Available online at www.sciencedirect.com
ScienceDirect
Earth and Planetary Science Letters 251 (2006) 33–43
EPSL
www.elsevier.com/locate/epsl

Transport of low $^{240}Pu/^{239}Pu$ atom ratio plutonium-species in the Ob and Yenisey Rivers to the Kara Sea

Ole Christian Lind [a,*], Deborah H. Oughton [a], Brit Salbu [a], Lindis Skipperud [a], Morten A. Sickel [b], Justin E. Brown [b], L. Keith Fifield [c], Steven G. Tims [c]

[a] *Department of Plant- and Environmental Sciences, Norwegian University of Life Sciences, P.O. Box 5003, 1432 Ås, Norway*
[b] *Environmental Protection Department, Norwegian Radiation Protection Authority, P.O. Box 55, 1332 Østerås, Norway*
[c] *Department of Nuclear Physics, Australian National University, Canberra, ACT 0200, Australia*

Received 6 January 2006; received in revised form 18 August 2006; accepted 22 August 2006
Available online 3 October 2006
Editor: S. King

Abstract

Plutonium (Pu) isotope ratios can be used to differentiate between sources of Pu contamination such as nuclear weapon production, weapon fallout as well as accidental and routine releases from nuclear installations. To obtain information on the contamination level, speciation and sources of Pu in the Ob and Yenisey river systems (Siberia, Russia) and the adjacent Kara Sea, water was size fractionated onboard ship and the concentrations and atom ratios of ^{240}Pu and ^{239}Pu in obtained water fractions (i.e. particles, colloids and low molecular mass species) were determined by accelerator mass spectrometry (AMS). Results show a clear difference in speciation between high $^{240}Pu/^{239}Pu$ atom ratio Pu derived from global weapon fallout and low $^{240}Pu/^{239}Pu$ atom ratio Pu, presumably originating from weapons grade Pu. In particular, the $^{240}Pu/^{239}Pu$ atom ratios (mean 0.18 ± 0.06) for particles (>0.45 μm) could not be distinguished from global fallout Pu (0.17–0.19), whereas for low molecular mass (LMM; <8 kDa) species the Pu ratio was much lower than for global fallout Pu in both rivers. The difference was especially well pronounced in the Ob (mean $^{240}Pu/^{239}Pu$ atom ratio 0.052 ± 0.023), where the difference was statistically significant (paired *t*-test, $P=0.02$, $n=4$). The low $^{240}Pu/^{239}Pu$ atom ratios in filtered (<0.45 μm) water and especially in the LMM fractions were observed at stations along the whole length of the two sampling transects, extending from the lower parts of the Ob and Yenisey Rivers and into the northern Kara Sea. This provides evidence of long-range transport of Pu from low burn-up or non-civil sources into the Arctic Ocean. Pu appears to be predominantly in a dissolved form (<0.45 μm) throughout the investigated area. The colloidal fraction (8 kDa–0.45 μm) ranged within 24–78% in the river systems and 8–53% in the Kara Sea. Concentrations of $^{239,240}Pu$ in filtered (<0.45 μm) water were very low, ranging from 2.6 to 40.6 mBq m^{-3} in the rivers, somewhat higher than in the open Kara Sea (2.4–7.7 mBq m^{-3}) in agreement with previously reported values.

Keywords: Ob; Yenisey; Weapons grade plutonium; Global fallout; Speciation; AMS

1. Introduction

The Kara Sea receives more than one-third of the total fresh water discharge to the Arctic Ocean, mainly via the two Siberian rivers Ob and Yenisey, Russia [1].

* Corresponding author. Tel.: +47 64 96 5545; fax: +47 64 94 8359.
E-mail address: Ole-Christian.Lind@umb.no (O.C. Lind).

0012-821X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.epsl.2006.08.023

The extensive watersheds of both rivers have received radioactive contaminants from global fallout caused by nuclear weapons tests, local and tropospheric fallout from nuclear weapons tests at Novaya Zemlya and Semipalatinsk, as well as accidental and routine releases from three major nuclear facilities located in the river catchment areas [2–6]. The nuclear facilities include Mayak Production Association (Mayak PA), Siberian Chemical Combine (SCC) and Krasnoyarsk Mining and Chemical Combine (KMCIC), all of which have been involved in the production of weapons grade Pu (Fig. 1).

The relative abundances of ^{239}Pu and ^{240}Pu can be used to trace the specific Pu source because Pu isotopic ratios can vary with reactor type, nuclear fuel burn-up time, neutron flux and energy, and, for fallout from nuclear detonations, weapon type and yield [7]. Weapons grade Pu is produced by leaving the nuclear fuel in the reactor for only a short time in order to minimize neutron activation of ^{239}Pu, and is therefore characterised by a low content of the ^{240}Pu isotope, with ^{240}Pu/^{239}Pu atom ratios usually less than 0.07 [7,8]. Because the isotopic composition of Pu is changed only slightly upon detonation of low yield nuclear devices, tropospheric fallout (^{240}Pu/^{239}Pu atom ratio ~0.04) is indistinguishable from weapons grade Pu [9], unless additional isotope ratios such as ^{241}Pu/^{239}Pu and ^{242}Pu/^{239}Pu are determined. In contrast, ^{240}Pu/^{239}Pu atom ratios from both global weapons fallout (0.17–0.19) and spent fuel from civil reactors (0.2–0.8) are higher [8], providing the possibility to distinguish between the different sources of Pu contamination using mass spectrometry.

Pu released from a source can also be present in different physico-chemical forms (e.g. low molecular mass (LMM) species, colloids, particles), and these can influence the mobility and potential ecosystem transfer [10]. A variety of fractionation techniques can be used to differentiate radionuclide species released from a source or a mixture of sources. The combination of fractionation techniques and isotope ratio determination in the obtained fractions can provide a significant improvement in the interpretation of data compared to analysis of total samples.

In view of the potential long-range river transport of radionuclides to the Arctic Ocean from landbased sources within the catchments of the Ob and Yenisey rivers [11], this study was undertaken to improve the current knowledge on the provenance, quantity and behaviour of Pu contamination in the area. The objectives were to determine the ^{239}Pu and ^{240}Pu concentrations in the Ob and Yenisey rivers and the adjacent Kara Sea, to quantify the amount of the particulate, colloidal and LMM Pu species in the study area, and to use ^{240}Pu/^{239}Pu atom ratios to identify sources contributing to the Pu contamination. Samples were collected during the «SIRRO 2001» expedition [12,13], and filtration (<0.45 μm) and tangential flow ultrafiltration (<8 kDa) were performed onboard ship shortly after sampling. Subsequently, the concentrations and atom ratios of ^{239}Pu and ^{240}Pu in samples and obtained fractions (particles, colloids and

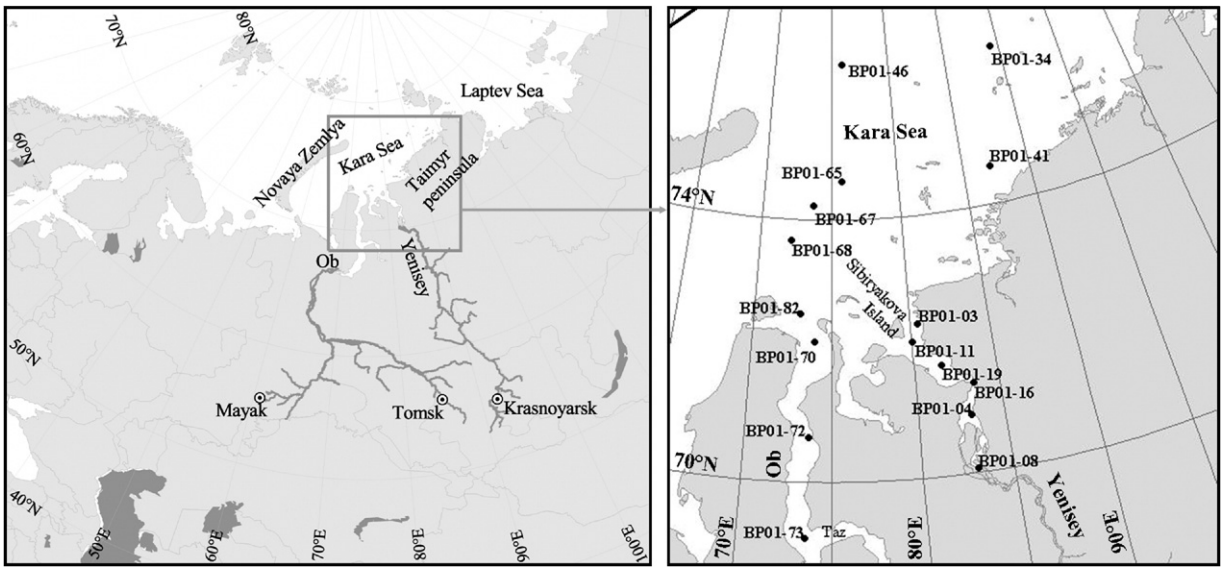

Fig. 1. Study area. Geographical position of the study area with the three major nuclear installations indicated (left). Sampling stations in the Ob and Yenisey rivers and the adjacent Kara Sea are indicated with station numbers (right).

LMM species) were determined by accelerator mass spectrometry (AMS).

2. Background to the investigation

2.1. Study area

Together, the Siberian rivers Ob and Yenisey represent a major fresh water input to the Arctic Ocean. The Yenisey is Siberia's largest river and among the ten largest rivers of the world, with an annual discharge of 620 km^3 yr^{-1} [14,15], drainage area of 2.58×10^6 km^2, length of 3844 km and the delta extends over 800 km [16,17]. The Ob is Siberia's third largest river in terms of annual discharge (429 km^3 yr^{-1}) and the longest Arctic river (6370 km including the Ob Bay) with the largest catchment area (2.99×10^6 km^2) [14–16]. The delta is nearly 100 km long with about 50 islands. The Kara Sea is a marginal shelf sea of the Arctic Ocean receiving all discharges from both rivers and its riverine surface waters are underlain by highly saline deep waters with a pycnocline separating the two water masses [18,19]. Water with salinity >30 psu enters the estuaries as salt intrusions, forming a very stable salt wedge in the Yenisey, which penetrates at least as far south as 71°24′N (just south of St. 16; Fig. 1). The salt intrusion into the Ob is less pronounced, reaching south to 72°N, and is more mixed with the overlying surface water [18]. The riverine Yenisey water flows towards the northeast along the coast and finally enters the Laptev Sea through the Vilkitsky Strait [20]. On the way to 75°N the Yenisey derived water loses about 50% of its total suspended matter (TSM) [21]. The River Ob discharges mainly to the north, and from the river mouth to 75°N, TSM is reduced by about 50%, largely because of conservative mixing of marine surface water [21].

Most of the sedimentation in the two estuaries is associated with a reduction in flow as the Ob widens into the Ob Bay and the Yenisey into the southern Kara Sea. Flocculation and coagulation of colloidal and suspended matter in the area of fresh and salt water mixing add to sedimentation in the estuaries [22].

2.2. Sources of Pu contamination

Several sources may contribute to the contamination of Pu in the Ob and Yenisey river systems in addition to global fallout, including the nuclear installations at Mayak, Tomsk and Krasnoyarsk as well as local and tropospheric fallout from nuclear weapons testing. Tropospheric sources include close in fallout from Novaya Zemlya and the river transport of Pu (e.g. from Semipalatinsk).

The Mayak PA which, in the 1970s, comprised seven nuclear reactors and two reprocessing plants, was established in 1948 in order to produce Pu for the Soviet nuclear weapons programme [23]. The complex is situated in the southern Urals within the catchment of the Techa river, which is a tributary to the Iset–Tobol–Irtysh–Ob river system, about 2800 km from the Kara Sea. Since 1949, both routine discharges and accidental releases of radioactive waste have led to severe contamination of Mayak and surrounding areas. It is estimated that about 100 PBq of radioactive liquid waste including about 2 TBq of alpha emitters was released directly to the River Techa during 1949−1951 [24]. Based on recent investigations, the Pu inventory in the Mayak reservoirs is at least 40 TBq [23]. Isotope ratios in sediments reflected a change in the discharge composition with time. In the deep sediment profiles Pu originating from the early discharges was present, while in the upper sediment profiles Pu was derived from recent reprocessing of civil nuclear fuel [8].

The Siberian Chemical Combine (SCC) is situated at Seversk on the River Tom, a major tributary of the river Ob [25]. The downstream distance from the site to the outlet of the Ob River into the Kara Sea is about 2700 km [25]. At SCC, the production of Pu, U and other transuranic elements has generated large amounts of radioactive waste that are stored in underground disposal sites and in severely contaminated storage ponds [25]. Since 1956, the plant has released contaminated cooling water into the river Tom. An accident occurred at the site in 1993, when an explosion in a storage tank containing fission products, Pu and U nitrate solution contaminated an area of about 90 km^2 [26].

The Krasnoyarsk Mining and Chemical Industrial Complex (KMCIC), formerly known as Krasnoyarsk-26 and now renamed Zheleznogorsk, was established in 1958 and is located at the Yenisey river 2400 km from the Kara Sea outlet [25]. At KMCIC, Pu production in three RBMK-type graphite-moderated reactors, Pu reprocessing, and storage of radioactive wastes have taken place. Commissioned in 1958 and 1961, respectively, the first two reactors used open-loop core cooling. Coolant entered into the reactors from the Yenisey River and was discharged into the river. Therefore, activation products, corrosion products from the fuel cladding and the reactor, and fission products entered the river with the cooling water [27]. These past releases have resulted in radioactive contamination of river water and sediments north of the complex. The two oldest reactors were shut down in 1992. The third reactor, which is still in use, has a closed primary cooling cycle [28]. However, the control rods are cooled in a once-through

coolant loop, and together with migration of radionuclides from a liquid radioactive waste disposal site (Severny), represent sources of continuing discharge of radioactivity to the Yenisey [29–31]. About 20 and 30 yrs ago, respectively, two reactor accidents occurred, causing U fuel particles to be released into the Yenisey along with the cooling water [32]. According to Sukhorukov et al. [33], a third accident occurred in 1966 when nuclear waste storage ponds were affected by a large flooding event in the river Yenisey. No information is available on either the magnitude of released radionuclides or on the environmental impact that the accident may have had.

2.3. Pu isotope ratios

Apparently, no data has previously been published on $^{240}Pu/^{239}Pu$ atom ratios in water samples from the area investigated in the present work. Josefsson, however, reported low $^{238}Pu/^{239+240}Pu$ and $^{241}Am/^{239+240}Pu$ activity ratios in a water sample collected outside the mouth of the Yenisey, suggesting a riverine influence of unfissioned nuclear weapons material [34]. Furthermore, the impact of sources other than the ubiquitous global fallout has been documented on the basis of low $^{240}Pu/^{239}Pu$ atom ratios in suspended sediments (0.12–0.18) and sediment cores (0.016–0.21) from the upper reaches of the Ob River system [5,6], as well as in bottom sediments from the Yenisey River (0.05–0.12) [35,36]. However, Pu in sediments from the lower parts of the River Ob and its estuary, as well as in sediments from the open Kara Sea, including the area adjacent to the Yenisey estuary is dominated by global fallout (0.16–0.18) [36].

2.4. Speciation

The speciation or physico-chemical form of Pu released from a source can have a significant impact on its subsequent mobility and transfer. In general, low molecular weight (LMM) species are believed to be mobile, whereas Pu associated with particulate material is relatively quickly removed from the water column by gravitational settling. Colloids and pseudocolloids may affect the behaviour of Pu in two ways. Colloids act as transporting agents in natural water systems [10,37], especially in the fresh water end member of rivers [38]. In estuaries, however, aggregation and sedimentation of river transported colloids and particles can take place upon mixing with high ionic strength seawater, and associated radionuclides are removed from the water phase [38]. The distribution of Pu species will change over time due to transformation processes or interactions with other components in the system, for example, redox sensitive elements like Fe and Mn. Co-precipitation, and particle growth mechanisms such as hydrolysis and aggregation increase the nominal molecular mass of LMM species and reduce mobility, while desorption, dissolution and dispersion processes (e.g., weathering of radioactive particles) mobilise LMM species from colloids or particles [10].

Filtration (μm range) and ultrafiltration (nm range) are frequently applied to separate Pu-species into size or nominal molecular mass categories [38–41], and changes in the size distribution pattern can reveal information on processes influencing the Pu-speciation, such as particle growth mechanisms or dispersion processes.

3. Methods

Sampling was carried out in August and September 2001 onboard the Vernadsky Institute's research vessel *Akademik Boris Petrov*, along a transect from the fresh water of the rivers Ob and Yenisey through the estuaries and into the higher salinity Kara Sea water (Fig. 1; Table 1). The sampling route in the Kara Sea mainly followed the flow of riverine Ob (North of the estuary) and Yenisey waters (North-East of the estuary along the coast).

Surface waters (~1 m depth) were sampled with a standard pump, while a large-volume water sampler (batomat, 200 L) was used for pycnocline and deep water samples. Fractionation of water samples was carried out on board (see flow chart in Fig. 2), less than 2 h after collection.

During processing, all samples were temporarily stored in plastic containers (300 L). About 400-litre water samples (A) were pre-filtered through 0.45 μm Millipore nitrocellulose filters to yield the dissolved fraction (B). Filters (C) were changed frequently to avoid clogging. Immediately after the pre-filtration, half the filtrates (B) were ultrafiltered to give about 200 L ultrafiltration permeate (D) which passed through a Millipore tangential flow system consisting of 4 polysulphone membrane cassettes each with a nominal molecular mass cut-off of 8 kDa [10,42]. The membrane cassettes were carefully washed between each sample with 0.1 M NaOH, 0.1 M HCl and MilliQ water prior to pre-conditioning with (~2 L) of sample water prior to sample collection.

Thus, each sample was divided into 3 operationally-defined size categories;

1. Particles: >0.45 μm, retained on 0.45 μm filters (C).
2. LMM-species: <8 kDa, obtained from ultrafiltration permeate (D).

Table 1
Samplings station and characteristics

Area	Station no.	Depth (m)	Latitude (N)	Longitude (E)	Sample category	Sampling depth (m)	Temperature (°C)	Salinity (‰)	pH	Alkalinity (mg l^{-1} HCO_3^-)	TSM (mg l^{-1})
Yenisey	3	17	72°56.00	80°31.80	Surface, mixing zone	1	10.5	4.4	7.69	49.94	2.9
	4	22	71°05.50	83°06.20	Surface, fresh water	1	13.8	<0.1	7.86	64.43	3.0
	8	28	70°04.10	83°03.90	Surface, fresh water	1	14.4	<0.1	7.86	62.53	1.6
	8	28	70°04.10	80°31.80	Near bottom, fresh water	27.4	14.3	<0.1	7.64	63.29	3.5
	11	12	72°05.60	81°41.80	Surface, mixing zone	1	13	<0.1	7.87	51.9	2.9
	11	12	72°56.00	80°31.80	Near bottom, mixing zone	8.4	5.5	22.4	7.16	110.9	4.3
	16	28	71°41.70	83°31.20	Surface, fresh water	1	13.1	<0.1	7.81	62.1	3.7
	19	28	72°35.70	80°06.40	Surface, mixing zone	1	9.6	6.1	n.m.	56	3.9
	19	28	72°35.70	80°06.40	Pycnocline, mixing zone	3.5	n.d.	27.6	7.66	127.7	n.m.
Kara Sea	34	91	77°54.29	89°20.15	Near bottom, sea water	90	−1.4	34.3	n.m.	n.m.	1.3
	41	42	75°41.40	87°07.80	Surface, sea water	1	4	23.8	n.m.	n.m.	1.2
	46	323	77°55.43	75°57.35	Surface, sea water	1	4.2	26.4	7.9	118.6	1.6
	65	63	75°42.98	75°50.79	Pycnocline, mixing zone	15	4.2	28	7.87	125.1	n.m.
	67	49	75°14.65	73°45.78	Pycnocline, mixing zone	1	7.4	11.3	7.92	86.9	2.5
	68	31	74°35.05	72°14.97	Pycnocline, mixing zone	7	5.8	24.3	7.64	110.6	2.9
Ob	70	22	72°40.16	74°00.22	Surface, fresh water	1	9.2	0.9	7.46	42.3	11.8
	70	22	72°40.16	74°00.22	Pycnocline, mixing zone	7	6.2	29.9	7.41	130.01	12.5
	72	26	70°49.88	73°44.34	Surface, fresh water	1	11.5	<0.1	7.42	39.3	13.0
	73	15	68°54.89	73°39.99	Near bottom, fresh water	10	12.5	<0.1	7.64	53.8	11.8
	82	29	73°11.83	73°01.65	Surface, mixing zone	1	6.7	9.9	7.7	77.4	5.6
	82	29	73°11.83	73°01.65	Near bottom, mixing zone	22	−1.3	32.9	7.49	139.54	n.m.

TSM data obtained from [22].
n.m. = not measured.

3. Colloids: between < 0.45 μm and <8 kDa, obtained by difference between filtration (B) and ultrafiltration permeate (D).

Water samples (B and D) were reduced in volume (from about 200 L to about 5 L) by a chemical precipitation procedure onboard the ship, which includes the use of ^{242}Pu and ^{243}Am yield monitors and measures to ensure complete equilibration [43]. The resulting ~5 L slurries were taken to the home laboratory for further processing. Filter paper samples (C) were also transported to the home laboratory and ^{242}Pu tracer was added prior to ashing at 500 °C, digestion with aqua regia (3:1 mix of 12 M HCl and 14 M HNO_3), filtration of extracts and evaporation of filtrate to dryness. Following radiochemical separation and purification based on selective sorption on anion exchange resins (Dowex AG 1×8) to separate U and Am from Pu [44], Pu activities and isotope ratios were determined by AMS which enabled us to measure the Pu concentrations and Pu isotope ratios of the low level samples with high sensitivity. Iron(III) nitrate was added to the Pu eluate from the anion exchange chromatography and the solutions evaporated, then ashed at 500 °C to give final preparates for AMS measurements as Fe_2O_3 (2 mg Fe), with ^{242}Pu:Fe atom ratios between 10^{-10} and 10^{-9} by design. AMS measurements were carried out during several runs in 2002 and 2003 using the 14UD tandem accelerator at the Australian National University, Canberra, full details of the analytical technique have been reported elsewhere [8,45]. The three Pu isotopes (mass 242, 240 and 239) were counted sequentially using repeat cycles for each sample [8,46]. In-house standards and certified reference material for Pu and Pu isotope ratios (UKAEA No. UK Pu 5/92138) were determined for each run. $^{239+240}$Pu activities in the samples were calculated from the measured 239/242 and 240/242 atom ratios. The 242/239 isotope ratio precision of the

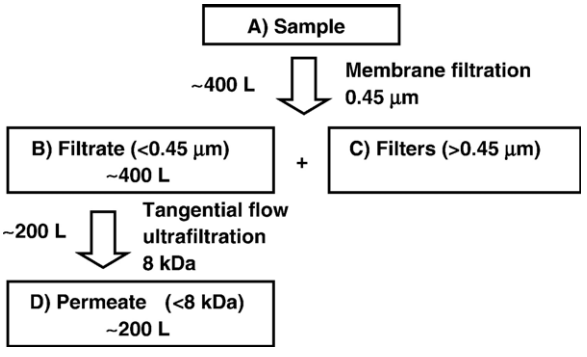

Fig. 2. Schematic outline of the size fractionation processes used in the present study.

CRM was 0.7% (relative standard deviation, $n=5$). Determination of an in-house standard over four runs in a three-month period showed reproducibility to within 5%. The accuracy of 242/239, 240/242 and 239/240 ratios was within at least 5% of the reference values, hence errors on sample measurements were dominated by counting statistics.

4. Results and discussion

4.1. Concentrations and size distribution

The results from AMS Pu analysis of the size fractioned samples are given in Table 2. The atom concentrations of ^{240}Pu and ^{239}Pu have been converted to activity concentrations (mBq m^{-3}) and summed to facilitate comparison with previous work.

Both the concentration of $^{239+240}$Pu and ^{240}Pu/^{239}Pu atom ratios show considerable variability between samples, exceeding factors of 10. The highest $^{239+240}$Pu concentrations were found in the estuary mixing zones and the lowest in the fresh water end member of the Ob and in the open Kara Sea (Fig. 3).

The concentration of ^{239,240}Pu in 0.45 μm filtered water in the lower parts of the Yenisey and Ob river systems ranged from 6.5 to 29 mBq/m^3 and 2.6 to 40.6 mBq/m^3, respectively, somewhat higher than in the open Kara Sea (2.4–7.7 mBq/m^3). These results are within the same range as previously published data based on α-spectrometry [47,48], although Josefsson reported concentrations as high as 90 mBq/m^3 ^{239,240}Pu outside the mouth of Yenisey during early summer flooding [34].

Estimates of annual input of ^{239,240}Pu to the Kara Sea from the rivers can be made using mean annual discharges from the Ob (429 km^3 yr^{-1}) [14] and Yenisey (625 km^3 yr^{-1}) [40] as well as mean total concentrations (sum of >0.45 μm and <0.45 μm fractions) obtained in the present work from the river and estuary sampling stations; 18.5±15.3 mBq m^{-3} (Ob; $n=5$) and 20.1±7.7 mBq m^{-3} (Yenisey; $n=9$). This gives an estimated annual ^{239,240}Pu flux to the Kara Sea of about 8±7 GBq and 13±5 GBq from the Ob and Yenisey, respectively. However, these numbers are probably underestimated as they do not take into account the observed strong interannual and intra-seasonal variability of the fresh water discharges [22], which influences the input of radionuclides associated with colloidal and particulate matter from the rivers [20]. It should also be noted that peak releases of suspended matter by the rivers during flooding is probably more pronounced than the fresh water discharge itself because the spring break-up of river ice is usually a very turbulent event [49].

According to Vakulovsky [50], the Yenisey has received a total of about 5 GBq $^{239+240}$Pu through controlled releases from the KMCIC during 1994–2000, with the highest annual discharges reported for 1999 (1.9 GBq) and 2000 (1 GBq). This is low compared with our estimates, suggesting that there must be other sources to the Kara Sea besides the controlled releases, for example, transport of global fallout from the catchment or from other sources within the catchment area of the Yenisey.

A large fraction of the Pu in the fresh water section of the rivers was associated with particulate material (45–76%), whereas in the estuaries and the Kara Sea, Pu was predominantly present in dissolved forms, i.e. colloids and LMM species. The colloidal fraction (i.e., 8 kDa–0.45 μm) in the rivers ranged from 25 to 78% and 24 to 73% in the Yenisey and the Ob, respectively, with the highest concentrations being seen in bottom waters. In Kara Sea surface waters influenced by the Yenisey (St. no. 41), the low colloidal fraction (8%) of Pu may be explained by the long travel distance from the river mouth, whereas in the pycnocline Kara Sea waters influenced by the Ob (St 68) 53% was associated with colloids. In general, the colloidal fraction in the study area was significantly higher than previously reported for the Arctic seas [51]. High levels of colloidal Pu (59–62% in the river, 17–41% in the mixing zone) have also been observed in the River Rhone [38]. Thus, colloids are important transport agents for river transported Pu.

LMM Pu-species varied from 16 to 39% in the fresh water end members of the rivers, 13–56% in the estuaries, and 40–67% in the Kara Sea. Data suggests an estuary maxima for LMM Pu-species, similar to those observed for most trace metals in estuaries [52–54]. To conclude, the main difference in Pu-speciation between sites was the overall predominance of particulate forms in the river waters and dissolved forms in the Kara Sea. Although the data shows evidence of a change in concentration, speciation and isotope ratios along the river transects, no correlation could be observed with salinity (expected to be indicative of dilution) or location. Additional confounding factors such as the relatively high concentrations in estuarine bottom waters, and contributions from resuspension and/or catchment run-off, probably override any dilution or salinity effect on concentration or speciation. Hence, the data do not provide the spatial resolution required to see systematic changes or correlations.

4.2. ^{240}Pu/^{239}Pu atom ratios

Atom ratios of ^{240}Pu/^{239}Pu show significant variations between sites and, more importantly, between size fractions. The results show a clear difference in

Table 2
Results from AMS measurements

Sample depth (m)	Sal. (psu)	>0.45 μm		<0.45 μm		<8 kDa		Sum fractions
		$^{240+239}$Pu (mBq m^{-3})	^{240}Pu/^{239}Pu	$^{240+239}$Pu (mBq m^{-3})	^{240}Pu/^{239}Pu	$^{240+239}$Pu (mBq m^{-3})	^{240}Pu/^{239}Pu	$^{240+239}$Pu (mBq m^{-3})
Yenisey River and Estuary and Eastern Kara Sea (influenced by the Yenisey)								
St. 8 (70°04.10′N, 83°03.80′E, depth 28 m)								
1	<0.1	4.6±0.3	0.120±0.023	14.4±0.4	0.062±0.006	n.m.	n.m.	19.0±0.5
27.4	<0.1	1.2±0.1	0.177±0.024	8.7±0.6	0.116±0.019	3.9±0.2	0.115±0.015	9.9±0.6
St. 4 (71°05.50′N, 83°06.20′E, depth 22 m)								
1	<0.1	5.2±0.5	0.202±0.044	6.5±0.3	0.212±0.024	2.4±0.2	0.093±0.028	11.7±0.6
St. 16 (71°41.70′N, 83°31.20′E, depth 28 m)								
1	<0.1	23.7±3.3	0.077±0.031	7.4±0.2	0.138±0.011	n.m.	n.m.	31.1±3.3
St. 11 (72°05.60′N, 81°41.80′E, depth 12 m)								
1	<0.1	1.9±0.3	0.238±0.076	17.0±0.8	0.069±0.010	n.m.	n.m.	18.9±0.8
8.4	22.4	3.0±0.2	0.108±0.019	29.0±0.5	0.032±0.002	4.0±0.3	0.130±0.025	32.0±0.5
St. 19 (72°35.70′N, 80°06.40′E, depth 28 m)								
1	6.1	3.5±0.5	0.208±0.062	16.3±0.4	0.094±0.007	n.m.	n.m.	19.8±0.6
4.7	27.6	2.9±0.1	0.151±0.016	12.0±0.5	0.138±0.013	8,2±0.3	0.108±0.011	14.8±0.5
St. 03 (72°56.00′N, 80°31.80′E, depth 17 m)								
1	4.4	6.3±1.2	0.297±0.109	16.8±0.8	0.188±0.019	n.m.	n.m.	23.2±1.4
St. 41 (75°41.40′N, 87°07.80′E, depth 42 m)								
1	23.8	2.6±1.2	n.d.	7.7±0.3	0.104±0.010	6.9±0.3	0.073±0.009	10.3±1.2
St.34 (77°54.29′N, 89°20.15′E, depth 90 m)								
90	34.3	n.d.	n.d.	6.4±0.2	0.158±0.010	n.m.	n.m.	>6.4
Ob River and Estuary and Kara Sea north of the Ob River (influenced by the Ob)								
St. 73 (68°54.894′N, 73°39.99′E, depth 15 m)								
10	<0.1	n.m	n.m	4.4±0.2	0.114±0.012	3.4±0.1	0.069±0.014	>4.4
St. 72 (70°49.88′N, 73°44.34′E, depth 26 m)								
1	<0.1	2.9±0.2	0.219±0.034	2.6±0.2	0.123±0.030	0.9±0.1	0.027±0.020	5.5±0.3
St. 70 (72°40.16′N, 74°00.22′E, depth 22 m)								
1	0.9	9.1±0.4	0.197±0.019	11.1±0.4	0.052±0.007	n.m.	n.m.	20.2±0.6
7	29.9	6.3±0.3	0.172±0.018	10.9±1.2	0.125±0.014	5.1±0.3	0.056±0.011	17.2±1.3
St. 82 (73°11.83′N, 73°01.65′E, depth 29 m)								
1	9.9	2.6±0.2	0.120±0.018	4.0±0.2	0.096±0.011	n.m.	0.030±0.007	6.6±0.2
22	32.9	2.7±0.1	0.147±0.024	40.6±0.9	0.019±0.003	8.8±0.4	0.077±0.009	43.3±0.9
St. 68 (74°35.05′N, 72°14.97′E, depth 31 m)								
7	24.3	0.6±0.2	0.165±0.064	7.7±0.3	0.073±0.009	3.3±0.3	0.143±0.031	8.3±0.4
St. 67 (75°14.65′N, 73°45.78′E, depth 49 m)								
1	11.3	5.8±1.6	n.m.	n.m.	n.m.	n.m.	n.m.	>5.8
St. 65 (75°42.98′N, 75°50.79′E, depth 63 m)								
15	28	0.5±0.1	0.142±0.089	2.4±0.3	0.231±0.056	n.m.	0.132±0.023	2.9±0.3
St. 46 (77°55.43′N, 75°57.35′E, depth 323 m)								
1	26.4	0.4±0.1	0.265±0.078	2.9±0.2	0.095±0.014	n.m.	n.m.	3.3±0.2

n.a. = not applicable, n.d. = not detected, n.m. = not measured. Errors are based on counting statistics (±1 SD). Pu activity concentrations refer to AMS measurements. Total activities (^{239}Pu+^{240}Pu) were calculated from the measured 239/242 and 240/242 atom ratios, using half-lives of 24 119 yrs for ^{239}Pu, 6564 yrs for ^{240}Pu, and 3.76×10^5 yrs for ^{242}Pu.
^{239,240}Pu activity concentrations, ^{240}Pu/^{239}Pu atom ratios and % distribution of total ^{239,240}Pu activity within size fractions. Sampling station data listed according to increasing latitude.

^{240}Pu/^{239}Pu atom ratios between the different Pu size fractions. At most stations a rather low ratio was observed for the dissolved fractions (colloids and LMM), while the ratio was higher for the particulate fraction (Fig. 3). This difference was observed in both rivers, but most pronounced in the Ob where LMM (<8 kDa) was significantly lower (paired *t*-test, $P=0.02$, $n=4$) than the particulate fraction. Thus, the ^{240}Pu/^{239}Pu atom ratios indicate that particulate Pu (mean for all stations 0.18±0.06) is global fallout related and that LMM Pu-species (mean Ob, 0.052± 0.023; mean Yenisey, 0.112± 0.015) originate from low atom ratio sources such as nuclear weapon production facilities or close-in/tropospheric fallout (Fig. 4).

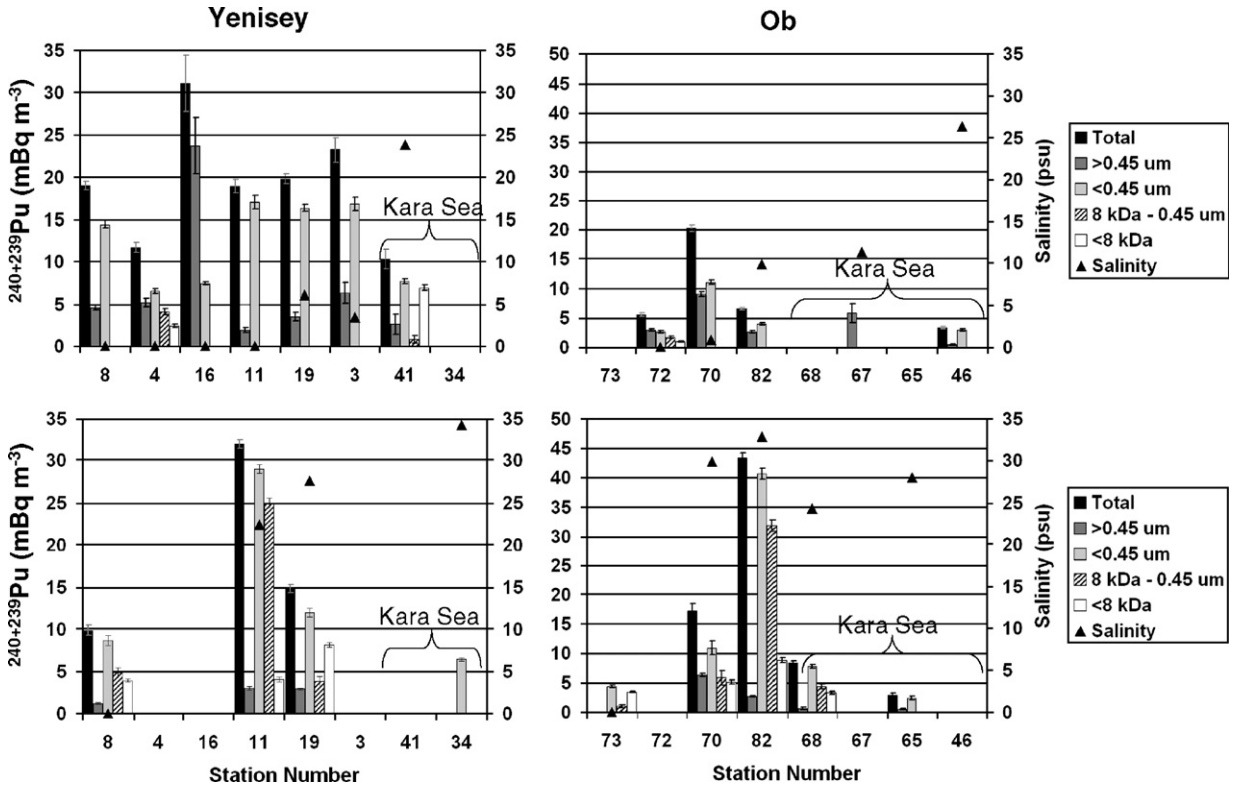

Fig. 3. ^{239,240}Pu concentrations (mBq m^{-3}) in obtained size fractions of surface (upper) and pycnocline and near bottom (lower) waters. Uncertainties given as 1 SD (n=3) or deviation from mean (n=2). Salinities (psu) are also shown. Note different left axes.

These findings imply that the speciation of global fallout derived Pu is different compared to Pu originating from low ^{240}Pu/^{239}Pu atom ratio sources. In particular, global fallout Pu appears to be particle-reactive, whereas the non-civil, non-global fallout Pu is more mobile. Variation in the ^{238}Pu/$^{239,\ 240}$Pu activity ratios with respect to Pu-speciation has also been observed by Mitchell and co-workers in the Irish sea, reporting a small, but significant difference between the mean ^{238}Pu/$^{239,\ 240}$Pu activity ratios in the filtered and suspended particulate fractions at locations well removed from Sellafield (Western/North Western Irish Sea) [55]. This was related to the existence of two separate source-terms: i.e., resuspension of mainly older Pu (discharged in earlier years from Sellafield and characterised by lower ratios) from western Irish Sea sediments, and desorption of a mixture of older and more recently discharged Pu from eastern Irish Sea sediments (characterised by somewhat higher ratios).

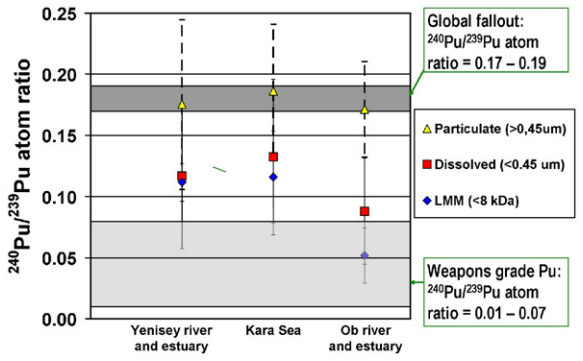

Fig. 4. Pooled ^{240}Pu/^{239}Pu atom ratios in the particulate, dissolved and LMM fractions in the Yenisey (river and estuary; particles n=9; dissolved n=9; LMM n=4), Kara Sea (particles n=4; dissolved n=5; LMM n=3) and Ob (river and estuary; particles n=5; dissolved n=6; LMM n=5), respectively.

In the present study, an input from global fallout derived Pu would be expected along the whole of the river catchment, and includes terrestrial erosion and surface run-off. Weapons grade Pu sources include the Krasnoyarsk site for Yenisey and Mayak, Tomsk and the Semipalatinsk test site within the Ob catchment area. Several researchers have suggested that run-off from the Semipalatinsk test site to the neighbouring Irtysh River could supply low ^{240}Pu/^{239}Pu atom ratio Pu from low yield nuclear explosions to the Irtysh–Ob river system which ultimately discharges into the Arctic Ocean [2,7]. The $^{239+240}$Pu concentration (2.0± 0.2 mBq/L) recently measured in

filtered Irtysh river water collected near the Semipalatinsk test site [56] is a factor of 100 higher than our data from the lower Ob. The $^{238}Pu/^{239+240}Pu$ activity ratio was ~ 0.15, indicating an expected non-global fallout influence. However, whichever source is responsible for the low isotope ratios seen in the river and estuary waters, they all suggest a long-range transport of relatively stable LMM Pu-species.

4.3. Water versus previously reported sediment data

Because the isotope ratios of Pu in deposited sediments is expected to reflect the observed isotope ratios of particulate Pu in the water column, the $^{240}Pu/^{239}Pu$ ratios observed in Ob and Yenisey water are compared with those reported for bottom sediments collected by us from the same area [36]. The sedimentation of suspended matter from the Yenisey is low until it reaches the main deposition area just north of Sibiryakova Island (Fig. 1) [22]. AMS measurements of sediment cores from this main deposition area show that the Pu deposited is mainly derived from global fallout with $^{240}Pu/^{239}Pu$ atom ratios of 0.16±0.01 [36]. Outside the main deposition area south of Sibiryakova Island, however, the $^{240}Pu/^{239}Pu$ atom ratios of surface sediments were significantly lower, ranging between 0.09 and 0.13 in the estuary and 0.05 and 0.12 in the fresh water end-member of the river [36], with the lower values dominating close to the KMCIC facility. Thus, the global fallout dominated particulate Pu appears to be the source of most of the Pu in the main sediment deposition area. This seems to be the case also for the Ob, although it exhibits a depositional regime different to the Yenisey. Indeed, sedimentation in the Ob takes place all the way along the Ob Bay, through the river mouth and north to 76°N [22], an area where Pu in (recently deposited) surface sediments has been reported to be of global fallout origin [36]. As the suspended particulate material (SPM) discharge is almost three times higher in the River Ob than the Yenisey [57], the Ob clearly carries a greater input of suspended sediments from terrestrial erosion and run-off. These high loads of suspended sediments may, if predominantly from areas subjected to inputs of global fallout, dilute any influence of a low $^{240}Pu/^{239}Pu$ atom ratio source in suspended and deposited sediments.

4.4. Long-range transport of Pu

Low $^{240}Pu/^{239}Pu$ atom ratio signals were observed in Kara Sea surface waters (<0.45 μm and LMM) even at two of our farthest sampling points, St. no. 46 (77°55.43′ N, 75°57.35′E) and St. no. 41 (75°41.40′N, 87°07.80′E), several hundred km from the estuaries. Our AMS measurement data are supported by the fact that the surface water samples featured relatively low salinity and high DOC concentrations reflecting riverine influences. The high salinity bottom water sample (<0.45 μm) at a third station in the Northern Kara Sea (St. no. 34; 77°54.29′N, 89°20.15′E) did not significantly deviate from the global fallout signal. In addition, indications of Pu from non-European nuclear fuel reprocessing sources have been reported in the Laptev Sea which is connected to the north eastern parts of the Kara Sea [4]. Thus, a significant amount of mobile Pu-species is apparently transported long distances with Kara Sea surface waters.

5. Conclusions

At site size fractionation of Pu in water samples from the lower parts of the Ob and Yenisey Rivers, their estuaries and the adjacent Kara Sea revealed that $^{240}Pu/^{239}Pu$ atom ratios in dissolved forms (<0.45 μm), in particularly for LMM Pu-species (<8 kDa), were lower than global fallout, reflecting a low burn-up or non-civil Pu, such as weapons grade Pu, as a key source. This observation was especially pronounced in the Ob where the $^{240}Pu/^{239}Pu$ atom ratio for LMM Pu (0.027–0.077) was significantly lower than the global fallout ratio. For Pu associated with particles the $^{240}Pu/^{239}Pu$ atom ratio could not be distinguished from global fallout. This finding reflects the fact that global fallout derived Pu and the low $^{240}Pu/^{239}Pu$ atom ratio sources of Pu exhibit different environmental behaviour, indicating that the Pu derived from the global fallout source is particle-reactive, whereas the non-civil, non-global fallout sources of Pu are more mobile. The signal from low $^{240}Pu/^{239}Pu$ atom ratio Pu was observed in fractioned samples (<0.45 μm) as far north as 78°N in the Kara Sea, indicating that mobile riverine Pu can be transported far into the Arctic Ocean.

The very low concentrations of Pu previously reported for the study area were confirmed by our data. Pu was predominantly present in dissolved forms; however, the Pu colloidal fraction in the rivers and estuaries of Ob and Yenisey and the adjacent Kara Sea was much larger than previously reported for the Arctic. For size fractioned water samples with ultra low Pu concentrations, AMS has proved to be a powerful analytical technique. The results should improve the understanding of Pu speciation in estuaries, and be of relevance for impact assessments in case of accidental releases from nuclear installations in the Urals and Siberia.

Acknowledgements

We gratefully acknowledge the support provided by the European Commission (contract no. ICA2-CT-2000-10008) and the Norwegian Research Council (project no. 141479/720). We thank the captain and the crew of the R.V. Akademik Boris Petrov for their excellent help during the expedition and we gratefully acknowledge R. Stein and O. Stepanets for organizing the expedition. The analytical work by M.N. Pettersen and H. Mobbs, UMB is also appreciated.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.epsl.2006.08.023.

References

[1] K. Aagaard, E.C. Carmack, The role of sea ice and other fresh water in the Arctic circulation, J. Geophys. Res. 94 (1989) 14485–14498.
[2] F.L. Sayles, H.D. Livingston, G.P. Panteleyev, The history and source of particulate Cs-137 and Pu-239, Pu-240 deposition in sediments of the Ob river delta, Siberia, Sci. Total Environ. 202 (1997) 25–41.
[3] S.M. Vakulovsky, I.I. Kryshev, A.I. Nikitin, Y.V. Savitsky, S.V. Malyshev, E.G. Tertyshnik, Radioactive contamination of the Yenisei River, J. Environ. Radioact. 29 (1995) 225–236.
[4] L.W. Cooper, T. Beasley, K. Aagaard, J.M. Kelley, I.L. Larsen, J.M. Grebmeier, Distributions of nuclear fuel-reprocessing tracers in the Arctic Ocean: indications of Russian river influence, J. Mar. Res. 57 (1999) 715–738.
[5] J.K. Cochran, S.B. Moran, N.S. Fisher, T.M. Beasley, J.M. Kelley, Sources and transport of anthropogenic radionuclides in the Ob River system, Siberia, Earth Planet. Sci. Lett. 179 (2000) 125–137.
[6] T.C. Kenna, F.L. Sayles, The distribution and history of nuclear weapons related contamination in sediments from the Ob River, Siberia as determined by isotopic ratios of plutonium and neptunium, J. Environ. Radioact. 60 (2002) 105–137.
[7] T.M. Beasley, J.M. Kelley, K.A. Orlandini, L.A. Bond, A. Aarkrog, A.P. Trapeznikov, V.N. Pozolotina, Isotopic Pu, U, and Np signatures in soils from Semipalatinsk-21, Kazakh Republic and the Southern Urals, Russia, J. Environ. Radioact. 39 (1998) 215–230.
[8] D.H. Oughton, L.K. Fifield, J.P. Day, R.C. Cresswell, L. Skipperud, M.L. Di Tada, B. Salbu, P. Strand, E. Drozcho, Y. Mokrov, Plutonium from Mayak: measurement of isotope ratios and activities using accelerator mass spectrometry, Environ. Sci. Technol. 34 (2000) 1938–1945.
[9] J.M. Kelley, L.A. Bond, T.M. Beasley, Global distribution of Pu isotopes and Np-237, Sci. Total Environ. 238 (1999) 483–500.
[10] B. Salbu, Speciation of radionuclides in the environment, in: R.A. Meyers (Ed.), Encyclopedia of Analytical Chemistry, John Wiley & Sons Ltd, Chichester, 2000, pp. 12993–13016.
[11] AMAP, AMAP assessment report: Arctic pollution issues, Arctic Monitoring and Assessment Programme, Oslo, Norway, 1998.
[12] ESTABLISH, Estuarine specific transport and biogeochemically linked interactions of selected heavy metals and radionuclides, NRPA, Final Report for the EU Project ICA-CT-2000-10008, 2004 Østerås.
[13] O.V. Stepanets, R. Stein, Introduction, in: R. Stein, O.V. Stepanets (Eds.), Scientific Cruise Report of the Kara-Sea Expedition 2001 of RV "Akademik Boris Petrov": The German–Russian Project on Siberian River Run-off (SIRRO) and the EU project "ESTABLISH", Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, 2002, pp. 1–2.
[14] V.V. Gordeev, River input of water, sediment, major ions, nutrients and trace metals from Russian territory to the Arctic Ocean, in: E.L Lewis (Ed.), The Freshwater Budget of the Arctic Ocean, Kluwer Academic Publisher, 2000, pp. 297–322.
[15] J.D. Milliman, Flux and fate of fluvial sediment and water in coastal seas, in: R.F.C. Mantoura, J.-M. Martin, R. Wollast (Eds.), Ocean Margin Processes in Global Change, Wiley, Berlin, 1991, pp. 69–89.
[16] S.A. Telang, R. Pocklington, A.S. Naidu, E.A. Romankevich, I.I. Gitelson, M.I. Gladyshev, E.T. Degens, S. Kempe, J. Rickey, Carbon and mineral transport in major North American, Russian Arctic, and Siberian rivers: the St. Lawrence, the Mackenzie, the Yukon, the Arctic Alaskan, the Arctic Basin rivers in the Soviet Union and the Yenisei, Biogeochemistry of Major World Rivers, SCOPE, , 1991, pp. 75–104.
[17] J.D. Milliman, R.H. Meade, World-wide delivery of river sediment to the oceans, J. Geol. 91 (1983) 1–21.
[18] I.H. Harms, U. Hübner, J.O. Backhaus, M. Kulakov, V.V. Stanovoy, O.V. Stepanets, L.A. Kodina, R. Schlitzer, Salt intrusions in Siberian river estuaries: observations and model experiments in Ob and Yenisei, in: R. Stein, K. Fahl, D.K. Fütterer, E.M. Galimov, O.V. Stepanets (Eds.), Siberian River Run-off in the Kara Sea: Characterisation, Quantification, Variability, and Environmental Significance, Elsevier, Amsterdam, 2003, pp. 281–308.
[19] V.I. Burenkov, A.P. Vasilkov, Influence of river discharge on spatial-distribution of hydrological characteristics in the Kara Sea, Okeanologiya 34 (1994) 652–661.
[20] I.H. Harms, M.J. Karcher, D. Dethleff, Modelling Siberian river runoff-implications for contaminant transport in the Arctic Ocean, J. Mar. Syst. 27 (2000) 95–115.
[21] B. Beeskow, V. Rachold, Geochemical processes in the Yenisei River and Estuary, in: R. Stein, K. Fahl, D.K. Fütterer, E.M. Galimov, O.V. Stepanets (Eds.), Siberian River Run-off in the Kara Sea: Characterisation, Quantification, Variability, and Environmental Significance, Elsevier, Amsterdam, 2003, pp. 125–148.
[22] A.C. Gebhardt, B. Gaye-Haake, D. Unger, N. Lahajnar, V. Ittekkot, Recent particulate organic carbon and total suspended matter fluxes from the Ob and Yenisei Rivers into the Kara Sea (Siberia), Mar. Geol. 207 (2004) 225–245.
[23] Joint Norwegian–Russian expert group for investigation of radioactive contamination in the Northern areas, Sources contributing to radioactive contamination of the Techa River and areas surrounding the "Mayak" production association, Urals, Russia, Norwegian Radiation Protection Authority, Østerås, 1997.
[24] M.I. Vorobiova, M.O. Degteva, D.S. Burmistrov, N.G. Safronova, V.P. Kozheurov, L.R. Anspaugh, B.A. Napier, Review of historical monitoring data on Techa River contamination, Health Phys. 76 (1999) 605–618.
[25] AMAP, AMAP assessment 2002: radioactivity in the Arctic, Arctic Monitoring and Assessment Programme, Oslo, Norway, 2004.
[26] V. Tcherkezian, B. Galushkin, T. Goryachenkova, L. Kashkarov, A. Liul, I. Roschina, O. Rumiantsev, Forms of contamination of

the environment by radionuclides after the Tomsk Accident (Russia, 1993), J. Environ. Radioact. 27 (1995) 133–139.
[27] R.D. Waters, K.L. Compton, V.M. Novikov, F.L. Parker, Releases of radionuclides to surface waters at Krasnoyarsk-26 and Tomsk-7, International Institute for Applied Systems Analysis, RR-99-3, Laxenburg, Austria, 1999.
[28] V.G. Linnik, J.E. Brown, M. Dowdall, V.N. Potapov, V.V. Surkov, E.M. Korobova, A.G. Volosov, S.M. Vakulovsky, E.G. Tertyshnik, Radioactive contamination of the Balchug (Upper Yenisey) floodplain, Russia in relation to sedimentation processes and geomorphology, Sci. Total Environ. 339 (2005) 233–251.
[29] A. Bolsunovsky, Artificial radionuclides in aquatic plants of the Yenisei River in the area affected by effluents of a Russian plutonium complex, Aquat. Ecol. 38 (2004) 57–62.
[30] A. Bolsunovsky, L.G. Bondareva, Tritium in surface waters of the Yenisei River basin, J. Environ. Radioact. 66 (2005) 285–294.
[31] A.Y. Bolsunovsky, A.I. Ermakov, B.F. Myasoedov, A.P. Novikov, A.I. Sobolev, New data on the content of transuranic elements in bottom sediments of the Yenisei River, Dokl. Earth Sci. 387 (2002) 971–974.
[32] A.Y. Bolsunovsky, V.O. Tcherkezian, Hot particles of the Yenisei River flood plain, Russia, J. Environ. Radioact. 57 (2001) 167–174.
[33] F.V. Sukhorukov, A.G. Degermendzhi, A. Bolsunovsky, V.M. Belolipetskii, L.G. Kosolapova, Distribution and Migration Behaviours of Radionuclides in the Yenisei River Floodplain, SB RAS Publishers, Novosibirsk, 2004 1–286 pp.
[34] D. Josefsson, Anthropogenic radionuclides in the Arctic Ocean—distribution and pathways. PhD thesis, Lund University, (1998).
[35] L.W. Cooper, J.M. Kelley, L.A. Bond, K.A. Orlandini, J.M. Grebmeier, Sources of the transuranic elements plutonium and neptunium in arctic marine sediments, Mar. Chem. 69 (2000) 253–276.
[36] L. Skipperud, D.H. Oughton, L.K. Fifield, O.C. Lind, S. Tims, J. Brown, M. Sickel, Plutonium isotope ratios in the Yenisey and Ob estuaries, Appl. Radiat. Isotopes 60 (2004) 589–593.
[37] A.B. Kersting, D.W. Efurd, D.L. Finnegan, D.J. Rokop, D.K. Smith, J.L. Thompson, Migration of plutonium in ground water at the Nevada Test Site, Nature 397 (1999) 56–59.
[38] F. Eyrolle, S. Charmasson, Importance of colloids in the transport within the dissolved phase (<450 nm) of artificial radionuclides from the Rhone river towards the Gulf of Lions (Mediterranean Sea), J. Environ. Radioact. 72 (2004) 273–286.
[39] B. Salbu, D.H. Oughton, Analytical strategies for the determination of physico-chemical forms of trace elements in natural waters, in: B. Salbu, E. Steinnes (Eds.), Trace Elements in Natural Waters, CRC Press, 1994, pp. 41–69.
[40] M.H. Dai, J.M. Martin, First data on trace-metal level and behavior in 2 major Arctic river–estuarine systems (Ob and Yenisey) and in the Adjacent Kara Sea, Russia, Earth Planet. Sci. Lett. 131 (1995) 127–141.
[41] M.H. Dai, K.O. Buesseler, J.M. Kelley, J.E. Andrews, S. Pike, J.F. Wacker, Size-fractionated plutonium isotopes in a coastal environment, J. Environ. Radioact. 53 (2001) 9–25.
[42] M. Krosshavn, H.E. Bjornstad, L. Engh, H.N. Lien, B. Salbu, Speciation of Cs-137 and Sr-90 in discharges from the pulp industry and the Marine recipient, J. Environ. Radioact. 32 (1996) 157–164.
[43] Q.J. Chen, Determination of Plutonium in Environmental Samples by Controlled Valence in Anion Exchange, Risø National Laboratory, 1991 RISØ-M-2856, Risø.
[44] A. Clacher, Development and application of analytical methods for environmental radioactivity. PhD. thesis, University of Manchester, (1995).
[45] L.K. Fifield, R.G. Cresswell, M.L. diTada, T.R. Ophel, J.P. Day, A.P. Clacher, S.J. King, N.D. Priest, Accelerator mass spectrometry of plutonium isotopes, Nucl. Instrum. Methods B 117 (1996) 295–303.
[46] D.H. Oughton, L. Skipperud, L.K. Fifield, R.G. Cresswell, B. Salbu, P. Day, Accelerator mass spectrometry measurement of Pu-240/Pu-239 isotope ratios in Novaya Zemlya and Kara Sea sediments, Appl. Radiat. Isotopes 61 (2004) 249–253.
[47] O.V. Stepanets, A. Ligaev, G. Solovjeva, A.P. Borisov, T.V. Danilova, A. Spitzy, H. Köhler, Role of suspended matter and dissolved organic substances in behaviour and migration of anthropogenic radionuclides in river-sea aquatic systems, Radiochemistry 45 (2003) 414–419.
[48] L. Leon Vintro, C.A. McMahon, P.I. Mitchell, D. Josefsson, E. Holm, P. Roos, Transport of plutonium in surface and sub-surface waters from the Arctic shelf to the North Pole via the Lomonosov Ridge, J. Environ. Radioact. 60 (2002) 73–89.
[49] S.L. Pfirman, H. Eicken, D. Bauch, W.F. Weeks, The potential transport of pollutants by Arctic Sea-Ice, Sci. Total Environ. 159 (1995) 129–146.
[50] S.M. Vakulovsky, Annual Report on ISTC Project 1404 — Estimation and Prediction of the Consequences for the Environment and Population of Radioactive Contamination of the River Yenisei by Discharges of the Krasnoyarsk Mining and Chemical Industrial Complex, Science and Production Association, TYPHOON, Obninsk, 2001.
[51] P.I. Mitchell, L. Leon Vintro, K.J. Smith, M. Sickel, S. Gerland, J.E. Brown, D.H. Oughton, B. Salbu, O.C. Lind, Size fractionation of plutonium in Arctic Waters and implications for its mobility, in: P. Strand, T. Jølle, Å. Sand (Eds.), Environmental radioactivity in the Arctic & Antarctic, NRPA, Østerås, 2002, pp. 39–42.
[52] G.E. Millward, Processes affecting trace-element speciation in estuaries — a review, Analyst 120 (1995) 609–614.
[53] G.E. Millward, A. Turner, Trace metals in estuaries, in: B. Salbu, E. Steinnes (Eds.), Trace Elements in Natural Waters, CRC Press, 1994.
[54] D.R. Ackroyd, A.J. Bale, R.J.M. Howland, S. Knox, G.E. Millward, A.W. Morris, Distributions and behavior of dissolved Cu, Zn and Mn in the Tamar Estuary, Estuar. Coast. Shelf Sci. 23 (1986) 621–640.
[55] P.I. Mitchell, O.M. Condren, L. Leon Vintro, C.A. McMahon, Trends in plutonium, americium and radiocaesium accumulation and long-term bioavailability in the western Irish Sea mud basin, J. Environ. Radioact. 44 (1999) 223–251.
[56] EU ADVANCE FINAL REPORT, Source-specific ecosystem transfer of actinides utilising advanced technologies, Contract FIGE-2000-00108, Dublin, 2004.
[57] V.V. Gordeev, J.M. Martin, I.S. Sidorov, M.V. Sidorova, A reassessment of the Eurasian river input of water, sediment, major elements, and nutrients to the Arctic Ocean, Am. J. Sci. 296 (1996) 664–691.