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Changes in speciation and kinetics of Po-210 in produced water from oil industry when it is mixed with seawater

Valeriya Mekhonina
Master of Science in Radioecology

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Valeriya Mekhonina

LIST OF ABBREVIATIONS

CERAD – Centre for Environmental Radioactivity

DTPA – Diethylenetriamine-pentaacetic acid

LMM – Low molecular mass

NCS – Norwegian continental shelf

NMBU – Norwegian University of Life Sciences

NORM – Naturally occurring radioactive materials

PW – Produced water

ROI – Region of interest

SW – Seawater

TDS – Total dissolved solids

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ABSTRACT

Petroleum production on the Norwegian continental shelf is accompanied by the production of the largest by volume waste stream called *produced water*. Produced water discharged to the North Sea can contain elevated level of naturally occurring radionuclides (Ra-228, Ra-226, Po-210) causing concerns over its long-term effects on marine biota. However, to represent ecological risk the radionuclides in produced water should be available for biological uptake by marine biota. Biological uptake of radionuclides is determined by *speciation* or *physico-chemicals* forms of radionuclides. Radionuclides associated with low molecular mass species (LMM) are available for active uptake; radionuclides present as particles and colloids are usually biologically inert although could be available for passive uptake. Studies on speciation of the radionuclides present in produced water are limited and have been mainly focused on Ra-226. Speciation of Po-210, which is the major contributor to the radiation dose to marine organisms and humans via seafood, in the marine environment remains poorly studied and almost nothing is known about its speciation in produced water. Therefore, it seemed obvious to undertake a study that could somewhat fill this gap. Thus, a major objective of the present work was to characterize produced water from the oil-producing platform Troll C with respect to polonium size speciation and to study how polonium speciation might change with time after mixing with seawater. The results indicated that produced water from Troll C contained elevated level of Po-210 amounted to 0.0612 Bq/l. Size fractionation of the produced water shown that more than 90% of Po-210 in the produced water was present as particles. Size fractionation of mixtures of produced water with seawater indicated that polonium speciation changed to some extent after 24 hours and 1 month of mixing, however in both cases the particulate Po-210 was still dominant over the colloidal and LMM species fractions. Although, seawater did not contribute to substantial solubilization of the particulate Po-210 neither 24 hours nor 1 month after mixing, it should be noted that a small fraction of the particulate Po-210 was mobilized just in the first 24 hours of mixing and no mobilization was observed after 1 month in seawater. Moreover, the LMM species fraction of Po-210 had a tendency to decrease with time. These things could be important with respect to time period when Po-210 might be most bioavailable for marine biota upon discharge. Overall, it could be concluded that seawater did not contribute to solubilization of the particulate Po to the extant that we expected suggesting that there were other factors responsible for Po dissolution, for example, anoxic conditions. Finally, it is important to note that the produced water was fractionated a few months after sampling, therefore some changes in Po speciation might had already occurred. We think that fractionation should be performed immediately after the produced water has been brought to the surface from the well while storage effects do not change Po speciation. This can be done only on the platform.

Keywords: offshore oil industry, produced water, Po-210, speciation, kinetics, seawater

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1. INTRODUCTION

In 2012, Norway was ranked the third largest gas exporter and the tenth largest oil exporter in the world (MPE, 2014). The petroleum activity accounts for almost one-third of the State's total revenues, what makes the industry highly important for the Norwegian economy and supporting the Norwegian welfare state (MPE, 2014). However, the production of oil and gas on the Norwegian continental shelf (NCS), may affect the environment, in particular continental shelf ecosystem, the most biologically productive area of the ocean as well as an important source of seafood. One of the causes for concern is associated with continuing discharges of *produced water (PW)* from the Norwegian platforms and its long-term effects (NPD, 2009).

Produced water is water extracted from the well together with oil and gas during production and represents the largest waste stream by volume in oil and gas production operations (Neff et al., 2011). In 2015, the total discharges of produced water on the NCS were 148 million m^3 (NOROG, 2016). Produced water is a complex mixture that includes oil, dissolved hydrocarbons, organic acids, inorganic ions, heavy metals that are toxic to marine biota at high concentrations (Neff et al., 2011). However, the potential toxicological impact of produced water is not the only reason to worry. Produced water contains naturally occurring radioactive materials (NORM) (Ra-226, Ra-228, Pb-210 and Po-210), which are discharged with it into the sea. This causes concerns over the potential radiological impacts of produced water on marine biota and human health.

Radium isotopes (Ra-226, Ra-228) comprise over 90% of the total radioactivity of produced water (Snavely, 1989). Moreover, the activity concentrations of these radionuclides in produced water are often significantly higher compared to the natural background (NRPA, 2004). However, Po-210 in produced water is recognized the most important radionuclide with respect to potential environmental impact and doses to human (Simmonds et al., 2003). This is likely due to its biomagnification along marine food chains (Kristan et al., 2015). Po-210 is effectively accumulated by marine organisms and is the major contributor to the radiation dose received by humans via seafood consumption (Wildgust et al., 1999). In 2000 the contribution of Po-210 to the collective dose rate received by the European Union population was 82% of the total with Ra-228 giving 11%, Ra-226 6% and Pb-210 1% (Simmonds et al., 2003). The contribution of the anthropogenic radionuclides is considered to be negligible (Wildgust et al., 1999). For example, concentrations of plutonium isotopes in fish will add less than 0.01% to the dose delivered by Po-210 to consumers (Carvalho et al., 2011). According to the MARINA II study (MARINA II, 2002), oil production is the major contributor to the collective dose to the population of the European Union.

The main source of naturally occurring Po-210 in the sea is *in situ* production from the decay of Pb-210 via Bi-210 (Cherrry and Heyraud, 1988 cited by NRPA, 2004). Besides, Po-210 comes to the sea from direct discharges of this radionuclide and from the decay following discharges of Ra-226 and Pb-210 (Simmonds et al., 2003). It has been estimated that even if discharges continue until 2020 at 2000 discharge rates, the collective dose rates will still increase (Simmonds et al., 2003). This is because of the ingrowth of Po-210 from the earlier discharges of Ra-226 and Pb-210 (Simmonds et al., 2003). Taking into account a contribution of Po-210 from the decay of Ra-226, radium content in produced water is of importance.

Thus, produced water discharges contribute to the release of natural radionuclides to the marine environment what increases potential for unwanted exposure to marine animals themselves and humans via marine food. The problem is that the long-term effects of the radionuclides present in produced water on marine ecosystem remain unclear.

In order to assess the long-term effects of produced water discharges, it is required to understand the behavior of the radionuclides after they enter the sea. The behavior is determined by *physico-chemical forms* or *speciation* of the radionuclides.

Salbu (2007) highlights that radionuclides may exist in different physico-chemical forms such as particles having diameters larger than 0.45 µm, colloids ranging in size from 1 nm to 0.45 µm, low molecular mass (LMM) species in size less than 1 nm. The gist of it is that the behavior of the radionuclides, particularly biological uptake and accumulation of the radionuclides is determined by their physico-chemical forms (Salbu, 2007). Radionuclides present as LMM species are available for active uptake; radionuclides present as particles and colloids are considered biologically inert, however they are of importance with respect to passive uptake (Salbu, 2007). Therefore, in order to determine whether radionuclides present in produced water represent ecological risk to marine biota, it is essential to know what radionuclide species are present in the produced water. It has been truly stated that this information cannot be obtained from the measurements of total concentration of radionuclides in the environment (Salbu and Skipperud, 2009). This information can be obtained from speciation analysis.

According to Salbu and Skipperud (2009), physico-chemical forms may change with time due to transformation processes caused by interactions of the discharged radionuclides with other components of the receiving environment. As a result, the behavior of a radionuclide will be different from initially expected. That is why, the study of both radionuclide speciation and changes in speciation with time is essential in order to produce more realistic estimates of the risk associated with produced water discharges.

To date information on physico-chemical forms of the radionuclides present in produced water is scarce. Moreover, available information is limited mainly to the study of a single radionuclide – Ra-226 (Snavely, 1989, Hamilton et al., 1992, NRPA, 2004, Rye et al., 2009, Eriksen et al., 2009, Skancke, 2014). Scarce data on activity concentration of Po-210 in produced water was reported by NRPA in a survey of 2003 (NRPA, 2004). As far as we are aware, nothing is known about physico-chemical forms of Po-210 in produced water and their changes with time. This information is highly important to overall assessment of the long-term effects of produced water discharges. Po-210 is recognized the most important natural radionuclide in produced water due to its radiological impact on the environment and human health, however polonium speciation still remains poorly studied.

Thus, the need to enhance our knowledge on speciation of Po-210 present in produced water along with interest in studying processes that result in changes in its speciation, led to the present study.

2. HYPOTHESES AND OBJECTIVES

The study addresses the following **hypotheses**:

1. Size speciation of Po-210 changes when produced water is mixed with seawater.
2. Size speciation of Po-210 present in mixture of produced water with seawater changes with time.

The **objectives** of the study were as follows:

1. To characterize produced water from the oil-producing platform Troll C with respect to size speciation of Po-210 and its activity concentrations.
2. To determine the size speciation changes of Po-210 in produced water when it is mixed with seawater using 24 hours and 1 month as exposure time.

3. BACKGROUND

What is produced water?

Produced water is extracted from the well along with oil and gas during hydrocarbon production. It includes formation water naturally present in the oil and gas reservoir, or a mixture of seawater and formation water, if seawater is injected in order to maintain pressure in the reservoir during oil and gas production, or re-injected produced water (NRPA, 2004). Produced water represents the largest operational discharges resulting from oil and gas production (Neff et al., 2011). On the platform, produced water is separated from oil and gas, treated and discharged to the sea or re-injected into the reservoir. In 2015 on the NCS, 148 million m^3 of produced water were discharged to the sea and 44 million m^3 were re-injected into the reservoir (NOROG, 2016). Usually the quantity of produced water increases as the field becomes mature and oil and gas production decreases. In this case seawater is injected to increase oil recovery and maintain reservoir pressure. In an old field the production stream can consist of 5 % oil and 95 % produced water (NRPA, 2004).

Produced water is a complex mixture. Its composition widely varies within and between reservoirs and is determined by such factors as geological characteristics of the reservoir, its age and depth, the type of hydrocarbons produced, and operating conditions (NRPA, 2004). Generally, produced water contains such natural components as dispersed hydrocarbons in the form of oil droplets; dissolved hydrocarbons like BTEX (benzene, toluene, ethyl benzene, xylene), aromatic and polycyclic aromatic hydrocarbons (PAHs); organic compounds (alkylphenols, naphthenic acids); inorganic salts; heavy metals and naturally occurring radionuclides (Neff et al., 2011). A number of these chemicals may be found in produced water at concentrations higher than in seawater what raising concerns over potential ecological harm (Neff et al., 2011). In addition to the natural components, produced water can contain different production chemicals, for example, to protect the production system from corrosion and scale, to aid in recovery and pumping of oil and gas, to aid in the separation of oil, gas and water (Neff et al., 2011). Some of these chemicals, for example scale inhibitors, corrosion inhibitors are soluble in water, therefore remain in produced water and discharged with it (Neff et al., 2011). For example, the estimated amount of scale inhibitors discharged in produced water to the North Sea is 1143 t/y (Neff et al., 2011).

Most produced waters are highly saline (Hamilton et al., 1991). The salinity of produced water may reach a few hundreds parts per thousand (‰) compared to salinity of seawater which is 32–36‰ (Neff et al., 2011). For example, salinity of produced water from the Hibernia oil-producing platform varies from 46‰ to 195‰ (Neff et al., 2011). The salinity of produced water is determined mainly dissolved sodium and chloride ions followed by calcium, magnesium, potassium, sulfate, bromide and bicarbonate (Table 1).

Table 1. Chemical data for selected elements and inorganic ions in produced waters of different geologic ages. Data reported in units of milligram per kilogram or parts per million (Collins, 1975 cited in Neff et al., 2011)

Element / inorganic ion	Seawater	Produced water	
		Highest concentration (Age[1])	Range of Mean concentrations
Salinity	35,000	---	5,000 – 300,000,000
Sodium	10,660	120,000 (J)	23,000 – 57,300
Chloride	19,353	270,000 (P)	46,100 – 141,000
Calcium	416	205,000 (P)	2530 – 25,800
Magnesium	1294	26,000 (D)	530 - 4300
Potassium	387	11,600 (D)	130 - 3100
Sulfate	2712	8400 (T)	210 - 1170
Bromide	87	6000 (J)	46 - 1200
Strontium	0.008	4500 (P)	7 - 1000
Ammonium	---	3300 (P)	23 - 300
Bicarbonate	142	3600 (T)	75 - 560
Iodide	167	1410 (P)	3 - 210
Boron	4.45	450 (T)	8 - 40
Carbonate	---	450 (M)	30 - 450
Lithium	0.17	400 (J)	3 - 50

[1] D. Devonian, J. Jurassic, M. Mississippian, P. Pennsylvanian, T. Tertiary.

Radioactivity in produced water

Certain rocks and clays in the hydrocarbon reservoir contain high concentration of naturally occurring uranium and thorium. Both U-238 and Th-232 decays to stable lead isotopes via several radionuclides of which Ra-226, Pb-210, Po-210 and Ra-228 are key with respect to the potential environmental impact and human exposure. Ra-226 is an alpha emitter with a half-life of 1602 y belongs to the U-238 decay series; Ra-228 is a beta emitter with a half-live of 5.76 y belongs to the Th-232 decay series (Figure 1). Thus, the concentration of Ra-226 and Ra-228 in reservoir rock is determined by the abundance of uranium and thorium there. Decay of Ra-226 leads to the production of its daughter nuclides such as Pb-210, a beta emitter with a half-life of 22 y and Po-210, an alpha emitter with a half-life of 138,4 d (Figure 1).

Hydrocarbon reservoirs also contain naturally present formation water. Radium is considered more soluble in water than uranium and thorium and can be dissolved in the

$${}^{238}_{92}U \xrightarrow{\alpha,4{,}5\ 10^{9}y} {}^{234}_{90}Th \xrightarrow{\beta,24{,}1d} {}^{234}_{91}Pa \xrightarrow{\beta,1{,}2m} {}^{234}_{92}U \xrightarrow{\alpha,2{,}5\ 10^{5}y} {}^{230}_{90}Th \xrightarrow{\alpha,8\ 10^{4}y} \boldsymbol{{}^{226}_{88}Ra} \xrightarrow{\alpha,1600y} \boldsymbol{{}^{222}_{86}Rn}$$

$$\xrightarrow{\alpha,3{,}8d}$$

$${}^{218}_{84}Po \xrightarrow{\alpha,3{,}05m} {}^{214}_{82}Pb \xrightarrow{\beta,26{,}8m} {}^{214}_{83}Bi \xrightarrow{\beta,19{,}8m} {}^{214}_{84}Po \xrightarrow{\alpha,214\mu s} \boldsymbol{{}^{210}_{82}Pb} \xrightarrow{\beta,22y} {}^{210}_{83}Bi \xrightarrow{\beta,5{,}0d} \boldsymbol{{}^{210}_{84}Po}$$

$$\xrightarrow{\alpha,138{,}4d} {}^{206}_{82}Pb$$

$${}^{232}_{90}Th \xrightarrow{\alpha,1{,}4\ 10^{10}y} \boldsymbol{{}^{228}_{88}Ra} \xrightarrow{\beta,5{,}7y} {}^{228}_{89}Ac \xrightarrow{\beta,6{,}13h} {}^{228}_{90}Th \xrightarrow{\alpha,1{,}9y} {}^{224}_{88}Ra \xrightarrow{\alpha,3{,}64d} {}^{220}_{86}Rn \xrightarrow{\alpha,55{,}6s} {}^{216}_{84}Po$$

$$\xrightarrow{\alpha,0{,}15s}$$

$${}^{212}_{82}Pb \xrightarrow{\beta,10{,}6h} {}^{212}_{83}Bi \xrightarrow{\beta,60{,}6m} {}^{212}_{84}Po \xrightarrow{\alpha,0{,}3\mu s} {}^{208}_{82}Pb$$

FIGURE 1. TWO RADIOACTIVE SERIES FROM U-238 AND TH-232 WITH THEIR MAIN BRANCHES OF DECAY. THE DECAY MODE (ALPHA OR BETA) AND THE HALF-LIFE OF THE NUCLIDE ARE SHOWN (HYLLAND AND ERIKSEN, 2013)

formation water. When oil and gas are pumped from the hydrocarbon reservoir, formation water is pumped together with them and brought to the platform as produced water. Therefore, when produced water is brought to the platform, it brings radium and its decay products.

Up to now, not much data has been published on the activity concentrations of Ra-226 and Ra-228 in produced water from Norwegian platforms. Far less data has been reported for Pb-210 and Po-210. According to the NRPA (2004), average activity concentrations of Ra-226 and Ra-228 in produced water samples collected in 2003-2004 from 41 Norwegian platforms were 3.3 Bq/l and 2.8 Bq/l, respectively; the activity concentrations of Po-210 in produced water from 12 Norwegian platforms were less than 0.01 Bq/l; the activity concentrations of Pb-210 in almost all analyzed samples were below the detection limit.

Typical background concentrations of Ra-226 in the North Sea are 1.5 mBq/l and 1 mBq/l for Ra-228 (Van der Heijde et al., 1990, cited by Hosseini et al., 2012). The reported average concentration of Po-210 in the North Sea is 0.8 ± 0.23 mBq/l (Cherrry and Heyraud, 1988 cited by NRPA, 2004).

In 2011 the total releases of Ra-226, Ra-228 and Pb-210 on the NCS were estimated to be 451.3 GBq, 356.2 GBq and 35.4 GBq, respectively (IAF and Zpire, 2012). The total annual release of Po-210 has not been reported.

Polonium: exposure risk in the marine environment

Po-210 is a major source of natural radiation to marine organisms (Cherry and Shannon, 1974 cited by Carvalho, 2011). Studies in the Irish Sea indicated that marine organisms received higher doses from naturally occurring Po-210 rather than from anthropogenic radionuclides present in the discharges from the Sellafield nuclear fuel reprocessing plant (Pentreath and Allington 1988 cited by Stewart and Fisher, 2003*a*).

Polonium is highly radiotoxic even at low concentrations due to its high specific activity (1.66 x 10^{14} Bq/g) and its relatively effective accumulation into soft tissues where a high-energy alpha particle ($E\alpha = 5.304$ MeV) has a high linear transfer (about 100 keV/μm) (Ansoborlo et al., 2012, Kristan et al., 2015) and thus can cause considerable damage and cell death.

Polonium is in the same group elements as sulfur (S), selenium (Se) and tellurium (Te), therefore it has similar chemical properties (NRPA, 2012). However, in contrast to S and Se that are essential elements for living organisms, Po does not perform any biological function (NRPA, 2012) but nevertheless behaves as a nutritional element due to its association with sulfur-containing compounds and proteins (Jones et al., 2015). Cherry and Shannon (1974 cited by NRPA, 2012) suggested that elevated Po-210 concentrations in marine organisms are linked to sulfur uptake. Fisher et al. (1983) found that Po-210 enters the cytoplasm of phytoplankton cells and distributes within the cell in a way similar to that of protein and sulfur. Moreover, it has been suggested (Carvalho et al., 2011, Carvalho, 2011) that Po-210 follows protein transfer in marine food web.

It is noteworthy to say that although Po-210 is a particle-reactive radionuclide, its particle affinity and binding mechanism is different from those of other particle-reactive radionuclides, for example, Pb-210. Pb-210 is associated more with the surface of particles and its sorption is extracellular (Fisher et al., 1983, Stewart and Fisher, 2003*a*). It is adsorbed to sedimentary particle surfaces and removed from water column via particle scavenging (Jones et al., 2015). Pb-210 can be also removed from surface waters by zooplankton, but the radionuclide is not assimilated in animal tissue and sinks in fecal material (Stewart and Fisher, 2003*a*). In contrast to Pb-210, Po-210 has high affinity for organic matter inside cells therefore its sorption is intercellular (Fisher et al., 1983). As a result, Po-210 is relatively rapidly removed from the water column via adsorption onto organic particles and uptake in phytoplankton and zooplankton (Strålberg et al., 2003), what usually leads to deficit of the dissolved Po-210 in the upper ocean relative to Pb-210 (Jones et al., 2015). In fact, there was found a strong correlation between the dissolved Po-210 removal rate constant and chlorophyll *a* concentration (Nozaki et al., 1997 cited by Stewart and Fisher, 2003*a*). It has been suggested that since Po-210 penetrates the cytoplasm of phytoplankton cells, much of Po-210 bound to the cells would be efficiently assimilated by zooplankton who feeds on phytoplankton cells (Stewart and Fisher, 2003*a*). Zooplankton greatly concentrates Po-210 in its tissues and becomes an effective carrier of Po-210 from phytoplankton to higher trophic levels that are consumed as seafood (Stewart and Fisher, 2003*b*). By doing so, zooplankton increases the residence time of Po-210 spent in surface waters what contributes significantly to polonium bioaccumulation in marine food chains (Stewart and Fisher, 2003*a*). It has been detected that higher trophic levels (mussels and sardines) feeding upon zooplankton indicate the high enrichment of Po-210 (Carvalho, 2011, Jones et al., 2015). The exceptionally elevated concentrations of Po-210 have been found in the hepatopancreas of crustaceans and fish liver and gonad, which are consumed in many countries (Carvalho et al., 2011).

Po-210 is accumulated by phytoplankton from the dissolved phase (Stewart and Fisher, 2003*a*), and then is transferred to the next trophic level along marine food chains (Carvalho, 2011). Carvalho and Fowler (1994) studied the importance of water and food as a source of polonium to prawns and fish and found that:

(1) food ingestion was the main pathway of Po uptake in both prawns and fish;
(2) ingested polonium was readily accumulated in internal tissues in both prawns and fish with the highest concentration measured in hepatopancreas and gut for prawns (about 71% of the whole-body burden of Po); and liver for fish (about 85% of the whole-body burden of Po);
(3) in fish polonium dissolved in water was only weakly accumulated either on external surfaces or within internal organs;
(4) in prawns polonium dissolved in water was mainly adsorbed on external surfaces, but did not contribute significantly to Po accumulation in internal organs;
(5) the efficiency of polonium absorption was much higher when the radionuclide was incorporated into the organic matrix of food rather than weakly bound to food particles (Carvalho and Fowler, 1994).

Thus, it could be assumed that absorption of the dissolved Po-210 from water is the primary route of polonium uptake for phytoplankton, while food ingestion is the main exposure pathway for higher trophic levels.

The elevated levels of Po-210 in marine organisms may lead to elevated doses to human through seafood consumption. In fact, Po-210 found in fish and shellfish is the major contributor to the radiation dose received by humans via food consumption; anthropogenic radionuclides such as Cs-137 make only a small contribution (Wildgust et al., 1999). It has been estimated that around 4 kg of scallop flesh intake would be sufficient to reach the annual permissible intake of 1 mSv of Po-210 for humans (Bustamante et al., 2002 cited by Jones et al., 2015). Of course, the radiation dose will depend on human dietary habits: the radiation dose would be higher in nations with a high consumption of seafood (Carvalho et al., 2011). For example, it will be higher in Portugal where the annual seafood consumption is around 60 kg/year per capita than in the UK where it is around 10 kg/year per capita (Carvalho et al. 2011).

Polonium speciation in the marine environment

The marine geochemistry of polonium still remains poorly known and polonium speciation remains a challenge. In most natural waters polonium is found at extremely low concentrations, therefore much relevant data should still be derived from studies at trace concentrations (Swarzenski et al., 1999).

Polonium has 25 radioactive isotopes with mass numbers of 192 to 218, of which Po-208, Po-209 and Po-210 have half-life longer than 1 day (IAEA, 2009). Decay data for these three isotopes is given in Table 2. Po-210 is most widely available isotope of polonium in nature (Ansoborlo et al., 2012).

Polonium can exist in several oxidation states (−II, +II, +IV, and +VI), of which tetravalent Po (IV) is the most stable in solution (Ansoborlo et al., 2012). It is assumed that in well-oxygenated, pH neutral waters, aqueous polonium is predominantly present in form of Po (IV) (in insoluble form), while Po (II) (in soluble form) prevails under reducing conditions (Swarzenski et al., 1999). One of the most important chemical properties of polonium, in particular Po (IV), is its tendency to hydrolyze and form colloids $Po(OH)_4$ (Ansoborlo et al., 2012). Polonium reacts with sulfide to form PoS_2 (LaRock et al., 1996). It can also form soluble salts with chlorides, bromides, acetates, nitrates, and other inorganic anions (Ansoborlo et al., 2012).

It is important to note that Po-210 is a redox-sensitive particle-reactive radionuclide and the redox state is the major parameter that controls its sorption/desorption and behavior across the O_2 / H_2S interface (Ansoborlo et al., 2012, Swarzenski et al., 1999). In surface waters dissolved Po-210 is rapidly scavenged by biogenic particles (plankton) but also by

Table 2. Decay modes, half-life, radiation energy and intensity for Po-208, Po-209, Po-210 (IAEA, 2009)

Radionuclide	Half-life	Decay modes	Eα (MeV)	Intensity (%)
Po-208	2.898 y	α: 99.99777%	5.115 4.220	99.9956 2.4E-4
Po-209	102 y	ε: 0.00223% α: 99.52%	4.885 4.883 4.622 4.310 4.110	20 80 0.551 1.5E-4 5.6E-4
Po-210	138.376 d	ε: 0.48% α: 100%	5.304 4.517	100 1.22E-3

manganese oxide (MnO_2) and then transported downward in the water column to the redox interface (Swarzenski et al., 1999). In the region above the redox interface where MnO_2 begins aerobic reduction and dissolution, MnO_2-bound Po-210 becomes solubilized (Swarzenski et al., 1999). The newly released dissolved Po-210 can then diffuse either upward in the water column towards the aerobic manganese reduction region or downward into anoxic waters where it can precipitate as sulfide polonium (Swarzenski et al., 1999). Within the aerobic manganese reduction region, the upward-diffusing Po-210 can be re-scavenged by freshly formed MnO_2 which can contribute to the particulate enrichment in this layer (Swarzenski et al., 1999) and a cyclic behavior of reduction-oxidation starts again. The process of dissolution and diffusion proceeds slowly, therefore only a small fraction of Mn undergoes this cyclic behavior while the rest is more or less permanently retained in the sediments (NRPA, 2012). Nevertheless, polonium release from sediments to the water column in relation to Mn-cycle under reducing conditions is one of the remobilization mechanisms for Po (Benoit and Hemond, 1990). Another remobilization mechanism is linked to the activity of sulfate-reducing bacteria (LaRock et al., 1996). In one study sulfate-reducing bacteria interacted with gypsum and by doing so released (solubilized) Po-210 contained in the gypsum (LaRock et al., 1996). Another study suggestedthat the water column profile of Po-210 in Framvaren Fjord, Norway is strongly affected not only by the Mn-cycle; but also by the presence of phototrophic sulfur bacteria at the O_2 / H_2S interface (Swarzenski et al., 1999).

4. MATERIALS AND METHODS

Laboratory work

Laboratory experiments with produced water were carried out at Isotope Laboratory at the Norwegian University of Life Sciences (NMBU), Norway. The experiments were conducted from August 2016 to March 2017 as part of a small project funded by the Centre for Environmental Radioactivity (CERAD).

4.1 Materials: Produced water and Seawater

Produced water (PW)

The oil-producing platform Troll C was selected for sampling of produced water. Troll C is one of the three platforms of the Troll field which is located in the northern part of the North Sea, 65 km west of Kollsnes, near Bergen (Figure 2) (Statoil, 2007). With respect to recoverable reserves, Troll is the largest gas field and the major oil field on the NCS (Statoil, 2016). The Troll field is neighbored to other large fields such as Oseberg, Statfjord and Gullfaks (Figure 2).

With respect to discharge volumes of produced water and radioactivity in produced water, Troll C is one the main contributors to emission to the North Sea (NRPA, 2004). In 2013, the volume of produced water discharged from Troll C was 6.3 million m^3 (Statoil, 2014). In 2011 Troll C alone counted for 20% of the total releases of Ra-226 and around 18% of the total releases of Ra-228 on the NCS (IAF and Zpire, 2012).

Samples of produced water from Troll C were collected in eight 25-L polyethylene containers. The samples were collected by personnel in Statoil on August 11, 2016 and delivered to Isotope Laboratory on August 18, 2016. All containers of produced water were stored at 4^0 C in the dark until used to minimize biological activity.

Produced water general characteristics

Information on sampling date was provided together with the samples of produced water. Conductivity, salinity and pH of the produced water were measured using Multi 3420 Multiparameter Meter; SenTix 940-3/TetraCon 925-3 (WTW, Germany). General characteristics of the produced water from Troll C are given in Table 3. As it seen, the produced water has pH close to neutral and a high conductivity reflecting a high salinity.

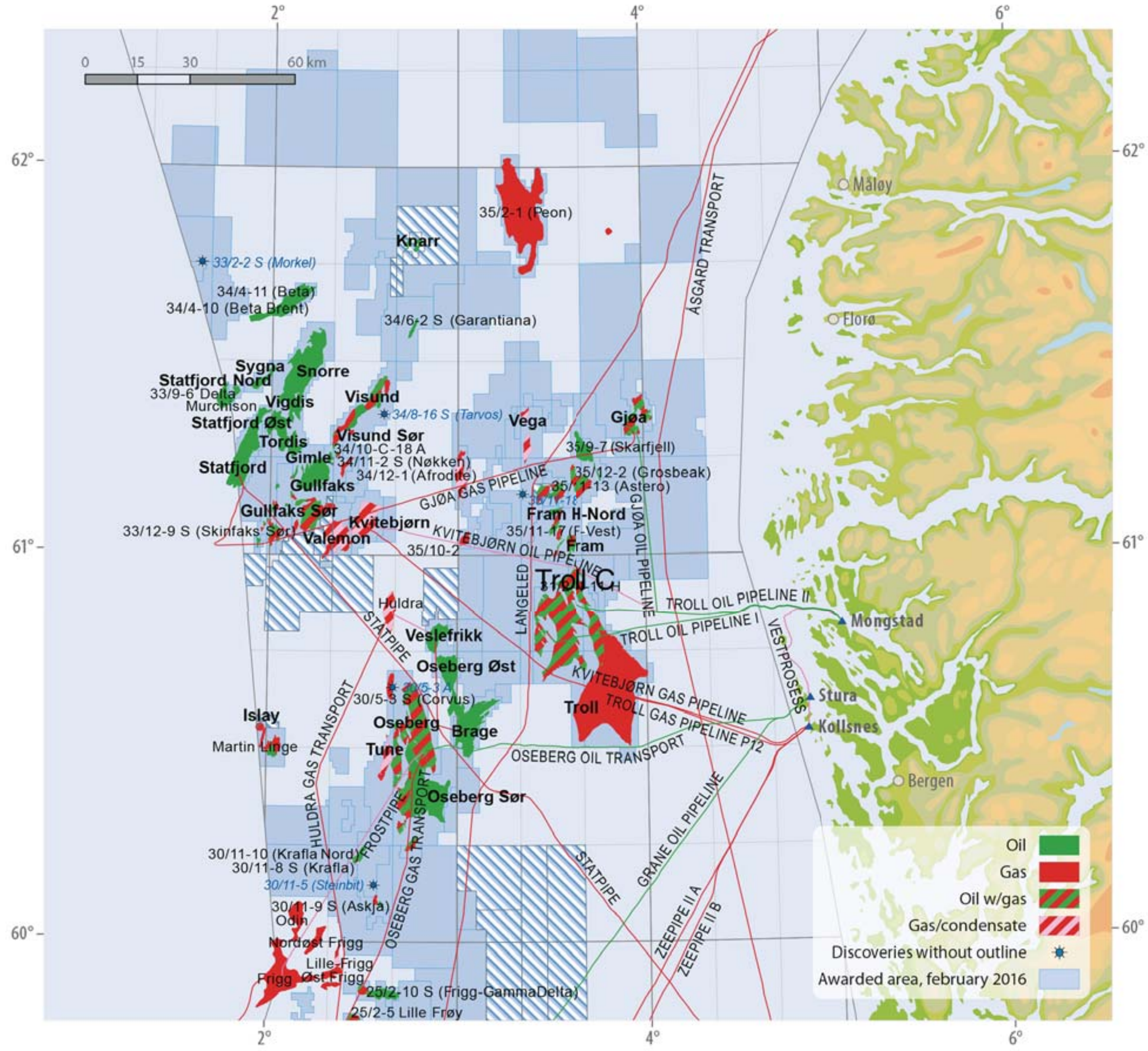

FIGURE 2. THE MAP OF THE NORWEGIAN NORTH SEA SECTOR WITH EMPHASIS ON TROLL C (NPD, 2016)

Table 3. Produced water general characteristics

Platform	Sample provider	Sampling Date	pH	Conductivity, mS/cm	Salinity, psu
Troll C	Statoil	11.08.2016	6.52	71.3	47.7

Seawater (SW)

About 75 L of seawater were collected at NIVA Marine Research Station at Solbergstrand, Drøbak for use in the mixing experiments with the produced water. The seawater was pumped from Oslo Fjord into three 25-L polyethylene containers. All containers of seawater were transported to Isotope Laboratory and stored at 4^0 C in the dark until used in the experiments.

4.2 Methods: Fractionation and Alpha Spectrometry

Fractionation technique

The original produced water and produced water mixed with seawater were fractionated to study particle size properties of polonium radionuclide. To follow the changes in speciation of Po-210 due to possible transformation processes, 24 hours and 1 month were selected as exposure time in the mixing experiments.

Size fractionation included the collection of the following fractions:

1) Total
2) Species less than 0.45 μm
3) Species less than 10 kDa

Each fraction was collected in one 2-L polyethylene container (Table 4).

Using the collected fractions, the following fractions were calculated:

1) Particles larger than 0.45 μm as (Total - <0,45 μm)
2) Colloids at 10 kDa to 0.45 μm as (<0,45 μm - <10 kDa)
3) LMM species less than 10 kDa as (< 10 kDa)

Table 4. Sample size and volume of each fraction collected during size fractionation of the original produced water (PW) and produced water mixed with seawater (PW + SW) after 24 hours and 1 month of exposure time

Fractions	PW	PW + SW, 24h	PW + SW, 1month
Total	1 x 2L	1 x 2L	1 x 2L
<0,45 μm	1 x 2L	1 x 2L	1 x 2L
<10 kDa	1 x 2L	1 x 2L	1 x 2L

Fractionation of the original produced water

The original produced water in the amount of 25 L was fractionated with respect to particle size. First, total concentration was directly pumped from the unfiltered original produced water sample using a peristaltic pump Longer Pump WT600-3J (Longer Precision Pump Co., Ltd, China). The centrifugation speed was 200 rpm. Next, the sample was fractionated using 100 μm filter and 0.45 μm membrane GWV (Pall Corporation, USA) and the radionuclide species less than 0.45 μm in size were collected. The centrifugation speed was 200 rpm, no pressure was applied. Further fractionation was performed using 10 kDa hollow fiber (Microza Ultrafiltration Module, Pall Corporation, USA). Using the peristaltic pump connected with the hollow fiber and pressure of 12 psi, the radionuclide species less than 10 kDa were collected. The centrifugation speed was 200 rpm.

Mixing experiments: Fractionation of produced water mixed with seawater

Fractionation of produced water mixed with seawater was performed in the same manner as fractionation of the original produced water.

The original produced water was mixed with seawater in a proportion of 1 : 3. Eventually, 6 L of produced water was mixed with 18 L of seawater and fractionated. Size fractionation was performed after 24 hours and 1 month of exposure time.

Determination of Po-210 in produced water and in mixture with seawater by alpha spectrometry

Determination of Po-210 in the produced water and in mixture with seawater by alpha spectrometry involved the following steps: sample preparation, source preparation, measurement in an alpha spectrometer and calculation of the activity concentration of Po-210 in the sample.

Po-209 was used as a yield tracer. It was selected by reason of availability and good energy peak resolution between Po-209 and Po-210 (Table 2 and Figure 3).

Sample preparation was based on a method proposed by Bojanowski et al. (1983). The method is developed for seawater samples and uses the ability of polonium to co-precipitate with MnO_2 at pH 8-9 from salt water samples (Skwarzec and Bojanowski, 1988). Since the produced water is a high salinity water sample (see Table 3), the MnO_2 precipitation method was applied.

Source preparation was based on a method used by Isotope Laboratory, NMBU. However, the main limitation of this method was the fact that it had been developed for the determination of polonium in fresh water samples but not high salinity water samples. Therefore, the initial result in terms of the deposition yield was unsatisfactory. To increase the deposition yield a series of experiments were undertaken.

In the paper by Grabowski and Bem (2010) was found that the addition of diethylenetriamine-pentaacetic acid (DTPA) to water samples with a high salty content reduced the concentration of the total dissolved solids (TDS). DTPA prevents the precipitation of $Ca(OH)_2$ and $Mg(OH)_2$ from a saline solution (Grabowski and Bem, 2010). Samples of produced water and tap water were prepared to test the effect of DTPA and ascorbic acid on the deposition yield. Usually ascorbic acid is added to a sample to remove iron (Fe) from the sample solution in order to eliminate the interference of Fe in the deposition process in case when iron hydroxide is used as precipitation technique (IAEA, 2009). The method used by Isotope Laboratory involves the addition of ascorbic acid. However, since we used the MnO_2 precipitation method, the need to add ascorbic acid to the samples of produced water was questioned. The results of the experiments are shown in Table 5. In case of produced water, the highest deposition yield (64%) was obtained after the addition of DTPA in the absence of ascorbic acid. In case of tap water, the highest deposition yield (41%) was obtained after the addition of ascorbic acid in the absence of DTPA. Based on the results, it was decided to employ DTPA for the samples of produced water and produced water mixed with seawater and not to use ascorbic acid involved in the original method.

Table 5. Effect of DTPA and ascorbic acid on the deposition yield in produced water and tap water depending on matrix composition. The deposition yield was calculated by assuming 15% efficiency of the alpha spectrometer detectors.

Type of sample	Matrix composition		Deposition Yield, %
	DTPA	Ascorbic acid	
Produced water	+	-	64
	_	+	22
	+	+	14
Tap water	-	+	41
	+	-	27
	+	+	18
	_	_	17

Sample preparation.

0.1 Bq of Po-209 (Eckert & Ziegler Isotope Products, USA) was added to 2 L sample to determine chemical yield and subsequently the activity of Po-210 on the date of sampling and on the date of fractionation in case of the mixing experiments. Po-210 was pre-concentrated from the sample by co-precipitation with MnO_2 at pH 8-9. In order to achieve the co-precipitation, 2 ml of 0.2M $KMnO_4$ and 2 ml of freshly made 0.3M $MnCl_2$ were added to the sample. In addition, 10 ml of 0,1M of DTPA dissolved in 250 ml of 1M HCl was added to the sample to deactivate Ca^{2+} and Mg^{2+} ions and keep them in solution. The solution was stirred for 1 hour to reach a tracer equilibration. After, the solution was adjusted to pH 8-9 using 25% HN_3, stirred for 4 hours and left for overnight precipitation.

Source preparation. The precipitate was carefully separated from the solution using a glass microfiber filter of 150-mm diameter (GF/C, Healthcare, UK); dissolved in 100-150 ml freshly made 1.2M HCl + 6% H_2O_2 and left for four days to evaporate to dryness at 60^0 C. The temperature was kept below 100^0 C to avoid volatility losses of polonium. To destroy the left organic component and residue, the dried sample was further heated on a hotplate at 170^0 C with 5 ml of 30% H_2O_2, 0.8 ml of 12M HCl and 15 ml of MilliQ water that were sequentially added to the sample at 10 minute intervals. In addition, 1 g of hydroxylamine hydrochloride was also added to the sample. Then, the sample was cooled off for 15 min and filtered through a circles/ashless 589/3 filter paper of 125-mm diameter (Whatman, Germany). The flask was rinsed 3 times with 3 ml of 0.3 M HCl containing 1 mg/ml of NaCl. The collected filtrate was placed in a water bath for polonium deposition. Deposition time was 5 hours at 85^0 C. Finally, polonium was spontaneously deposited onto a nickel disc of 25.4-mm diameter and 0.4-mm thickness (AC-D50-NI25, Triskem, France) from a hot hydrochloric solution. Prior deposition the nickel discs were thoroughly cleaned with soap and MilliQ water and gently wiped with a soft tissue. After deposition the nickel discs were rinsed with MilliQ water and dried in an oven at 60^0 C for 15 min for further alpha-spectrometric measurements.

To monitor the quality of the performance of a chemical procedure analytical blank free from any radioactive elements were prepared and subjected to the same steps as the analyzed samples during the source preparation step.

Measurement. The exposed nickel discs with Po-210 and the Po-209 tracer were counted by alpha-spectrometer (Canberra, model 7401, USA) to determine the deposition yield and calculate activity of Po-210 in the sample.

The Canberra model 7401 used in this work contained six counting stainless steel vacuum chambers equipped with Canberra's own passivated implanted planar silicon (PIPS) detectors. The PIPS detector provides high resolution and low background (Canberra, 2011). High resolution is ensured by two properties of the PIPS detector: the thin entrance window over the detector surface which minimizes energy straggling in the entrance window and the low leakage current which ensures a low electronic noise contribution (Canberra, 2011). When new, the PIPS detector has a low background count rate of 0.05 counts per hour (Canberra, 2011). However, with time this situation may change due to detector contamination caused by recoil contamination and/or nuclide evaporation (Skipperud, 2004).

Therefore, periodical background measurements should be carried out to check for possible contamination and make accurate background corrections (Skipperud, 2004). In this work possible contamination of the detector surface may occur because of volatilization of polonium at low pressure. Since we worked with the long-lived Po-209 (half-life 102 y.) tracer, the contamination could remain for a long time and result in higher background counts. In this work the chamber background was measured for 2500000 seconds and the background count rate was about 0.0001 counts per second.

Prior measurement, the system was energy calibrated using a certified calibration source (Standard Radionuclide Source, 67976-121, Analytics, USA), which contained such alpha emitters as U-238 (E = 4198 keV), U-234 (E = 4774 keV), Pu-239 (E = 5156 keV) and Am-241 (E = 5485 keV) with the total activity of 395 dpm.

Samples were counted until the statistical uncertainty in the count was less than 10%. To achieve it the counting time was long and varied from 247000 to 1470000 s. The observed alpha spectrum of Po-210 and the Po-209 tracer was similar to the one illustrated in Fig 3.

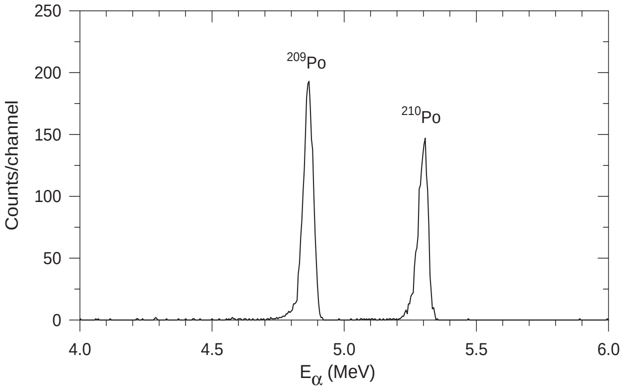

FIGURE 3. TYPICAL ALPHA SPECTRUM OF PO-210 WITH PO-209 AS YIELD TRACER (IAEA, 2009)

Calculation.

The activity concentration of Po-210 in the produced water was decay-corrected to the sampling date. Decay corrections were made to determine the initial activity of Po-210 in the produced water on the date of sampling. Because the time period between sampling (August 8, 2016) and Po measurements (January 24 and 25, 2017 and February 24, 2017) was long the initial activity of Po-210 had changed considerably from its initial value due to the decay of Po-210. The activity concentrations of Po-210 in produced water mixed with seawater were decay-corrected to the fractionation date since we were interested in observing possible changes in speciation after a certain time of mixing with seawater.

5. DISCUSSION AND RESULTS

In the present work only one sample representing one fraction was measured. Each sample was measured once, however, the counting time was long enough (247000 - 1470000 s) to achieve the required counting uncertainty less than 10%.

Prior measurements, the chamber background was counted for 2500000 s and a small background increase in the Po-209 region of interest (ROI) was detected in a few chambers. The increase in background could be an indication of detector contamination from Po-209 due to its inherent volatilization. The background count rate (0.0001 cps) was subtracted from the sample count rates and the corrected count rates were used to calculate the true activity of the count sample.

The analysis of analytical blanks that were free from any radioactive element did not indicate any radioactive contamination of glassware, chemical reagents and lab equipment used during sample preparation. Therefore, we assumed that the analyzed samples were not contaminated as well.

The deposition yield in the analyses of the produced water and produced water mixed with seawater was calculated by assuming 15% efficiency of the detectors and varied from 39 to 69%. The deposition yield in the analysis of the total fraction of polonium in the produced water was 62% what was comparable with 28 – 71% obtained by the NRPA in the analyses of Po-210 in produced water from the Norwegian platforms in 2003 (NRPA, 2004).

5.1 The activity concentration of Po-210 in the produced water from Troll C

The calculated activity concentration of Po-210 in the produced water collected from Troll C on August 11, 2016 is **0.0612** Bq/L, which is much higher than 0.0008 Bq/l reported for the background concentration of Po-210 in the North Sea (Cherrry and Heyraud, 1988 cited by NRPA, 2004) and higher than 0.002 Bq/l measured by IAF and Zpire (2012) in produced water sampled from the same platform Troll C. The calculated activity of Po-210 in produced water from Troll C is in the same range of those reported for produced water from the US Gulf Coast (0.022 - 0.085 Bq/l) (Lagera et al., 1999 cited by Hosseini et al., 2012).

5.2 Size speciation of Po-210 in the produced water from Troll C

Our results indicated that Po-210 in the produced water collected from Troll C and fractionated later in the laboratory was present as particles, colloids and low molecular mass species (LMM). As illustrated in Figure 4, more than 90% of Po-210 in produced water was

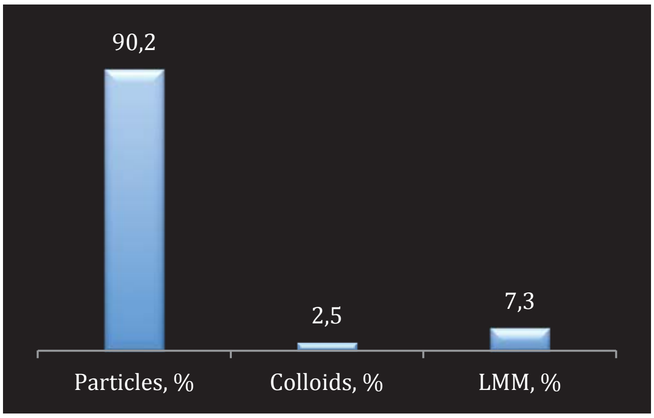

FIGURE 4. SIZE SPECIATION OF PO-210 IN THE PRODUCED WATER SAMPLED FROM TROLL C ON AUGUST 11, 2016. THE FRACTIONS WERE CALCULATED BASED ON THE TOTAL ACTIVITY OF PO-210 IN THE SAMPLE ON THE DATE OF SAMPLING. ONLY ONE SAMPLE WAS ANALYZED (N=1). THE COUNTING UNCERTAINTY FOR PO-210 WAS LESS THAN 10%

present as particles, 2.5% as colloids and 7.3% as LMM species. Predominance of the particulate fraction in the produced water could be related to a cycling behavior of polonium and manganese (Mn) depending on redox conditions. As described above, Po-210 is a very redox-sensitive element therefore its sorption/desorption is mainly controlled by redox conditions. In oxic conditions polonium is oxidized to the particulate Po (IV), in anoxic conditions polonium is reduced to Po (II) and it starts to dissolve (Ansoborlo et al., 2012). This is explained by the fact that Po adsorbs to MnO_2 and released when particulate Mn (IV) is reduced to dissolved Mn(II) when redox conditions change (Ansoborlo et al., 2012). It occurs because manganese is assumed one of the dominant carriers of many metals and radionuclides including polonium (Swarzenski et al., 1999).

Produced water consists of formation water, which is anoxic. Several metals, in particular manganese, are often present in formation waters at high concentrations (Neff et al., 2012). In anoxic waters Mn is found in dissolved state as Mn (II). When formation water rich in Mn is brought to the surface and exposed to the atmosphere, Mn becomes oxidized to the particulate Mn (IV) and precipitates as manganese oxide (MnO_2) (Neff et al., 2012). This process may affect the behavior of other elements present in formation water, for example, by co-precipitation. As a result, particle-reactive Po-210 present in formation water adsorbs to manganese oxide and it co-precipitates with it as MnO_2-Po.

Since the analyzed produced water was exposed to the atmosphere during the sampling, most of Po-210 became associated with particles. We can assume that in oxic surface water the particulate Po-210 discharged with produced water will not be available for biological uptake for marine biota. However, as mentioned above, the particulate Po-210 can start to dissolve when it transfers from oxic surface water to anoxic deep water. Then the dissolved Po will become available for biological uptake by aquatic biota, f. e. phytoplankton.

If it would be technically feasible, produced water should be collected and fractionated without exposure to the atmosphere in order to determine the truly size distribution of polonium in produced water. In addition, fractionation should be performed on the platform immediately after sampling in order to avoid storage effects (aggregation or dissolution processes) that could disturb the initial speciation (Salbu and Bjørnstaad, 1990). In our case the produced water was fractionated a few months after sampling and some changes to the speciation during storing might had already occurred.

Taking into account that Po-210 is introduced to marine food chain by phytoplankton who accumulates the radionuclide from the dissolved phase (< 0.45 μm), an important question arises: could seawater affect solubilization and mobilization of the particulate Po-210 in the produced water when it enters the sea? Since produced water discharges contribute to the additional release of naturally occurring Po-210 in elevated concentrations relatively to its natural level, this question is of great importance. To clarify it, produced water was mixed with seawater and 24 hours and 1 month were selected as exposure time to follow the possible changes in polonium size speciation.

5.3 Size speciation of Po-210 in the produced water mixed with seawater after 24 hours and 1 month of exposure time

The results obtained from both mixing experiments conducted in laboratory conditions indicated that polonium speciation changed to some extent. Unfortunately, there was no possibility to judge whether the changes in polonium speciation were statistically significant since replicate samples were not analyzed what did not allow us to perform one-way ANOVA.

Nevertheless, the results indicated that 24 h after mixing, most of Po-210 was still present as particles (87.8%), although a small decrease of particles was observed (Figure 5). It could be assumed that a small fraction of the particulate Po was mobilized upon the seawater contact due to polonium tendency to hydrolyze and form colloids. The results indicated that the colloidal fraction of Po-210 was increased substantially and represented 6.1% (Figure 5).

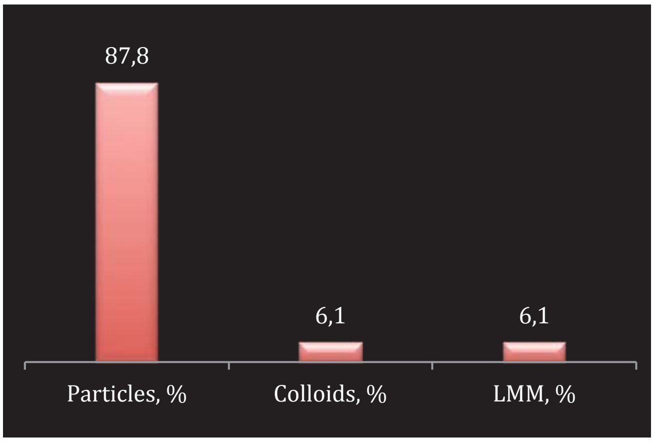

FIGURE 5. SIZE SPECIATION OF PO-210 IN THE PRODUCED WATER FROM TROLL C MIXED WITH SEAWATER AFTER 24 HOURS OF EXPOSURE TIME. THE FRACTIONS WERE CALCULATED BASED ON THE TOTAL ACTIVITY OF PO-210 IN A SAMPLE ON THE DATE OF FRACTIONATION. ONLY ONE SAMPLE WAS ANALYZED (N=1). THE COUNTING UNCERTAINTY FOR PO-210 WAS LESS THAN 10%

There was observed a small decrease in the low molecular mass fraction of Po-210, which accounted for 6.1% (Figure 5). The observed decrease could probably occur because the solubility of some polonium compounds was exceeded due to interactions with seawater compounds. It could be assumed that the decrease of the particulate and LMM fractions occurred in favor of the increase of the colloidal fraction (Figures 4 and 5).

Overall the results indicated that seawater did not cause a substantial solubilization of the particulate Po after 24 h of mixing. The particulate fraction still dominated and was relatively stable despite a small decrease.

One month after mixing the results indicated that the major part of Po-210 was still associated with particles (91.2%) (Figure 6). Moreover, a small increase in the fraction was observed compared to the unmixed produced water. There was observed a small increase in the colloidal fraction of Po-210 (3.8%) and a small decrease in the fraction of LMM species (5%) (Figure 6) compared to the unmixed produced water.

If we compare the results obtained from 1 month of mixing to the 24 h results, it is seen that the reaction of hydrolyze and the formation of colloids proceeded more rapidly in the first 24 hours after mixing (Figure 7). Probably this thing can matter with respect to polonium availability for marine organisms: this fraction of Po may be more bioavailable within the first hours upon produced water discharges. It is also seen that the colloidal fraction obtained after 24 h was quite metastable and some of colloids were probably coagulated 1 month after mixing (Figure 7). A small decrease in the fraction of LMM species observed after 24 h and its gradual decrease observed after 1 month of mixing could indicate that seawater

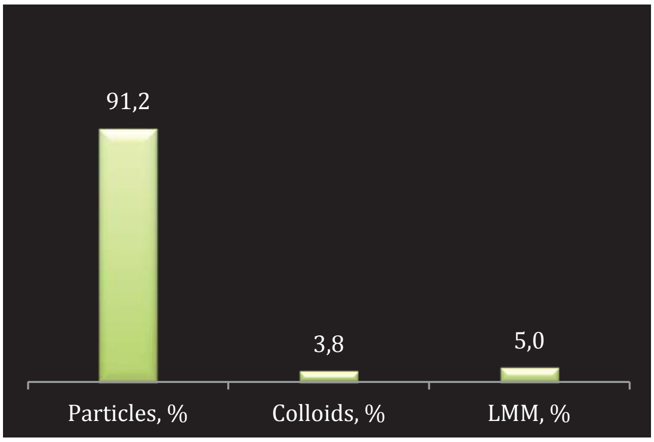

FIGURE 6. SIZE SPECIATION OF PO-210 IN THE PRODUCED WATER FROM TROLL C MIXED WITH SEAWATER AFTER 1 MONTH OF EXPOSURE TIME. THE FRACTIONS WERE CALCULATED BASED ON THE TOTAL ACTIVITY OF PO-210 IN A SAMPLE ON THE DATE OF FRACTIONATION. ONLY ONE SAMPLE WAS ANALYZED (N=1). THE COUNTING UNCERTAINTY FOR PO-210 WAS LESS THAN 10%

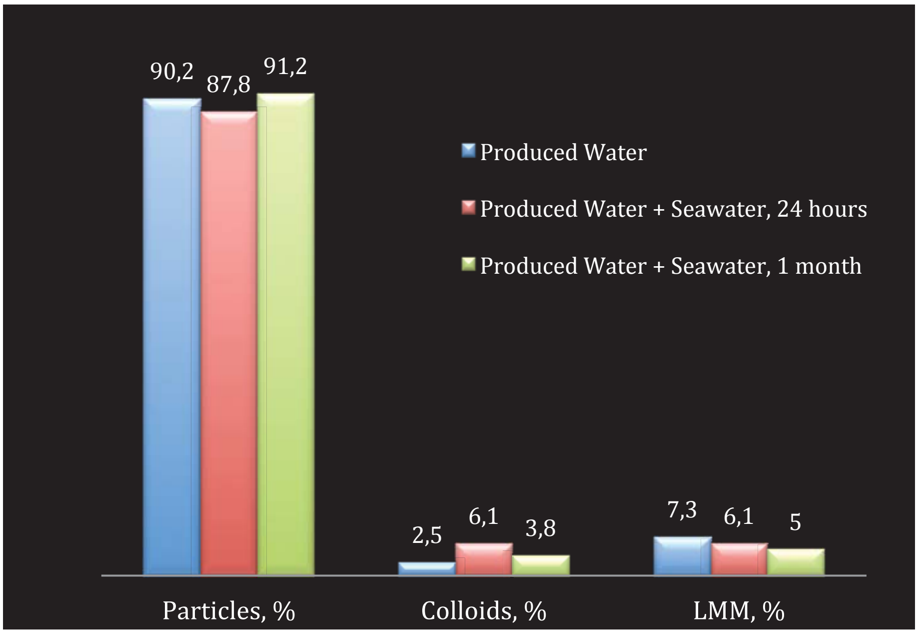

FIGURE 7. SIZE SPECIATION AND CHANGES IN SIZE SPECIATION OF PO-210 IN PRODUCED WATER AND IN MIXTURE WITH SEAWATER AFTER 24 HOURS AND 1 MONTH OF EXPOSURE TIME

contributed to the aggregation of species at least within one month (Figure 7).

Overall the results indicated that seawater did not contribute to solubulization and mobilization of the particulate Po even after 1 month of mixing. Contrary, it could be assumed that changes in polonium speciation after 1 month in seawater occurred in favor of the particulate Po (> 0.45 µm) rather than the dissolved Po (< 0.45 µm).

Kinetics of polonium present as particles, colloids and LMM species in the produced water and in mixture with seawater after 24 hours and 1 month of contact time are shown in Figures 8, 9 and 10, respectively.

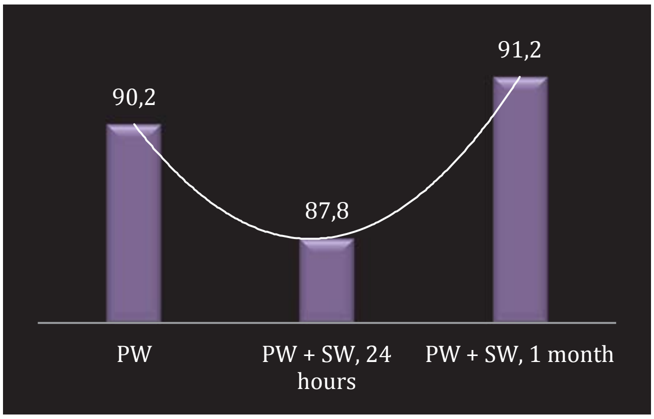

FIGURE 8. PERCENTAGE OF PO-210 PRESENT AS PARTICLES IN PRODUCED WATER AND IN MIXTURE WITH SEAWATER AFTER 24 HOURS AND 1 MONTH OF EXPOSURE TIME WITH A TREND LINE SHOWING THE PREVAILING DIRECTION OF THE PARTICULATE FRACTION

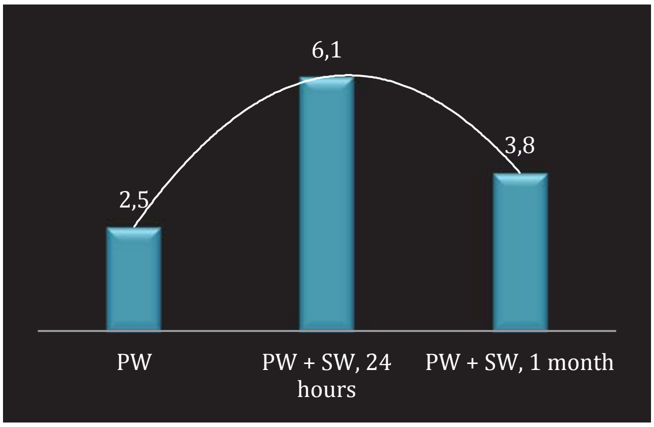

FIGURE 9. PERCENTAGE OF PO-210 PRESENT AS COLLOIDS IN PRODUCED WATER AND IN MIXTURE WITH SEAWATER AFTER 24 HOURS AND 1 MONTH OF EXPOSURE TIME WITH A TREND LINE SHOWING THE PREVAILING DIRECTION OF THE COLLOIDAL FRACTION

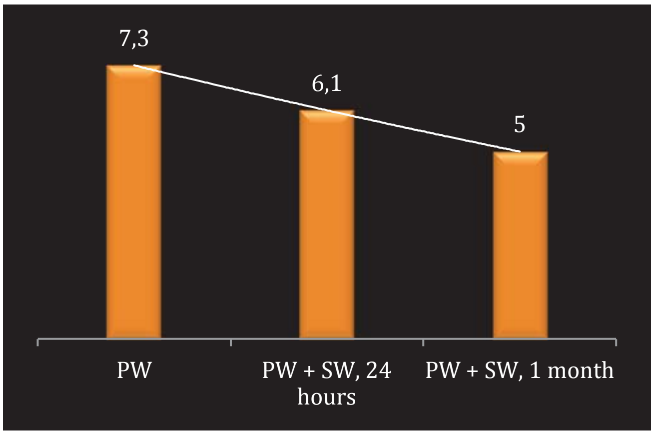

FIGURE 10. PERCENTAGE OF PO-210 PRESENT AS LOW MOLECULAR MASS (LMM) SPECIES IN PRODUCED WATER AND IN MIXTURE WITH SEAWATER AFTER 24 HOURS AND 1 MONTH OF EXPOSURE TIME WITH A TREND LINE SHOWING THE PREVAILING DIRECTION OF THE LMM SPECIES FRACTION

6. CONCLUSIONS

Produced water discharges from Troll C contribute to the elevated release of Po-210 in the North Sea. The calculated activity concentration of Po-210 in the produced water from Troll C was more than 70 times higher than its natural level in the North Sea.

More than 90% of polonium in the produced water collected from Troll C was present as particles (> 0.45 µm). We explain this phenomenon guided by the general behavior of Po-210 under different redox conditions and its link to Mn-cycling assuming that the analyzed produced water was exposed to the atmosphere during sampling and fractionation and, thus oxidation of soluble Po(II) to insoluble Po(IV) occurred.

The mixing experiments shown that seawater did not contribute to substantial solubilization and mobilization of the particulate Po-210 neither 24 hours after mixing nor 1 month after mixing. It could mean that there are other factors that are responsible for solubilization and mobilization of polonium in the sea, for example, the anoxic conditions.

In both mixing experiments the particulate fraction had absolute dominance over the colloidal and low molecular mass species fractions, although some changes in all three fractions took place. Unfortunately, one cannot determine whether these changes were statistically significant since no statistical analysis had been performed due to limited sample size (n=1).

It was interesting to note that polonium underwent to hydrolysis more rapidly in the first 24 hours after mixing rather than 1 month after mixing. This phenomenon can be important with respect to time period when Po-210 may be most bioavailable for marine biota upon discharge.

Overall, it could be concluded that dilution produced water with seawater in the laboratory did not contribute to solubilization of the particulate Po present in the produced water to the extant that we expected.

In this work the produced water was fractionated a few months after sampling, therefore some changes in Po speciation might had already occurred. We think that fractionation should be performed immediately after sampling while storage effects do not change Po speciation in the produced water. This can be done only on the platform.

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Norges miljø- og biovitenskapelig universitet
Noregs miljø- og biovitskapelege universitet
Norwegian University of Life Sciences

Postboks 5003
NO-1432 Ås
Norway