	1,20E-01
Ac-228	β	6,15 hours	1,0E-3	9,87E+02
Th-228	α	1,9 years	2,74	3,65E-01
Ra-224	α	3,7 days	1,46E-02	6,84E+01
Rn-220	α	56 seconds	2,56E-06	3,90E+05
Po-216	α	0,15 seconds	6,86E-09	1,46E+08
Pb-212	β	11 hours	1,81E-03	5,52E+02
Bi-212	β (64%) α (36%)	61 minutes	1,67E-04	5,97E+03
Tl-208	β	3,1 minutes	8,51E-06	1,18E+05
Po-212	α	310 nanoseconds	8,51E-13	1,18E+12

Since all decay products of Th-228 are characterized by a half life of $\leq$ 3,7 days the resulting concentrations of the respective decay products follow closely that of Th-228. This specific behavior manifests also in the time evolution of the total alpha und beta activities illustrated in Figure 5. The results show that both activities reach a maximum value around 4,5 years for the alpha activity and around 2,5 years for the beta activity. However, both maximum values for the alpha and beta activity concentrations reflect a real situation only under specific boundary condition of keeping the produced water in a closed container for several years.



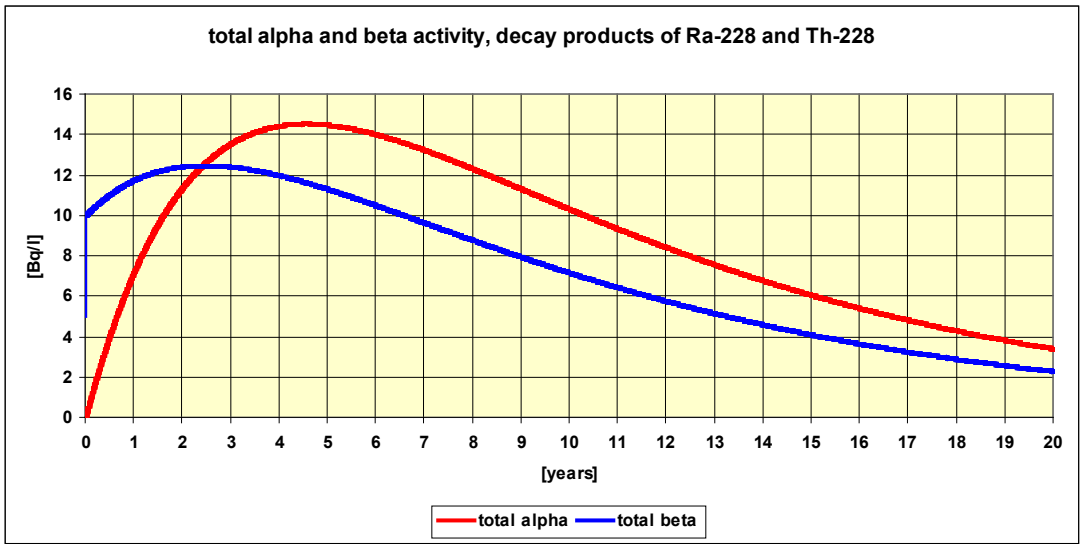
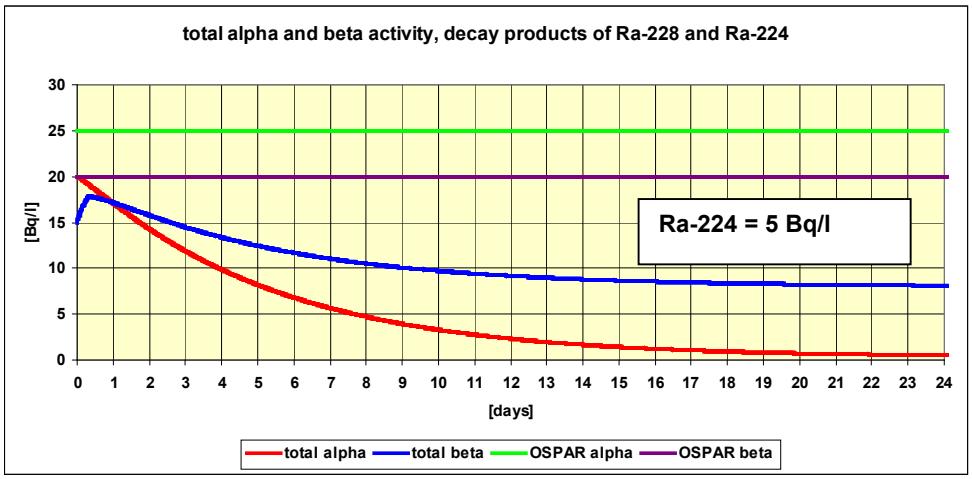
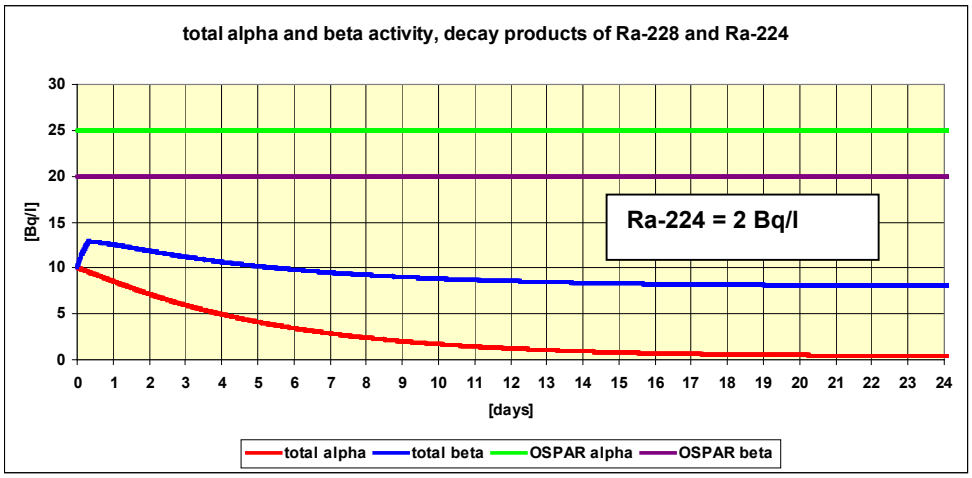


Figure 5: Time evolution of the Th-228 activity (upper panel) and of the alpha und beta activity (lower panel).
The initial concentrations are:
Ra-228 (t=0): 5 Bq/l and Th-228(t=0)=0.

The situation depicted in Figure 5 would change, when initially the activity concentrations of Ra-228 and Ra-224 together with its decay products have equally high activities. For this interesting case the resulting time evolution of the alpha and beta activities is shown in Figure 6. It can be seen, that the total alpha activity concentration decreases exponentially as Ra-224 does. So the particular result emerges, that the total alpha and beta activity concentrations are the smallest after about 1 month. Later on the respective activities would increase again due to the ingrowth of Th-228 and its daughters. As shown in Figure 5, the respective maximum values will be reached after around 4,5 years for the total alpha activity and at around 2,5 years for the total beta activity.
The time evolution of the total beta activities show a similar behavior, however they increase at the beginning a little bit due to the ingrowth of Ac-228 with a half life of 6,15 hours. The results will change with decreasing Ra-224 activity. In any case, as shown in Figure 6, the alpha and beta activity concentrations will differ most from the recommended values by OSPAR [1], when the Ra-224 concentration and its decay products are significantly smaller than that of Ra-228.





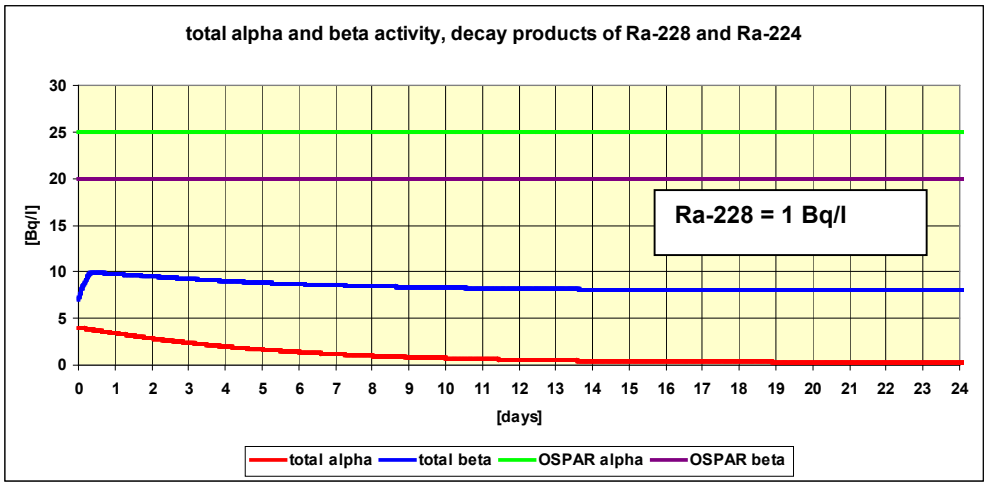
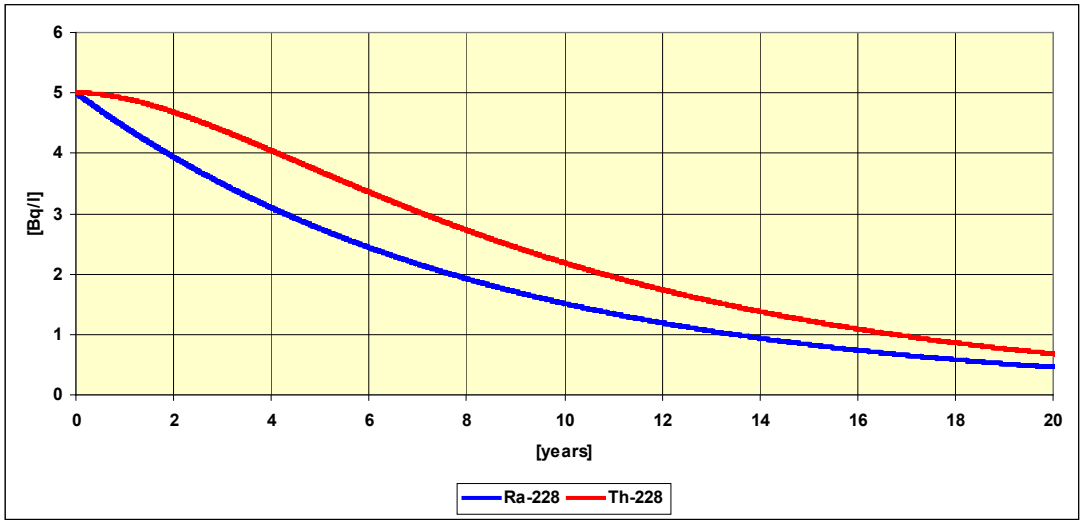
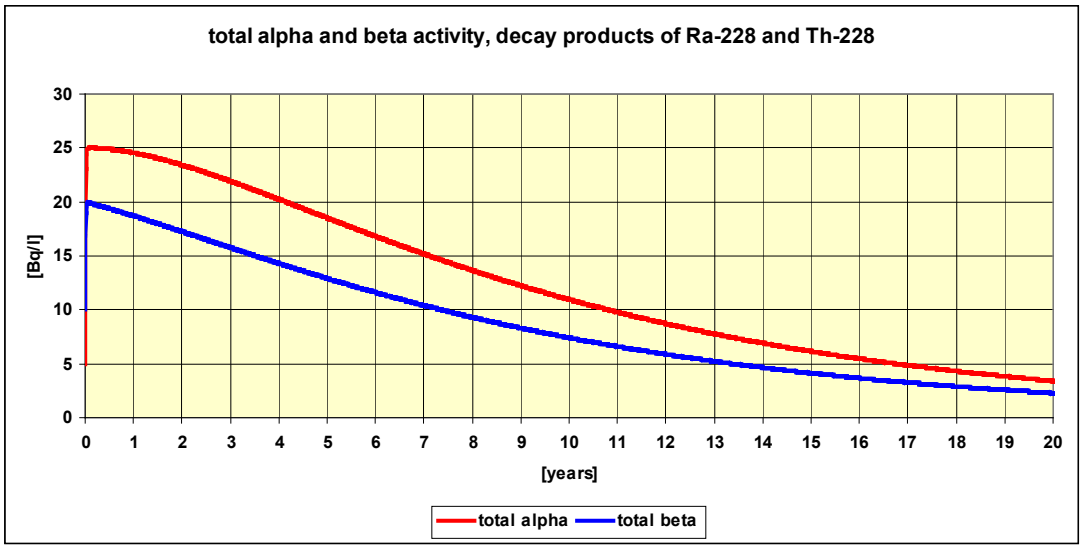


Figure 6: Same as Figure 5, however the activities of Ra-224 and its decay products are equal to 5, 2, 1 Bq/l. Also given are the respective estimates according to OSPAR [1].

The situation would also change significantly, if initially in the produced water the radionuclide Th-228 would be present to a large amount (s. Figure 7). The formula given by [1] is based on the assumption that initially the activity concentrations of Th-228 and all its decay products are in secular equilibrium with Ra-228. But this a hypothetical case that never happens and could therefore strongly overestimate the total alpha and beta activities. It is shown below by experimental analyses that there is practically no Th-228 present in the produced water at discharge (t=0).





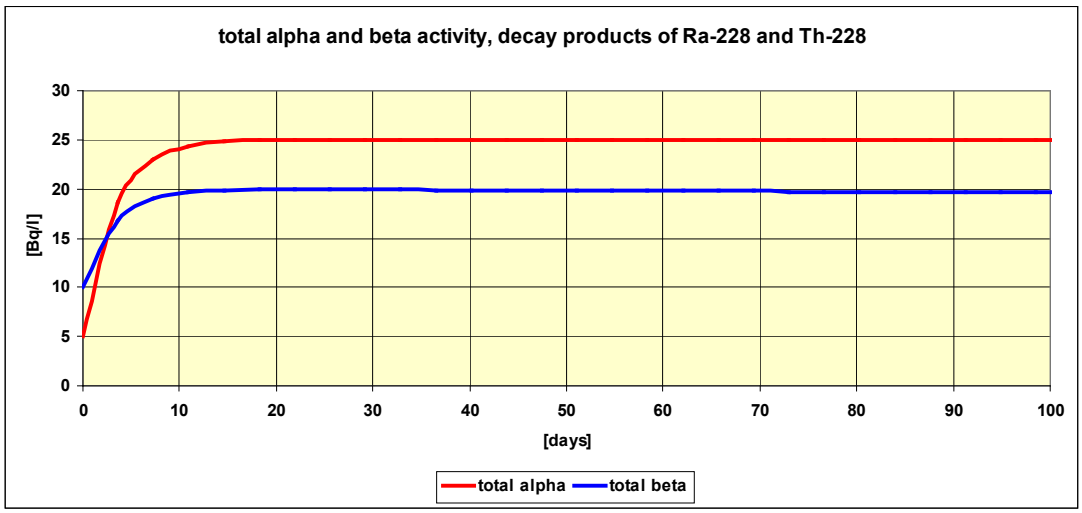


Figure 7: Same as Figure 5, however Th-228 (t=0)=Ra-228(t=0)=5 Bq/l

1.3.3 Total alpha and beta activity

According to [1] the total alpha activity in the produced water is given by (5xRa-228)+(4xRa-226)+(1xPb-210) and likewise for the total beta activity by (4xRa-228)+(2xRa-226)+(2xPb-210). This upper limit would be only reached if initially all the decay products of Ra-226, Ra-228 and Pb-210 are already in secular equilibrium with the respective parent nuclei. But this might be too conservative assumption. More realistic would be the case depicted in the Figure 8 at t=0. The total alpha activity and beta activity are the given by the initial activity concentration of Ra-226 and Ra-228. If the Pb-210 and the Ra-224 activities are not negligible, the resulting values for total alpha and beta activities have to be straightforwardly corrected. Nevertheless, the results suggest that the total alpha activity could be overestimated by using the recommended formula of [1] by almost one order of magnitude and by a factor of 6 for the beta activity.

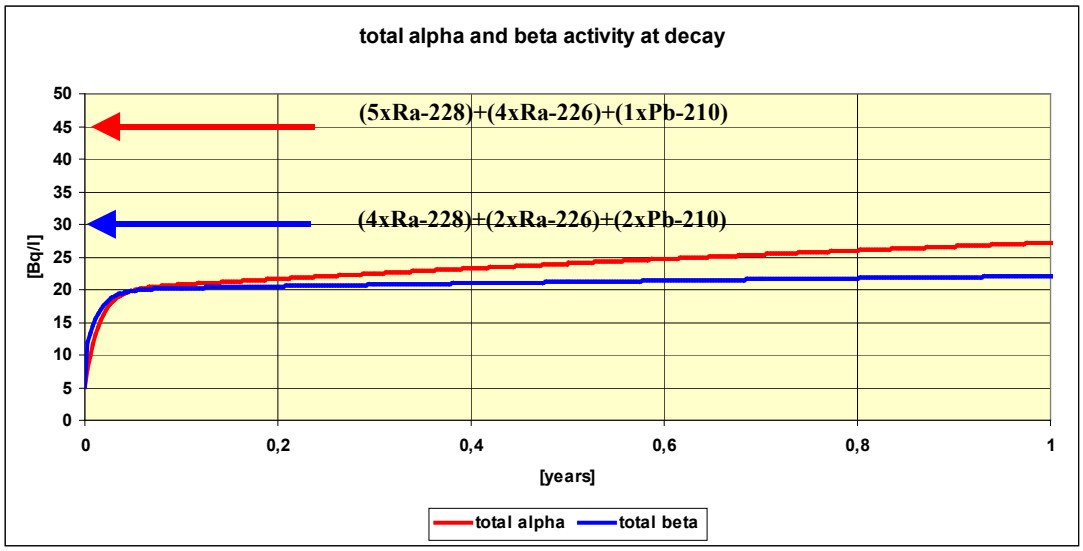


Figure 8: Time evolution of the total alpha and beta activity as a function of the elapsed decay for the first year. The initial concentrations are: Ra-226 (t=0) = 5 Bq/l, Ra-228(t=0)=5Bq/l, Pb-210(t=0)=20 mBq/l and Po-210(t=0)=10 mBq/l. The corresponding values according to the recommendation of [1] for the total alpha and beta activities (5xRa-228)+(4xRa-226)+(1xPb-210) and (4xRa-228)+(2xRa-226)+(2xPb-210) are indicated.

In Figure 9 the time evolution of the total alpha activity and beta activity are shown for 20 years. It is clearly seen that even for this unrealistic case the estimate recommended by [1] is still an upper bound, since the Ra-228 and likewise the Th-228 concentrations decay exponentially with increasing time, so that finally the corresponding curves will approach those given by Figure 3 for the alpha and beta decay of the Ra-226 and Pb-210 decay products belonging to the U-238 series. In other words, keeping the production water more than 50 years in a tightly closed container, then the alpha and beta activities are equal to those originating from the respective decays of the U-238 series.

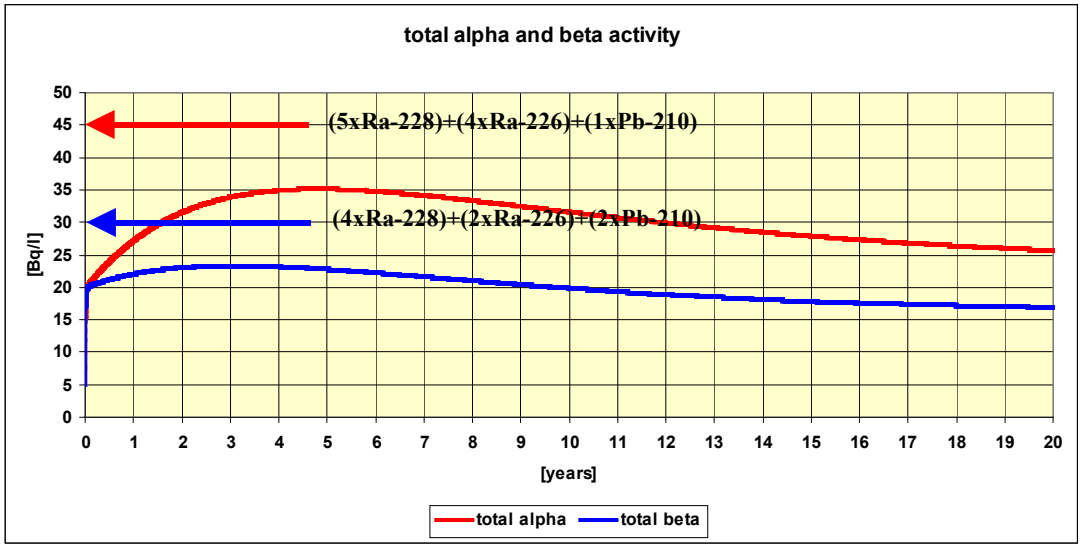


Figure 9: Same as Figure 8, however for the time evolution of 20 years.

2 Experimental Results and Discussion

2.1 Sampling and general results of the produced water

2.1.1 Sample locations

Ten installations were selected for sampling of produced water. The installations are spread along the Norwegian Continental Shelf (NCS) from Valhall and Ekofisk in the south North Sea Sector to Norne in the Norwegian Sea as shown in Figs. 8 - 11. The produced water samples were obtained from the following installations:

- Valhall (BP Norge AS)
- Ekofisk 2/4 J (ConocoPhillips Skandinavia AS)
- Varg (Talisman Energy Norge AS)
- Jotun A (ExxonMobil E&P Norge AS)
- Brage (Statoil Petroleum AS)
- Troll B (Statoil Petroleum AS)
- Troll C (Statoil Petroleum AS)
- Gullfaks C (Statoil Petroleum AS)
- Statfjord B (Statoil Petroleum AS)
- Norne (Statoil Petroleum AS)

Data on annual produced water discharges (m^3) for the installations for 2011 are given in Table 4. Other relevant information are available in Facts 2012 (www.npd.no).

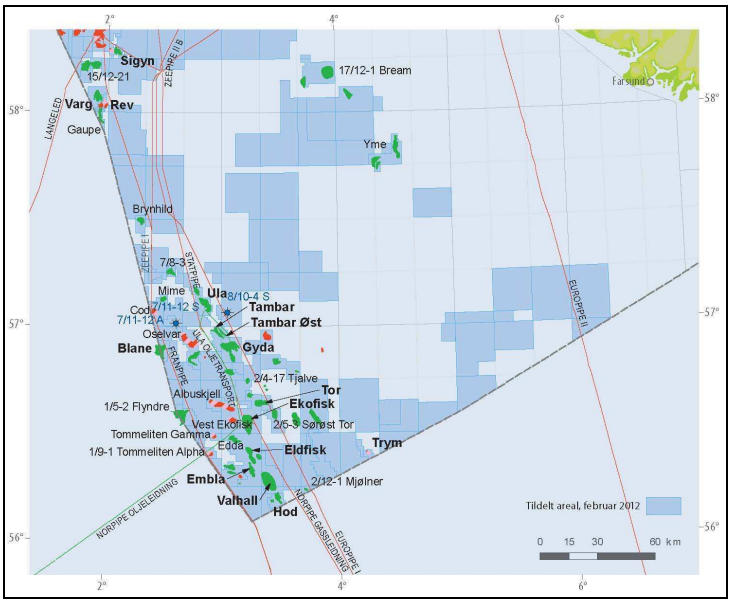


Figure 10: Map over the Norwegian North Sea South Sector showing Valhall, Ekofisk and Varg. (Map from Facts 2012, www.npd.no)

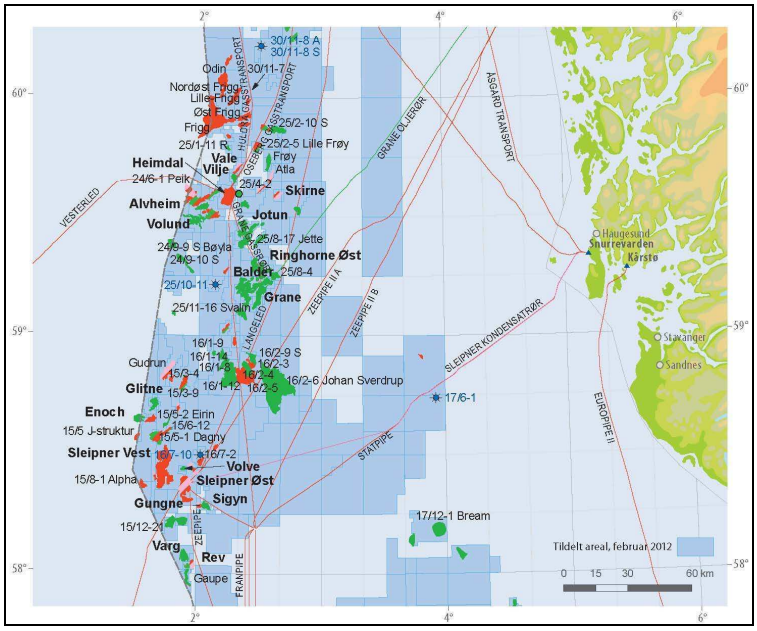


Figure 11: Map over the Norwegian North Sea Middle Sector showing Varg and Jotun. (Map from Facts 2012, www.npd.no)

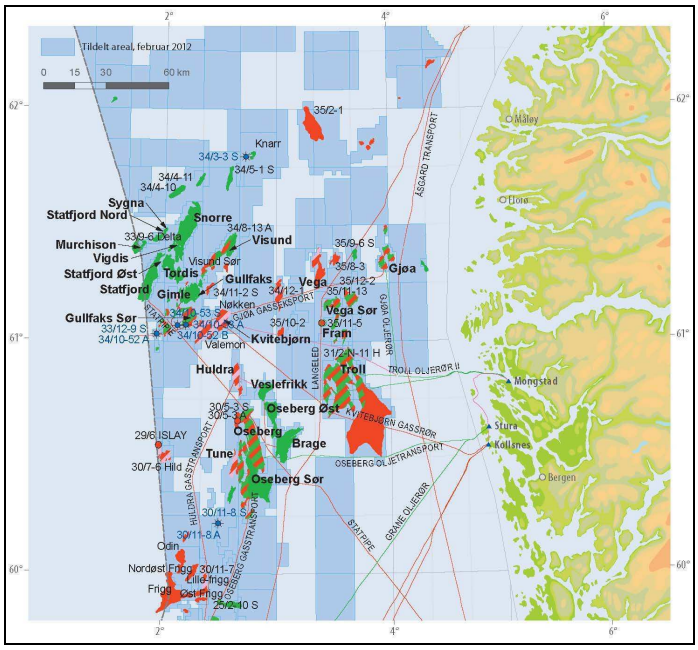


Figure 12: Map over the Norwegian North Sea North Sector showing Brage, Troll Gullfaks and Statfjord. (Map from Facts 2012, www.npd.no)

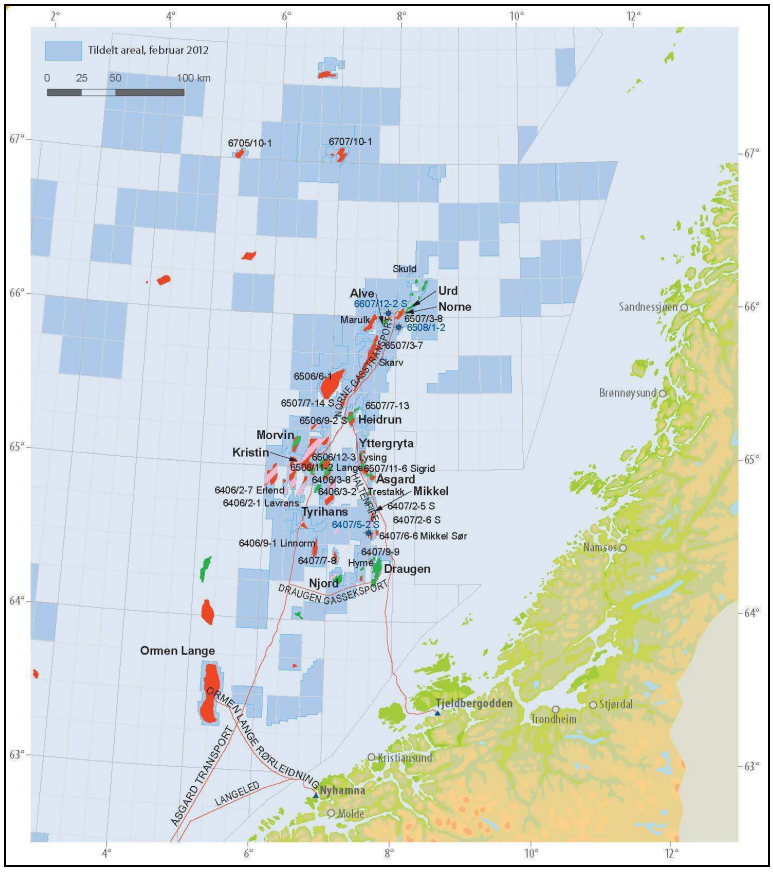


Figure 13: Map over the fields in the Norwegian Sea showing Norne. (Map from Facts 2012, www.npd.no)

2.1.2 Sampling method

Sample containers (2 × 2 litre plastic bottles) were sent to the installations. The samples were taken on each installation at the same sample point that is used for the ordinary monitoring samples. For most installations the sampling point is at or close to the Produced Water Degassing Tank. At this point no further treatment of the produced water is performed and the water is directly discharged to the sea. The bottles were filled completely to avoid unnecessary airspace at a time as close to transportation to land as possible. There were taken 2 samples at each installation with at least 15 minutes interval between the samples.
The samples were transported as quickly as practically possible to the laboratory. The transport from installation to laboratory usually took 3 - 6 days mostly depending on the transport method from installation to shore – helicopter or ship.

Together with the samples a few parameters were recorded:

- Sampling date and time (decay and ingrowth calculations)
- pH
- Conductivity
- Temperature
- Visual appearance (clear - milky)

The data are given in Table 5.

2.1.3 Produced water releases 2011

In Table 4 the produced water volumes for each installation in 2011 are given. As shown the produced water volumes vary from 0.3 million m^3 (Valhall) to almost 10 million m^3 (Troll B) contribution to 0.3 % to 7.6 %, respectively, of the total release of produced water on the Norwegian Continental Shelf. The installations contributing in this study represent 38.6 % (49.8 million m^3) of the total produced water releases on the NCS.

Table 4: Releases of produced water and radioactivity in 2011 from the installations in this study. Volumes in 10^6 m^3 , radioactivity data in giga Bequerel and the relative contribution to the total release on the Norwegian Continental Shelf (NCS) in % (brackets to the right).

Installation	**PW release 2011 (10^6 m^3)**	**Ra-226 (GBq)**	**Ra-228 (GBq)**	**Pb-210 (GBq)**
Troll B	9.849 (7.6)	99.4 (22.0)	86.6 (24.3)	3.5 (9.9)
Troll C	7.910 (6.1)	90.3 (20.0)	63.7 (17.9)	3.0 (8.5)
Statfjord B	6.623 (5.1)	5.0 (1.1)	2.6 (0.7)	2.7 (7.6)
Gullfaks C	3.466 (2.7)	16.8 (3.7)	14.7 (4.2)	1.7 (4.7)
Norne	8.544 (6.6)	6.8 (1.5)	7.5 (2.1)	1.5 (4.1)
Brage	3.941 (3.1)	36.0 (8.0)	31.4 (8.8)	1.6 (4.4)
Jotun A	1.563 (1.2)	10.2 (2.3)	10.7 (3.0)	0.6 (1.6)
Valhall	0.326 (0.3)	0.9 (0.2)	0.5 (0.1)	0.2 (0.6)
Ekofisk 2/4 J	7.065 (5.5)	8.5 (1.9)	2.8 (0.8)	2.2 (6.1)
Varg	0.500 (0.4)	3.2 (0.7)	1.9 (0.5)	0.4 (1.0)
Sum (study)	**49.788 (38.6%)**	**277.1 (61.4%)**	**222.4 (62.4%)**	**17.2 (48.6%)**
Total NCS	**129.000**	**451.3**	**356.2**	**35.4**

With respect to radioactivity, the 10 installations in this study represent more than 60 % of the total releases of radium in 2011. The two Troll installations alone, Troll B and Troll C, actually counts for 42.0 % of the Ra-226 releases on the NCS.
The reported releases for Pb-210 should not be given too much attention as all, or nearly all, releases of radioactive lead are based on estimates due to lesser than detection limit values.

2.1.4 Produced water general characteristics

General characteristics for the produced water from the 10 installations are given in Table 5. The characteristics is not specifically discussed in the context of this study, but is pointed out that the samples of produced water has a near neutral pH, a conductivity indicating a fairly high salinity (sea water conductivity 54 mS/cm) and elevated temperatures.

Table 5: Produced water general characteristics

Installation	Sampling Date	pH	Condensate	Temperature	Visual
			mS/cm	°C	
Troll B	25.07.12	6,71	70	40	Clear
Troll C	25.07.12	6,58	15,5	46,8	Clear
Statfjord B	17.07.12	7	45	70	Milky
Gullfaks C	20.07.12	6,92	47,4	69	Clear
Norne	13.07.12	6,8	59,5	61,5	Milky
Brage	06.08.12	6,68	na	81	Clear
Varg	17.07.12	7	na	83	Clear
Valhall	19.07.12	6,7	na	30,5	Clear
Ekofisk 2/4 J	21.08.12	6,5	33,4	23,7	Clear
Jotun A	19.07.12	6,3	na	47	Milky

2.2 Results and discussion

2.2.1 Specific activities of the radionuclides

The experimental results of the specific activities for the relevant radionuclides U-238, U-234, Ra-226, Pb-210, Po-210, Ra-228, Th-228 are collected in Table 6. The radionuclides U-238 and U-234 have been measured by alpha spectrometry. The detection limit was about 1 mBq/l. The experimental findings suggest that the uranium concentrations are almost negligibly small compared to those of Ra-226. The maximum concentration was only 30 mBq/l for U-234. Since the uranium concentrations are rather low, no further conclusion can be drawn about the activity ratio of U-2348/U-238 being for ordinary ground waters often significantly larger than 1.

The Ra-226 concentrations vary in a wider range from 0,5 to 10 Bq/l. The measured Rn-222 activity concentrations are comparable to those originating from the ingrowth since the moment of sampling until the time where the measurement begun in the laboratory. This means, that due to the separation process of oil and water at the platform the originally existing Radon has been nearly completely stripped out, so that the Rn-222 concentration at the sampling moment of the production water is almost negligible small compared to that of Ra-226. This has, as shown in chapter 1.3 in detail, far reaching consequences for the estimate of the de facto actual existing alpha and beta activities at the time point of sampling (see chapter 2.1.3).

It is also worthwhile to note, that the Pb-210 and Po-210 activity concentrations are negligibly small compared to those of radium. For Pb-210 only in a single case a small value of 30 mBq/l has been measured. In all the other cases only detection

limits of mostly < 20 mBq/l have been derived. This concerns also Po-210, but in most cases the detection limit was only 1 mBq/l.
Due to high quantification levels in ordinary produced water analyses, Pb-210 is most often reported as either equal to the quantification limit or equal to half of the quantification limit – typically in the range of 0.5 - 1.0 Bq/liter. Compared to the real level this means an over-reporting by at least an order of magnitude.
The Ra-228 activity concentrations follow very closely those of Ra-226 as illustrated by the results in Figure 14. Only in few cases the deviations are in the range of about 1 Bq/l. This implies that according to the general statements given in Chapter 1.3 the alpha and beta activities will also be almost equal to each other (cf. discussion in Chapter 2.1.3).

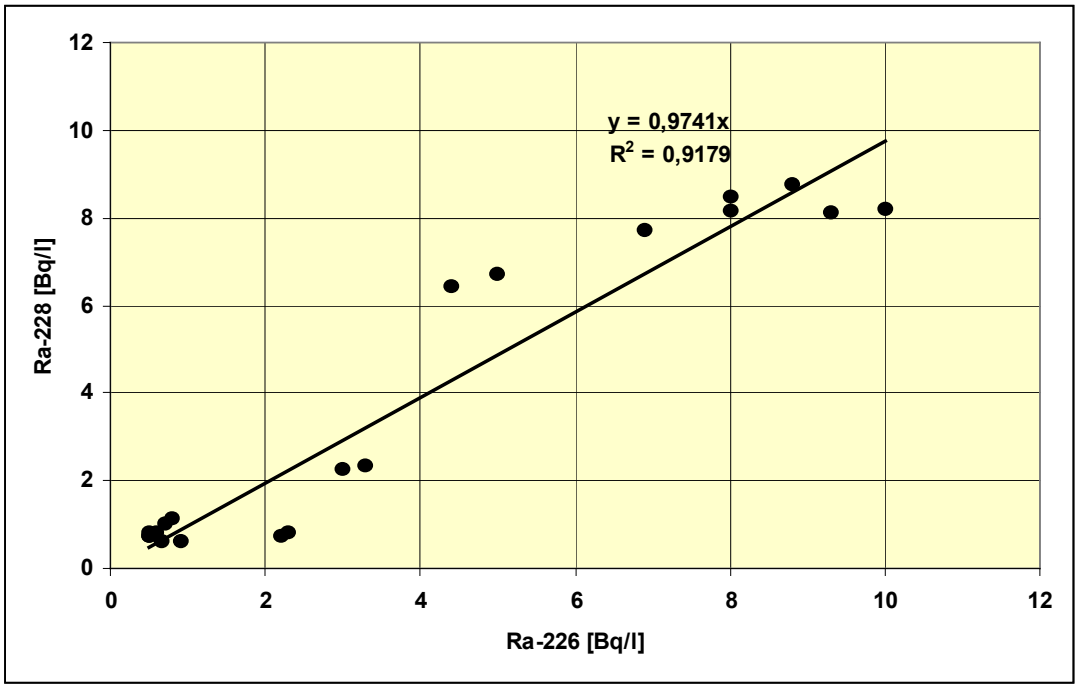


Figure 14: Ra-226 activity concentration versus that of Ra-228

One has to note that for Th-228 only fairly low detection limits could be given in Table 6. Even in the cases, where the Ra-228 concentrations were equal or above 5 Bq/l, no indications of Th-228 activity have been found. As expected, there is practically no Th-228 activity in the production water at all. The Th-228 activity generated since the time elapsed from the sampling until the measurements in the laboratory, is about 35 mBq/l for an initial Ra-228 activity concentration of 5 Bq/l after 7 days ingrowth time. In order to find out, to what very small extent Th-228 is in the production water after the separation process, we had to refine the experimental methods and/or to enlarge the water volume. However, for a more accurate measurement of the total alpha and beta activities such a refinement is not necessary.
It is not excluded that in some cases the Ra-224 activity at the point of discharge could even be comparable to that of Ra-226. However, since the respective time spans between the sampling and measurement were typically larger than 4 half lives of Ra-224, in the present study no special attention has been paid to the Ra-224 determination.

Table 6: Specific activities of the relevant radionuclides

Installation		**Specific activity (Bq/liter)**							
		U-238	U-234	Ra-226	Rn-222	Pb-210	Po-210	Ra-228	Th-228
Troll B	A	< 0.001	0.003 ± 0.001	8.0 ± 1.0	3.9 ± 0.3	< 0.15	< 0.001	8.0 ± 1.0	< 0.18
	B	< 0.001	0.004 ± 0.002	8.0 ± 1.0	4.0 ± 0.3	< 0.15	0.002 ± 0.001	8.3 ± 1.0	< 0.18
Troll C	A	0.003 ± 0.001	0.003 ± 0.001	9.3 ± 0.9	5.0 ± 0.3	< 0.1	< 0.001	8.0 ± 0.8	< 0.15
	B	< 0.001	< 0.001	10 ± 1.0	5.3 ± 0.4	< 0.1	0.002 ± 0.001	8.1 ± 0.8	< 0.12
Statfjord B	A	0.002 ± 0.001	0.005 ± 0.002	0.5 ± 0.1	0.3 ± 0.1	< 0.02	< 0.001	0.8 ± 0.2	< 0.01
	B	< 0.002	< 0.004	0.5 ± 0.1	0.3 ± 0.1	< 0.02	< 0.001	0.7 ± 0.2	< 0.02
Gullfaks C	A	< 0.002	< 0.002	0.6 ± 0.2	0.4 ± 0.2	< 0.02	< 0.001	0.8 ± 0.2	< 0.03
	B	< 0.002	0.002 ± 0.001	0.5 ± 0.1	0.4 ± 0.2	< 0.03	< 0.001	0.7 ± 0.2	< 0.02
Norne	A	< 0.001	0.002 ± 0.001	0.8 ± 0.2	0.5 ± 0.1	< 0.02	< 0.001	1.1 ± 0.2	< 0.03
	B	0.002 ± 0.001	< 0.002	0.7 ± 0.2	0.5 ± 0.1	< 0.02	0.002 ± 0.001	1.0 ± 0.2	< 0.05
Brage	A	< 0.001	< 0.001	6.9 ± 1.5	3.0 ± 0.3	< 0.20	< 0.001	7.5 ± 0.9	< 0.12
	B	< 0.001	0.002 ± 0.001	8.8 ± 1.2	3.6 ± 0.3	< 0.03	< 0.002	8.7 ± 0.9	< 0.10
Varg	A	< 0.001	0.002 ± 0.001	3.3 ± 0.3	2.3 ± 0.2	< 0.03	< 0.002	2.3 ± 0.3	< 0.04
	B	< 0.001	< 0.001	3.0 ± 0.3	2.3 ± 0.2	0.03 ± 0.01	0.005 ± 0.002	2.2 ± 0.3	< 0.03
Valhall	A	< 0.002	< 0.002	2.2 ± 0.3	1.8 ± 0.2	< 0.02	< 0.002	0.7 ± 0.2	< 0.02
	B	< 0.002	< 0.002	2.3 ± 0.3	1.8 ± 0.2	< 0.02	< 0.002	0.8 ± 0.2	< 0.02
Ekofisk 2/4 J	A	< 0.03	< 0.03	0.65 ± 0.15	0.55 ± 0.15	< 0.02	< 0.001	0.5 ± 0.2	< 0.20
	B	< 0.03	< 0.03	0.9 ± 0.4	0.8 ± 0.2	< 0.02	< 0.001	0.5 ± 0.2	< 0.20
Jotun A	A	0.027 ± 0.006	0.030 ± 0.008	5.0 ± 0.8	3.1 ± 0.3	< 0.02	< 0.001	6.7 ± 0.7	< 0.12
	B	< 0.001	< 0.001	4.4 ± 0.6	2.9 ± 0.3	< 0.03	< 0.001	6.4 ± 0.6	< 0.10

2.2.2 Total alpha and beta activities

The measurements of the total alpha and beta activities in the production water have been done with alpha spectrometry and low level liquid scintillation techniques, respectively. The respective results are collected in Table 7 for the different installations. Since the total alpha and beta activities were measured typically 10 - 15 days after sampling, the still at this moment eventually existing short living decay products giving rise to the total alpha or beta activity could not be accounted for. Moreover, since the activity concentrations of the key radionuclide Ra-226 and Ra-228 are nearly equal and the contributions from relevant daughter decay products of the two parent nuclei are de facto not present in the compound prepared for the measurement, the resulting resulting alpha and beta activities are also nearly equal. This can be seen from the correlation diagram shown in Figure 15. The nearly perfect correlation between the alpha and beta activity is practically the same as that for the two radium nuclides Ra-226 and Ra-228 shown in Figure 14. In order to achieve a fair estimate of the relevance of the short living decay products at the moment of discharge, the respective alpha and beta measurement have either to be done shortly after sampling or the results measured in the laboratory have to be related to the moment of sampling by utilizing elaborated models including, for instance, the solubility and the transport of thorium, lead and polonium in the water phase.

Table 7: The total alpha and beta activities at the measurement time

Installation		Total α-activity	Total β-activity
Troll B	A	8.0 ± 1.5	8.0 ± 1.5
	B	8.2 ± 1.5	8.5 ± 1.5
Troll C	A	9.3 ± 1.8	8.1 ± 0.9
	B	10.0 ± 2.0	8.2 ± 0.9
Statfjord B	A	0.5 ± 0.1	0.8 ± 0.2
	B	0.5 ± 0.1	0.7 ± 0.2
Gullfaks C	A	0.6 ± 0.1	0.8 ± 0.2
	B	0.5 ± 0.1	0.7 ± 0.2
Norne	A	0.8 ± 0.2	1.1 ± 0.2
	B	0,7 ± 0.2	1.0 ± 0.2
Brage	A	6.9 ± 1.5	7.7 ± 1.1
	B	8.8 ± 1.2	8.7 ± 0.9
Varg	A	3.3 ± 0.3	2.3 ± 0.3
	B	3.0 ± 0.3	2.2 ± 0.3
Valhall	A	2.2 ± 0.3	0.7 ± 0.2
	B	2.3 ± 0.3	0.8 ± 0.2
Ekofisk 2/4 J	A	0.7 ± 0.2	0.6 ± 0.2
	B	1.0 ± 0.4	0.6 ± 0.2
Jotun A	A	5.1 ± 0.8	6.7 ± 0.7

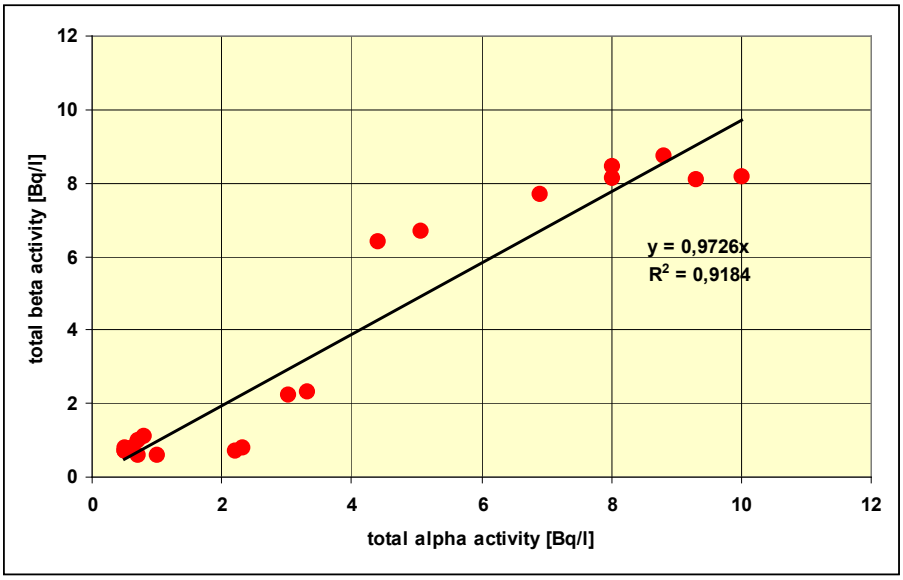


Figure 15: The total alpha versus total beta activity

It is worthwhile to note, that the sample compound prepared for the alpha and beta measurements do practically not contain any Rn-222. However, how big the fraction of the still existing progenies is, depends on the several circumstances. A key quantity is the for instance the time duration from the separation until the moment of discharge. In this respect the samples prepared for the measurement in the laboratory may not reflect the same situation as the samples taken at the platform.
However, despite the fact that there is practically no Th-228 activity in the sample, the inevitable ingrowth of the respective Th-228 decay products leads to additional alpha and beta activities not present at the beginning in the original sample just taken after finishing the separation of oil from water at the platform.
The best way of avoiding these unwanted effects is to begin the measurements right after the samples have reached the laboratory, whereby the time spans between sampling and measurements have to be kept as short as possible. Otherwise one has to correct for the contribution of the ingrowth of the respective decay products. The latter one can be accomplished by combining the results of the alpha and beta measurements with those of the single radionuclide measurements made by utilizing gamma spectroscopy. Concerning the beta activity the contribution of K-40 has in any case to be subtracted. In case that Rn-222 will not be pushed out during the oil-water separation process the above formula have to be changed according to the reasoning outlined in Chapter 1.3.
Our experience from many others cases show, that Th-228 is a poorly soluble compound at pH values above 4 and therefore not present in the production water phase at all. But Th-228 may well be contained in finest particle admixtures in secular equilibrium with Ra-228 within the oil-water mixture before separation.
It is also not excluded, that in the originally production water Ra-224 and its decay products are contained in a non-neglecting fraction. In order to quantify their contribution to the total alpha and beta activities the respective measurements have to be done shortly (less than 3 days) after the sampling.

3 The total alpha and beta release

According to the results given in Tables 6 and 7 the total alpha and beta activity release due to the discharge of production water is given in Table 8. In the table measured total alpha and total beta activities are compared with the corresponding total alpha and total beta activities using the "OSPAR formulas" (Ch. 1.3.3). It is clearly seen that the measured total alpha and total beta concentrations are almost an order of magnitude lower than the calculated ones: 88.7 % and 83.3 %, respectively.

Table 8: The total alpha and beta activity release

Installation	**Produced water release 2011 (m^3)**	**Measured activity (Bq/liter)I**		**Calculated activity (Bq/liter)**		**Measured Release (GBq)**		**Calculated Release (GBq)**		**Difference (%)**	
		Total α	Total β	Total α	Total β	Total α	Total β	Total α	Total β	Total α	Total β
Troll B	9 849 219	8.1	8.3	72.8	48.8	88.9	81.3	717.3	480.1	88.9	83.1
Troll C	7 909 804	9.7	8.2	78.9	51.6	87.8	64.5	624.1	408.1	87.8	84.2
Statfjord B	11 630 495	0.5	0.8	5.8	4.0	91.3	8.7	67.0	46.8	91.3	81.3
Gullfaks C	3 465 591	0.6	0.8	6.0	4.1	90.8	2.6	20.7	14.3	90.8	81.8
Norne	8 549 488	0.8	1.1	8.3	5.7	90.9	9.0	70.6	48.9	90.9	81.6
Brage	3 941 453	7.9	8.2	71.9	48.1	89.1	32.3	283.4	189.7	89.1	83.0
Varg	498 983	3.2	2.3	23.9	15.4	86.8	1.1	11.9	7.7	86.8	85.4
Valhall	326 241	2.3	0.8	12.8	7.5	82.4	0.2	4.2	2.5	82.4	90.0
Ekofisk 2/4 J	7 065 149	0.9	0.6	5.6	3.6	84.9	4.2	39.6	25.2	84.9	83.2
Jotun A	1 562 782	4.8	6.6	51.6	35.6	90.8	10.2	80.6	55.7	90.8	81.6
Sum activity/Mean difference						**216.9**	**214.2**	**1919.4**	**1278.9**	**88.7**	**83.3**

4 Recommendations for produced water sampling programme

The results in this study show that the two radium isotopes, Ra-226 and Ra-228, are the only radionuclides present in significant amounts in the produced water released from installations on the NCS. Both radium nuclides are practically not accompanied with the respective daughter nuclei. Therefore, only these two nuclides contributes to the quantification of radioactive release. It is however also important to document the non-presence of the other relevant nuclides.
The difference in analytical effort between a Ra-226 and Ra-228 determination performed by means of gamma analysis and an analysis determining also the radium daughters at low level, is large and the cost difference likewise. It is therefore suggested that a possible future monitoring programme should largely consist of a main bulk of straightforward Ra-226 and Ra-228 analysis supported by full scale analyses on specific samples at less frequent intervals of maybe one or two samples per year. This latter analysis will give better quantification of the level of Pb-210 that usually is not quantified through the ordinary analyses. It should be noted that the sampling method and transport of the full scale analyses will be different from the ordinary monitoring samples.

5 Summary and conclusion

This study comprises results from produced water samples from 10 installations representing 38.6 % of the total releases of produced water on the Norwegian Continental Shelf. The produced water samples have been analysed with respect to the relevant individual radionuclides (parent and daughter nuclei) utilizing low-level alpha- and gamma spectrometry and low level beta measurements. In addition the total alpha and total beta activities have been determined.
The results can be concluded as follows:

1. As the produced water is released, only Ra-226 and Ra-228 are present in significant amounts. All the daughter nuclei do practically play no role, since respective secular equilibrium stages are not reached.
2. Due to the apparent radioactive non-equilibrium the total activity releases as they are reported in OSPAR [1] are almost an order of magnitude higher than the actual releases as e.g. determined by total alpha and total beta analysis.
3. The level of Pb-210 is documented to be at least an order of magnitude lower than what is usually reported.

6 References

[1] OSPAR 2009. OSPAR Commission. RSC 09/3/2 Add.1-E (L). Assessment of the Liquid Radioactive Discharges from Non-Nuclear Sub-sectors in 2007. OSPAR Convention of the Protection of the Marine Environment of the North-East Atlantic. Meeting of the Radioactive Substances Committee (RSC), Oslo (Norway), 19-23 January 2009.