



The impact of the Russian oil industry on surface water quality (a case study of the Agan River catchment, West Siberia)

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Abstract

Water quality in the Agan River catchment (West Siberia, Russia) was assessed based on data obtained between 1993 and 2017 at 25 monitoring stations. The purpose of the research was to assess the impact of oil field development on the quality of surface waters. Monitoring stations were located in the oil fields characterized by various levels of impact, from “moderate” (number of wells < 0.5 per 1 km²) to “extreme” (number of wells > 1 per 1 km²). Comparisons with the thresholds indicated that metal (Ni, Hg Pb, Zn, Cu, Mn and Fe) concentrations exceeded the standard limits for fisheries in 10.8%, 14.5%, 22.3%, 24.7%, 54.7%, 88.6% and 99.2% of samples, respectively. The high contents of Mn, Fe and Cu can be generally regarded as the natural results of intensive leaching of elements from acid soils. The total petroleum hydrocarbons (TPH) value exceeds the threshold in 34.6% of samples. The water quality was estimated using the Canadian Council of Ministers of the Environment Water Quality Index (CCME WQI). The water quality of the Agan River catchment was classified as “poor” and “marginal”. The TPH values displayed a significant positive correlation with the density of wells and with the percentage of oil-contaminated lands. Positive correlations were found between Cl⁻ and the density of wells, the frequency of accidents and the area of contaminated lands. Trends of pollution are sensitive to changes of accident rate. The decrease in accident rate for the last decade resulted in declines in TPH and Cl concentrations.

Keywords West Siberia · Oil development · Hydrochemistry · Monitoring · River water quality · Trends of pollution

Introduction

The Agan River catchment (ARC) located within the West Siberian Plain, in the Khanty-Mansi Autonomous Okrug (KHMAO) according to the administrative division of Russia, is a region of intensive oil development. In 2019, the KHMAO produced about 236 million tons (6% of the World's crude oil). Past and recent mining and industrial activity in Siberia has resulted in the pollution of soils and water as well as damaging vegetation cover (Mueller et al. 2016). The following types of oil-related impacts on the environment are the most damaging: (1) infrastructure-related environmental impacts that lead to a destruction of soil cover and changes of hydrological regimes; (2)

ordinary environmental impacts caused by pollution during the extraction and transport of oil; (3) extraordinary environmental impacts caused by accidents and technogenic catastrophes; and (4) human impacts on ecosystems outside industrial areas (Groisman et al. 2013).

Oil development is the greatest contributor to point and non-point source pollution of stream waters in West Siberia (Moskovchenko et al. 2009; Soromotin 2011; Khoroshavin and Moiseenko 2014). Oil drilling rigs, wellhead equipment, industrial sites, motorized transport and pipelines are the main sources of pollution within this region (Opekunova et al. 2018). The relatively rapid pace of oil development has created large volumes of waste products including petroleum hydrocarbons, different forms of nitrogen, phosphorus, synthetic surfactants, particulate matter, chlorides and sulfates (Khoroshavin and Moiseenko 2014). Pipeline leakages and accidental oil spills are common problems in the petroleum industry (Jamrah et al. 2007). More than a half of currently operated Russian oil pipelines were designed for 20–25 years of service, which means that 80–90% of their service time has now elapsed (Slinko and Chernyanskii

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2007). As a result, accidents often occur along pipelines. According to official data sources, on average more than 2.5 thousand accidents per year occur in oil gathering systems within the Khanty-Mansi Autonomous Okrug (Soromotin 2011). In the early 2000s, between 700 and 840 thousand hectares of land were polluted by oil in the Northwest Siberia (IWACO 2001). Such factors have a strong direct impact on underground and surface water quality, ecological conditions and the quality of life. Thus, West Siberia is recognized as a “hot spot” of oil pollution (IWACO 2001; Hese and Schmullius 2009). Another matter of concern is increases in chloride concentrations in oilfield drainage waters resulting from the extraction of saline water from oil-bearing beds and its transfer onto the land surface (Moskovchenko et al. 2017).

There is an urgent need for improving water quality control and management within areas of oil production. During the Soviet period and early post-Soviet years, there was a sparse network of hydrochemical monitoring stations along West Siberian rivers. In 2003, the Regional Government of the KHMAO obliged oil companies to control water quality (Resolution 2003). Local programs for environmental monitoring of each oil field were adopted by the Environmental Control and Supervision Service (ECSS) of the KHMAO to obtain information on existing conditions and degrees of disturbance of ecosystems. Currently, such programs support the regular monitoring of water chemistry in about 800 streams and rivers, which drain the territory of 200 oil fields. The results of environmental monitoring within the Agan River catchment were used by us in the present article to evaluate the impact of oil development on surface water quality.

Study area

The Agan River is one of the longest (540 km) tributaries of the Ob River. The Agan River drains an area of more than 32,000 km² in the central part of the West Siberian Plain, within the administrative region of KHMAO (Fig. 1). Main tributaries of the Agan River include the rivers of Vat'egan (231 km), Amputa (152 km), Gun'egan (120 km), Negus'egan (95 km) and Lagrn'egan (80 km).

The Agan River catchment (ARC) is located in boreal latitudes (61.4–63.1° N) and generally characterized by a cold humid continental climate with a mean annual temperature of −4.1 °C. Average monthly temperatures range from −23 °C in January to +18 °C in July. A mean annual precipitation of 559 mm (approximately 36% of which is represented by snow) is recorded at the main meteorological station of Var'egan (Scientific 1998). The snow cover persists on the ground from late October to late April. Rivers

are covered with ice from mid-/late-November to May (Resources 1972).

The Agan River has a mean annual flow rate of 260 m³s^{−1} (Resources 1972). Within the ARC as well as other catchments in the taiga zone of West Siberia, river and stream waters originate from three main sources: (1) snowmelt, (2) runoff from surrounding lands dominated by ombrotrophic peat bogs and coniferous forests and (3) groundwater discharge (Alekin 1970). Rivers are characterized by a high hydrologic diversity and a large flow variability on a seasonal timescale. An average snowmelt season streamflow equals about a half of the annual flow. The highest water level is recorded in June (23% of the annual flow) and the lowest water level—in March (2.5% of the annual flow). Water level fluctuations have an amplitude of more than 4.5 m (Ljozin 1999).

The geology is characterized by the predominance of Pleistocene and Holocene fluviolacustrine, glacial and glaciofluvial sediments. The watershed (divide) area is almost completely covered with natural (or insignificantly disturbed) vegetation such as coniferous forests with a predominance of *Pinus sibirica*, *Pinus sylvestris*, *Picea obovata* and *Betula pubescens*, dwarf shrub–sphagnum moss peatlands and sedge-moss swamps. Those ecosystems are very fragile, and their rehabilitation after disturbance takes a long time because of the cold climate (Shvidenko et al. 2013). Most common soil types include Gelic Podzoluvisols, Haplic Podzols and Fibric Histosols (FAO 1988).

The ARC is a low-populated area with a total of about 72,000 permanent inhabitants in 2019, corresponding to a population density of 2.3 inhabitants per km². Most inhabitants live in the towns of Raduzhnyi and Pokachi. Effluents from these two municipalities are sent to wastewater facilities. In addition, there are several indigenous settlements within the catchment. Most of these settlements discharge their sewage into rivers without any treatment.

There are many oil fields within the ARC. The oldest field of Aganskoye has a long history of oil production since 1966. Anthropogenic pressure on ecosystems within the catchment has significantly increased with the oil industry expansion after 1980. A total number of 44 oil fields with a total production of about 33 million tons/year were registered within the catchment as of 2019.

Materials and methods

Monitoring stations and data

Data on land use, land disturbance and water quality were obtained from the ECSS-KHMAO (Environmental Control and Supervision Service of the Khanty-Mansi Autonomous Okrug) database. River water parameters including the total

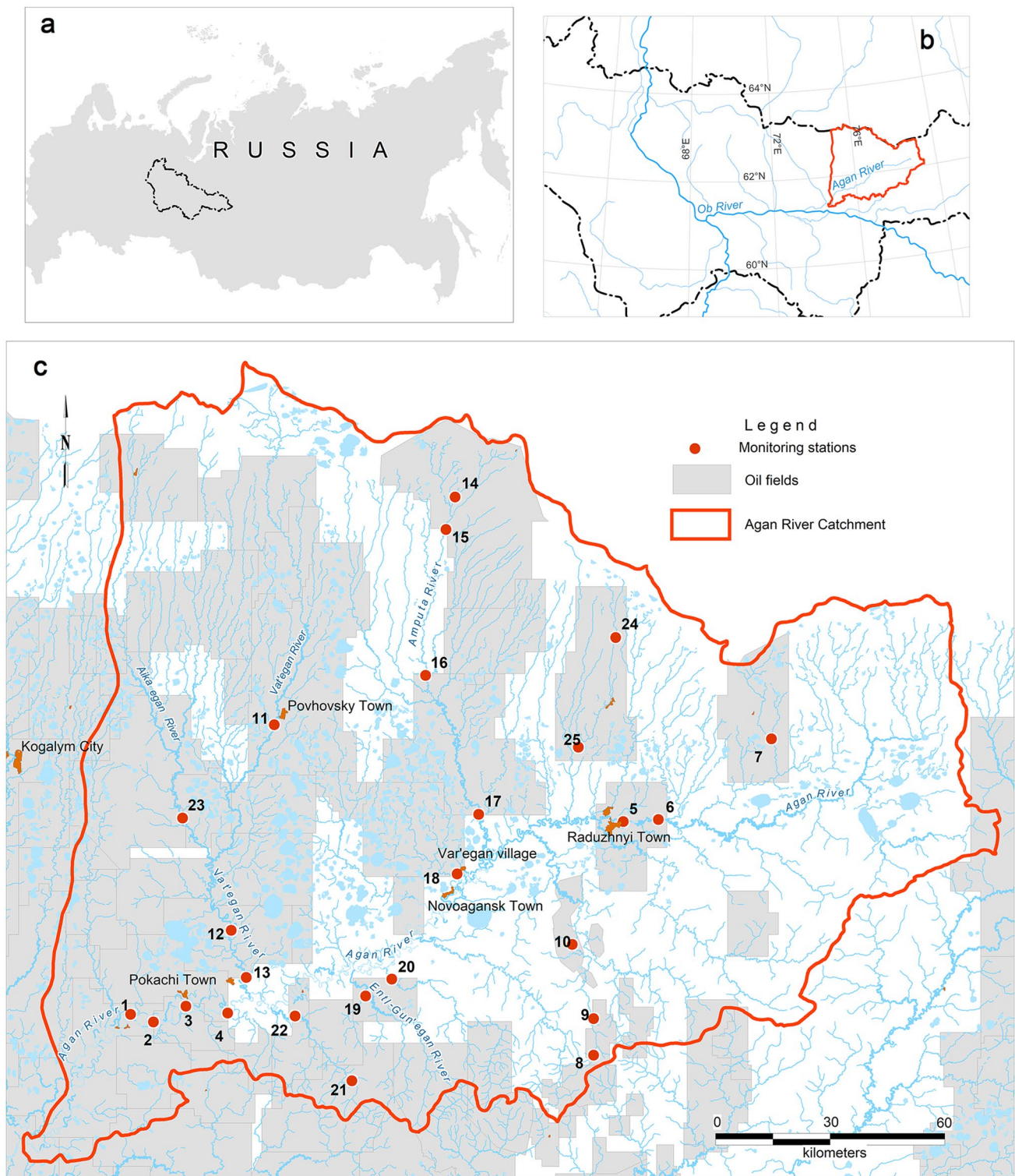


Fig. 1 The location of the Khanty-Mansi Autonomous Okrug (a); Agan River catchment (b); the hydrological network and monitoring stations (c)

petroleum hydrocarbons (TPH) and Cl^- concentrations were recorded at 25 monitoring stations (MS) during a period of 25 years, i.e., between 1993 and 2017, with more parameters

added to monitoring in 2006–2017. Each MS dataset contained at least three sampling events per year.

Monitoring stations were distributed throughout the ARC (Fig. 1). In particular, they were located along the main

channel of the Agan River (MSs 1–6) and its tributaries of Tagr'egan River (MS 7), Gun'egan River (8–10), Vat'egan River (11–13), Amputa River (14–17), Larkniegan River (18), Entl-Gun'egan River (19), Ai-Gun'egan River (20), On'egan-Vetlenya River (21, 22), Aika'Egan River (23) and Lagrn'egan River (24, 25) (Fig. 1). Water samples were collected at four seasonal stages of river dynamics over a year: (1) pre-ice (October–November), (2) ice (i.e., winter flow under ice, sampled in March–April), (3) meltflow (May–mid-July) and (4) summer baseflow (mid-July–September). Variations in timing of seasonal data collection at some monitoring stations were due to problems with traveling conditions in winter and spring, when it was often difficult to drive to monitoring stations.

Water samples were collected according to the Russian standards for sampling (GOST 2000). In the process of sampling, new plastic and glass bottles pre-washed in the laboratory were rinsed twice with river water prior to taking a water sample. Samples for trace element analysis were acidified to $\text{pH} < 2$ with about 2 mL ultra-pure HNO_3 . After collection, all samples were placed in a dark container. During summer periods, samples were placed in a cool box, with the temperature of $+4\text{ }^\circ\text{C}$. The samples were transported to the laboratory immediately after collection. Prior to analyses, water samples were filtered through 2- μm cellulose membrane filters.

Water quality assessments were based on analyzing 17 parameters as follows: pH, ammonium (NH_4^+), nitrate (NO_3^-), biological oxygen demand (BOD_{20}), chloride (Cl^-), sulfate (SO_4^{2-}), soluble reactive orthophosphate (PO_4^{3-} , referred to as “phosphates” in the text below), total petroleum hydrocarbons (TPH), phenols, dissolved Fe, Mn, Cu, Cr, Ni, Hg, Pb and Zn. All analyses were conducted in laboratories accredited by the Russian Federation Methods of analyses of water samples as listed in Table 1. The accuracy of determinations was verified using tests with standard solutions. The content of TPH was determined by infrared photometry in accordance with the environmental monitoring regulations certified by the regional government of the KHMAO (Regulations 2011).

Data analysis

The hydrochemical data were recorded and processed using statistical software packages of STATISTICA v.6.0 and MS Excel 2016. Values below detection limits were replaced by half of their limits (Fharnham et al. 2002). Descriptive statistics were calculated for dataset features. To meet the purpose of this research, the values obtained were compared with the guideline values of water quality set for fishery management (List 1999) and drinking water supply for public (WHO 2011). Then, the data were grouped by site and by season to determine spatial and temporal variations using graphical

Table 1 Analytical techniques and detection limits for physicochemical parameters of water quality

Parameter	Analytical technique	Unit	Detection limit
pH	Electrometric method	units of pH	0.1
NH_4^+	Photometric method	mg/l	0.05
NO_3^-	Ion chromatography	mg/l	0.1
PO_4^{3-}	Photometric method or ion chromatography	mg/l	0.05
BOD_{20}	20-Day BOD test	mg/l	0.375
Cl^-	Ion chromatography	mg/l	0.2
SO_4^{2-}	Ion chromatography	mg/l	0.2
TPH	Infrared photometry	mg/l	0.005
Fe	Atomic absorption	mg/l	0.05
Mn	Atomic absorption	mg/l	0.01
Cu	Atomic absorption	mg/l	0.001
Ni	Atomic absorption	mg/l	0.001
Pb	Atomic absorption	mg/l	0.0002
Zn	Atomic absorption	mg/l	0.001
Hg	Atomic absorption	$\mu\text{g/l}$	0.01

techniques such as boxplots. Data from each MS were divided into four seasonal periods: pre-ice (October–November), ice (December–April), meltflow (May–mid-July) and baseflow (mid-July–September).

The water quality was assessed using the Water Quality Index (WQI) calculated according to the Canadian environmental quality guidelines for the protection of aquatic life (CCME 2001) and specific guidelines for water quality assessment in terms of that index (Tyagi et al. 2013). Our reasons for choosing the CCME WQI were as follows: flexibility of selection criteria, tolerance for missing data and similarity between natural conditions of Canada and Siberia.

The values of CCME WQI were calculated using the following equation (CCME 2001; Lumb et al. 2006; Bilgin 2018):

$$\text{CCME CWQI} = 100 - \left(\frac{\sqrt{F_1^2 + F_2^2 + F_3^2}}{1.732} \right) \quad (1)$$

where

$$F_1 = \left(\frac{\# \text{ failed parameters}}{\text{total number of tests}} \right) \times 100 \quad (2)$$

$$F_2 = \left(\frac{\# \text{ failed tests}}{\text{total number of tests}} \right) \times 100 \quad (3)$$

$$F_3 = \left(\frac{\text{nse}}{0.01\text{nse} + 0.01} \right) \quad (4)$$

$$nse = \left(\frac{\sum \text{excursion}}{\text{total number of tests}} \right) \tag{5}$$

$$\text{Excursion} = \left(\frac{\text{failed test value}}{\text{guidance value}} \right)^{-1} \tag{6}$$

Computed values of CCME WQI were ranked into five categories characterizing water quality as follows: “poor” (WQI value 0–44), “marginal” (45–64), “fair” (65–79), “good” (80–94) and “excellent” (95–100) (CCME 2001).

In order to identify natural and human-induced changes in water chemistry, Agan River catchment was subdivided into 18 sub-basins using the data on local hydrography and topography. For the analysis, we selected ten sub-basins where monitoring stations are located. The parameters of landscape structure and human impact intensity were analyzed within ten sub-basins. The GIS data on land use, numbers of exploratory and development wells within oil fields, frequency of accidents, areas of disturbed and contaminated lands were provided by the ECSS of the KHMAO.

The land use data were grouped into three categories: forests, wetlands (bogs, mires and lakes) and disturbed lands (urban and rural settlements, industrial estates, pipelines, oil

wells, roads, etc.). Then, the level of ecosystem disturbance caused by oil development within sub-basins was estimated on the basis of the disturbed land area and the number (spatial density) of exploratory and development wells (Recommendations 2010). The analyzed sub-basins were ranked into three categories with moderate, high and extreme levels of disturbance, which were characterized by disturbed land areas of < 1%, 1–1.5% and > 1.5%, respectively, and oil well numbers of < 0.5, 0.5–1 and > 1 per 1 km², respectively.

Within each sub-basin, we calculated summary statistics of water quality variables from monitoring stations and established correlations between the water quality variables and the land disturbance parameters. Concentrations of TPH, trace metals, Cl⁻, PO₄³⁻, SO₄²⁻, NH₄⁺ and NO₃⁻ in water samples from polluted and non-polluted sites varied greatly, which resulted in a non-normal distribution. Spearman’s rank correlation coefficient was used to estimate strength and direction of relationships between variables.

Details of land use and disturbances within the whole Agan River catchment and its sub-basins are presented in Table 2. Wetlands, forests and disturbed lands occupy 64%, 34.7% and 1.3% of the total ARC area, respectively. There are about 19 thousand wells within the ARC, with their highest numbers found in the Vat’egan River sub-basin

Table 2 The land use and disturbances within the whole ARC and its ten sub-basins

Objects	Monitoring stations	Drainage area, km ²	Wetland %	Forest %	Disturbed %	Disturbances within (sub)basins			Level of disturbance
						Number of wells	Number of accidents 2006–2016	Area of polluted lands, ha	
ARC (whole basin)	1–4	32,140	64.0	34.7	1.3	18,955	1402	3919	High
Agan River (upper reaches)	5 and 6	1820	33.6	65.4	1.0	3001	718	59.8	High
Tagr’egan River	7	1104	44.2	54.7	1.2	741	89	112.1	High
Gun’egan River	8–10	1708	38.5	60.9	0.6	683	108	47.2	Moderate
Vat’egan River	11–13, 23	7379	53.7	44.6	1.7	6196	39	392	Extreme
Amputa River	14–17	4307	41.9	57.5	0.6	1834	108	136	Moderate
Larkniegan River	18	96	84.3	15.1	0.6	0	0	0	Moderate
Entl—Gun’egan River	19	750.4	28.0	70.6	1.4	212	18	35.6	High
Ai-Gun’egan River	20	664	25.4	74.5	0.1	25	4	2.59	Moderate
On’egan-Vetlenya River	21 and 22	575.5	16.3	81.8	1.9	760	12	12.6	Extreme
Lagrn’egan River	24 and 25	867.5	48.0	49.1	2.9	1194	141	76.3	Extreme

(particularly, oil fields of Povkhovsky and Vat'egansky with 2300 and 2100 wells, respectively, MSs 11 and 23).

Results and discussion

General hydrochemistry

Summary statistics for the surface water geochemistry dataset (minimum, maximum and median) are given in Table 3. Median values for each monitoring station are presented in Table 4. We used the median instead of the mean because it is resistant to and minimally affected by outliers (Kauffman and Belden 2010).

The pH values ranged from acidic (3.7) to alkaline (8.5), with the median value of 6.6. The 57.5% of the surface water samples were within the WQL range of 6.5–8.5 (Table 3). The median pH values of water samples from all monitoring stations, except 18, were within the interval of 6.3–6.9. Such waters could be described as moderately acidic to neutral, which is typical for surface waters of West Siberia (Uvarova 2000; Shvartsev et al. 2012). The sample from MS 18 had the lowest pH value, probably, due to the influence of acidic waters seeping from peatland. Wetlands (bogs, mires and lakes) occupy 84.3% of this sub-basin area (Table 2). The physicochemical properties of peatland waters of West Siberia include high acidity, high organic matter content, low

content of dissolved oxygen, low salinity and high oxygen demand (Moiseenko et al. 2013).

Ammonium (NH_4^+) concentrations ranged from 0.05 to 4.95 mg/l with the median value of 0.51 mg/l. Median ammonium levels in samples from over half of the monitoring stations exceeded the Russian threshold (0.5 mg/l) for fisheries. Ammonium concentrations in the ARC waters were significantly higher than those in the Ob River (0.21–0.47 mg/l) (Uvarova 2000). It is generally known that NH_4^+ concentrations in northern rivers depend on the local landscape and soil cover structure. The high concentrations of NH_4^+ recorded in the ARC waters could be linked to the accumulation of NH_4^+ in Histosols and Gelic Podzoluvisols. It is known that ammonium is actively produced in soils with a low redox potential (Nikanorov et al. 2010). NH_4^+ concentrations increase as a function of peatland percentage (Lepisto et al. 2004). According to Meybeck (1982), concentrations of ammonium in surface waters of background ecosystems of the world have a mean value of 0.015 mg/l, but a maximal value of 0.14 mg/l has been recorded in unpolluted streams of Alberta (Canada). In boreal landscapes, waters tend to have an increased ammonium content as a result of anoxic acidic conditions that have an inhibitory effect on nitrification in peatlands (Sikora and Keeney 1983) and/or non-effective retention of NH_4^+ by the soil (Lepisto et al. 2004). Therefore, high contents of ammonium in the ARC waters can be partly attributed to natural environmental conditions.

Table 3 Statistics summary of the ARC surface water chemical dataset in comparison with WQLs

Parameter	Unit	Period of sampling	<i>n</i>	Min	Max	Median	WQL ^a	PPWQL ^b (%)	WHOst ^c	PPWHOst ^d (%)
pH	units of pH	2006–2017	911	3.7	8.5	6.6	6.5–8.5	42.5	–	–
NH_4^+	mg/l	2006–2017	727	0.05	4.95	0.51	0.5	50.3	–	–
NO_3^-	mg/l	2006–2017	840	0.1	10.43	0.4	40	0	50	0
BOD_{20}	mg/l	2006–2017	685	0.383	10.0	2.26	3	8.0	–	–
PO_4^{3-}	mg/l	2006–2017	739	<0.05	1.3	0.14	0.2	31.0	–	–
Cl^-	mg/l	1993–2017	2440	0.50	1101	8.8	300	0.16	–	–
SO_4^{2-}	mg/l	2006–2017	861	0.22	14.26	1.1	100	0	–	–
TPH	mg/l	1993–2017	2484	0.005	2.2	0.040	0.05	34.6	–	–
Fe	mg/l	2006–2017	834	0.05	9.6	1.71	0.1	99.2	–	–
Mn	mg/l	2006–2017	806	<0.01	2.06	0.06	0.01	88.6	0.4	8.5
Cu	mg/l	2006–2017	784	<0.001	0.56	0.0012	0.001	54.1	2	0
Ni	mg/l	2006–2017	832	<0.001	0.04	0.005	0.01	10.8	0.07	0
Pb	mg/l	2006–2017	821	<0.0002	0.05	0.0025	0.006	22.3	0.01	1.2
Zn	mg/l	2006–2017	827	<0.001	1.93	0.0058	0.01	24.7	–	–
Hg	μg/l	2006–2017	781	<0.01	0.634	0.005	0.01	14.5	6	0

^aWQL Water quality limits for fishery are adopted from the State Committee of the Russian Federation for Fisheries (List 1999)

^bPercentage proportion (%) of water samples exceeding water quality limits for fishery

^cWHOst World Health Organization Guideline values for chemicals that are of health significance in drinking-water (2011)

^dPercentage proportion (%) of water samples exceeding World Health Organization standards

Table 4 Median values of measured surface water parameters (mg/l, pH = units of pH)

MS	pH	NH ₄ ⁺	NO ₃ ⁻	BOD ₂₀	PO ₄ ³⁻	Cl ⁻	SO ₄ ²⁻	TPH	Fe	Mn	Cu	Zn
1	6.91	0.56	0.20	2.24	0.15	12.9	1.1	0.025	1.6	0.040	0.0016	0.0059
2	6.68	0.84	0.16	2.33	0.18	10.1	5.0	0.06	1.9	0.050	0.0015	0.0062
3	6.60	0.77	0.17	2.44	0.19	14.8	1.0	0.04	3.0	0.065	0.0015	0.006
4	6.69	0.58	0.25	2.38	0.18	11.9	1.0	0.036	2.4	0.076	0.002	0.006
5	6.51	0.43	0.60	1.70	0.25	6.2	1.0	0.04	3.5	0.290	0.0005	0.008
6	6.50	0.46	0.55	1.70	0.23	5.0	1.0	0.04	3.3	0.245	0.0005	0.009
7	6.70	0.41	0.40	1.75	0.11	5.0	1.0	0.034	2.6	0.200	0.0005	0.007
8	6.50	0.61	0.33	1.40	0.10	7.1	2.0	0.03	0.6	0.040	0.002	0.016
9	6.40	0.50	0.29	1.73	0.10	12.6	2.0	0.035	0.5	0.050	0.0025	0.012
10	6.40	0.42	0.35	2.13	0.27	5.8	0.6	0.01	1.6	0.066	0.0022	0.0077
11	6.38	0.41	0.60	2.81	0.04	12.0	5.0	0.05	1.4	0.028	0.001	0.008
12	6.56	0.27	0.14	2.37	0.22	11.6	0.9	0.024	1.8	0.040	0.0011	0.0043
13	6.35	0.24	0.18	2.43	0.11	10.9	0.9	0.024	1.7	0.039	0.002	0.004
14	6.41	0.25	0.10	2.51	0.03	5.0	5.0	0.033	1.9	0.005	0.0005	0.001
15	6.44	0.25	0.11	2.59	0.03	5.0	5.0	0.03	2.0	0.005	0.0008	0.0025
16	6.70	0.35	0.40	1.80	0.12	5.0	1.0	0.025	2.0	0.120	0.0007	0.006
17	6.61	0.37	0.35	1.90	0.12	5.0	1.0	0.025	1.8	0.110	0.0005	0.0051
18	5.80	0.68	0.31	2.85	0.03	0.8	0.3	0.01	0.5	0.014	0.0008	0.0038
19	6.60	0.59	0.40	2.50	0.33	1.9	0.7	0.01	1.2	0.070	0.0019	0.0071
20	6.70	0.65	0.46	2.42	0.36	1.1	1.1	0.01	1.4	0.070	0.0019	0.007
21	6.76	0.96	0.34	2.10	0.08	10.9	2.4	0.028	1.5	0.044	0.0006	0.009
22	6.68	0.75	0.17	2.52	0.23	5.0	5.0	0.024	3.2	0.039	0.0026	0.0013
23	6.50	0.57	0.69	2.85	0.12	9.1	5.0	0.05	1.2	0.014	0.0008	0.005
24	6.50	1.15	0.21	2.20	0.15	7.4	0.5	0.025	1.6	0.054	0.001	0.002
25	6.65	1.05	0.32	1.70	0.11	26.4	0.5	0.025	1.8	0.139	0.001	0.0043

However, there was also a man-made contribution to the increase in ammonium concentrations, which was detected by analyzing the distribution of values across monitoring stations (Table 4). Maximal ammonium concentrations (1.05–1.15 mg/l) were detected at MSs 24 and 25, probably due to an input of anthropogenically polluted waters, judging from a high percentage of disturbed lands (Table 2). High concentrations of ammonium were also found at MSs 2,3 and 18, located downstream from settlements (Fig. 1). Ammonium contents in waters within sub-basins had a positive correlation ($r=0.59$) with higher percentages of disturbed lands, but the relationship with percentages of wetlands was insignificant ($r=0.01$). It is known that NH₄⁺ serves as an indicator parameter for serious water quality problems such as the presence of untreated sewage (Groeschke et al. 2017). Increased ammonium concentrations in studied samples were probably connected with domestic waste disposal into rivers from towns and villages including housing estates for personnel of the oil production industry. There was a common tendency for an increase in the ammonium concentrations in West Siberian rivers that correlates with population growth and oil industry development. For example, comparison of data from the periods of 1981–1990 and 1991–2000 showed that ammonium concentrations

increased by 1.2 times in the Ob River and almost doubled in the Pur and Taz rivers (Nikanorov et al. 2010).

Nitrate (NO₃⁻) concentrations in the ARC waters ranged from 0.1 to 10.43 mg/l, with a median value of 0.4 mg/l. Therefore, ammonium nitrogen prevailed over nitrate nitrogen compounds in most rivers of the ARC. A similar trend was reported by Nikanorov et al. (2010), i.e., the prevalence of ammonium over nitrate nitrogen compounds is a typical characteristic of waters draining from peatlands in West Siberia, which also implies the prevalence of ammonification over nitrification. It is known that nitrate concentration in acidic bog water is very low, as the biological synthesis of nitrates (nitrification) is suppressed (Gashkina 2011). In peatlands, nitrogen of nitrate compounds is either consumed by growing plants or removed through microbial reduction or denitrification. Such biogeochemical reactivity predetermines low NO₃⁻-N concentrations in peatland waters (Gorham et al. 1984; Lepisto et al. 2004).

Nitrate concentrations in rivers of the ARC were higher than those in the Ob River (0.05–0.33 mg/l) (Uvarova 2000). It is established that agriculture is the main source of nitrogen in surface waters of boreal regions (Evans et al. 2014; Varanka and Hjort 2017). Agriculture within the ARC is limited to small herds of reindeer bred by local people,

particularly, in the Var'egan–Novoagansk area (MS18). The median value of NO_3^- concentration at MS18 was below the average for the ARC; therefore, herd sizes of up to several thousand reindeer did not cause nitrate runoff to rivers. The other source of nitrates is sewage from towns and villages. Indeed, highest median values were recorded in the vicinity of Raduzhnyi and Povhovsky towns (MS 5 and 11, respectively) and an extremely disturbed oil development site (MS 23) (Table 4). Probably, nitrates were discharged with waste from housing estates of oil industry employees. However, the nitrate concentrations in all rivers of the ARC were below the Russian threshold of nitrate concentration in surface waters (40 mg/l).

It has been found that forest cutting can lead to nutrient losses from soils within catchments (Vuorenmaa et al. 2002). In our study, there was no correlation between nitrate concentrations and disturbed land areas ($r = -0.05$). Probably, disturbed land areas were too small to affect hydrochemical parameters of the biogeochemical cycle of nitrogen and the mobility of organic compounds and their derivatives. Increased concentrations of nitrate were found within areas of local pollution sources.

Phosphate (PO_4^{3-}) concentrations in river waters varied from 0.05 to 1.3 mg/l, with a median value of 0.14 mg/l. Comparing the recorded PO_4^{3-} concentrations in water with the Russian water quality standards (GOST 1977), rivers of the ARC can be subdivided into “moderately polluted” (0.04–0.3 mg/l) and “strongly polluted” (> 0.3 mg/l). About 31% of the analyzed samples had phosphate concentrations that exceeded the Russian standard for fishery (0.2 mg/l).

It is generally known that sources of phosphorus compounds in river water include phosphates leached from soils and products of microbiological decomposition of plant and animal residues. Sewage containing synthetic detergents with phosphates is an important man-made source in towns and villages. So, phosphates come into rivers from both non-point and point sources. A high phosphate concentration in river water may result from the predominance of acidic soils in surrounding landscapes. The rate of dissolution of phosphate minerals increases with decreasing soil pH (Bolan and Hedley 1990). Histosols are the most acidic soils; however, there was no positive correlation between wetland areas (including bogs, mires and lakes) and phosphate concentrations in river waters; instead, there was a negative correlation ($r = -0.36$). Varanka and Hjort (2017) also revealed a negative correlation between total phosphorus concentrations in surface waters and the percentage of lakes within catchments. Such a negative correlation established by us within the ARC showed that the rate of phosphate release from peaty soils was lower than that from mineral soils, which had higher contents of soluble phosphorus compounds. The highest phosphate concentrations in water were recorded at MSs 19 and 20 located in areas dominated by mineral soils.

Bayley et al. (1985) showed that phosphorus concentrations in water columns increased due to the increased solubility of phosphorus under reducing conditions. Therefore, leaching of phosphates is most intensive in acid gley soils such as Gelic Podzoluvisols.

An average content of PO_4^{3-} in the Ob River is estimated at 0.2 mg/l (Shvartzev et al. 1996) and its range is determined at 0.06–0.27 mg/l (Uvarova 2000). Therefore, phosphate concentrations in rivers of the ARC were generally lower than those in the Ob River, which has its upper reaches within the steppe zone with a very low percentage of bogs. This fact has confirmed the above conclusion about the negative correlation between the concentration of phosphates in river waters and the percentage of wetlands within basins.

The highest median values of PO_4^{3-} concentrations (above the Russian fishery-related threshold) were found in samples from MSs 5, 6, 10, 12, 19, 20 and 22 located in the lower reaches of rivers. Likewise, median phosphate concentrations increased from the upper to the lower reaches of the Amputa River (MSs 14–17) and the Gun'egan River (MSs 8–10) (Tab. 4). In the On'egan–Vetlenia River, median phosphate concentrations were 0.08 and 0.23 mg/l for the upper and lower reaches, respectively. It was previously noted that phosphorus concentrations in rivers generally increased with runoff from land (Tortorelli and Pickup 2006). It can be concluded that the content of PO_4^{3-} in water increases as a result of the interaction of river water with bedrock and soils. Low contents of phosphates in the upper reaches of rivers are associated with the dominance of peat bogs on surrounding lands, which minimize the contact between rainwater and bedrock.

Recorded values of biological oxygen demand (BOD_{20}) varied between 0.38 and 10 mg O_2 /l. According to the Russian water quality standards (GOST 1977), river water samples were categorized into groups with the following percentages: 35.5% “clean” ($\text{BOD}_{20} < 2$), 63.2% “moderately polluted” ($\text{BOD}_{20} 2\text{--}4$) and 1.3% “strongly polluted” ($\text{BOD}_{20} > 4$). Highest median values of BOD_{20} were recorded at MSs 11, 18 and 23. Large amounts of biologically degradable compounds could come from tributaries polluted with sewage from the nearby Povhovsky town and the Var'egan village. High values of BOD_{20} were periodically observed at MS 4 located on the river below the town of Pokachi. Thus, BOD values depended on the presence of sewage-type effluents from urban/rural settlements. An increase in BOD values commonly occurs due to population growth and economic and urban development (Tsuzuki 2013).

Salinization caused by sodium chloride water seepage from oil-bearing beds onto the land surface is one of the main forms of pollution within the oil development areas of West Siberia (Moskovchenko et al. 2017). The process of surface water salinization in West Siberia was first

described by Mikhailova et al. (1988), who found a considerable increase in the concentration of Cl^- in water of the Ob River in 1970–1980. Later studies (Moskovchenko et al. 2009) showed that some rivers and lakes within the Samotlor oil field had extremely high (> 1000 mg/l) chloride concentrations. Among dissolved solids, Cl^- is the easiest to interpret because of its conservative nature and limited number of potential sources (Grasby 1997). The concentration of Cl^- in precipitation is low, with the median value of 1.4 mg/l (Moskovchenko and Babushkin 2012), and neither bedrock nor till contain saliferous rocks within the ARC, so there are no significant natural sources of Cl^- . Man-made sources include the salt spread onto roads as an antifreeze, which is used only in the towns of Pokachi and Raduzhniy, with insignificant impact on surface waters. Therefore, surface water salinization results mainly from drilling activities, saline water leakage from injection wells and brine spillages.

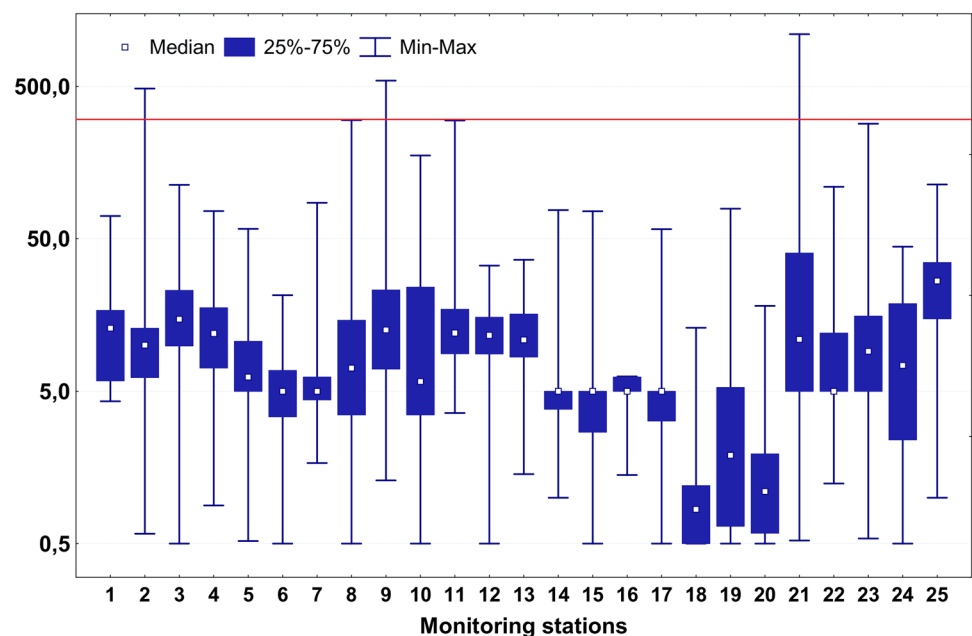
The concentration of chloride in the ARC waters ranged from 0.5 to 1101 mg/l, with a median value of 8.8 mg/l. The upper and lower quartiles were 5.0 and 16.6 mg/l, respectively. Only 0.16% of samples exceeded the 300 mg/l (limit for fisheries). Thus, extreme salt contaminations occurred only locally and temporarily within the ARC. However, in cases of extreme contamination by salt, Cl^- concentrations were more than ten times higher than the background level (≤ 5 mg/l) in surface waters of the KHMAO region (Moskovchenko et al. 2017). Maximum median values of 26.4 and 14.8 mg/l were recorded at MSs 25 and 3, respectively (Fig. 2). Generally, chlorides exhibited a wide concentration range, which may be attributed to accidents such as pipeline failures.

Sulfate (SO_4^{2-}) concentrations ranged from 0.22 to 14.26 mg/l, with a median value of 1.1 mg/l. All the values were below the limit of 100 mg/l, according to the Russian fishery-related standards (List 1999). Sulfate concentrations in rivers of the ARC were consistently lower than those in the Ob River [with a mean SO_4^{2-} concentration of 2.3–6.4 mg/l (Uvarova 2000)] as well as in the Vatinsky Egan River [with a mean SO_4^{2-} concentration of 0.8–4.4 mg/l (Moskovchenko et al. 2009)]. Therefore, sulfate contents in surface waters of the ARC were low and ecologically benign. Such levels were very close to the median value of sulfate concentration (1.0 mg/l) in melted snow within the whole KHMAO region (Moskovchenko and Babushkin 2012). This could be indicative of a high significance of meltwater runoff to rivers of the ARC and a weak interaction between atmospheric precipitation and frozen soils during snowmelt in spring (Alekin 1970). It should be mentioned that a low buffer capacity of soft waters of the ARC rivers predetermines their tendency for acidification, despite the low content of sulphates in precipitation.

In our previous study (Moiseenko et al. 2013), acidification of surface waters in the West Siberia caused by their man-made contamination by sulfates is mentioned. However, in a more recent study (Moiseenko et al. 2017) it is concluded that sulfates of anthropogenic origin have a very insignificant contribution to the acidification of surface waters in the West Siberia, because gaseous emissions from oil production in this region are low in sulfur.

Hydrocarbons have received much attention as important components of organic inputs that often have toxic, mutagenic and carcinogenic properties (Zhang et al. 2007). In the study area, water contamination by the total petroleum

Fig. 2 Box–whisker plot of Cl^- concentration values (1993–2017), with Y axis in a log scale. In Russia, chloride in surface waters has the threshold of 300 mg/l (List 1999)



hydrocarbons may arise from various accidents including pipeline breaks, leakages from storage tanks and oil production wells. Recorded values of TPH varied from 0.005 to 2.2 mg/l, with a median value of 0.04 mg/l. During the observation period, 34.6% of the samples had TPH concentrations of more than 0.05 mg/l corresponding to the “polluted” category of surface waters. The level of TPH pollution in the ARC rivers was higher than that in the Ob River, where TPH concentrations were often (in 28% of tests taken in 1993–2013) above the standard limit established for fisheries (Moskovchenko and Babushkin 2017).

The highest median concentrations of TPH were recorded in the main channel of the Agan River (MS 2) and in the Vat’egan River (MSs 11 and 23) (Fig. 3). The latter was characterized by a high density of oil wells and a large area of polluted lands (Table 1). The Agan River receives wastewater from all oil fields within the basin. It is necessary to take into account a low self-purification capacity of Siberian rivers due to low water temperatures, which leads to an aggravation of anthropogenic impact (Shchur et al. 2003). In particular, a low self-purification capacity implies low rates of TPH breakup in contaminated water. However, the TPH content may decrease upon dilution by unpolluted water, which was observed at the relatively undisturbed site of MS 16, where the concentration of TPH was significantly lower than in both upstream and downstream positions (Fig. 4).

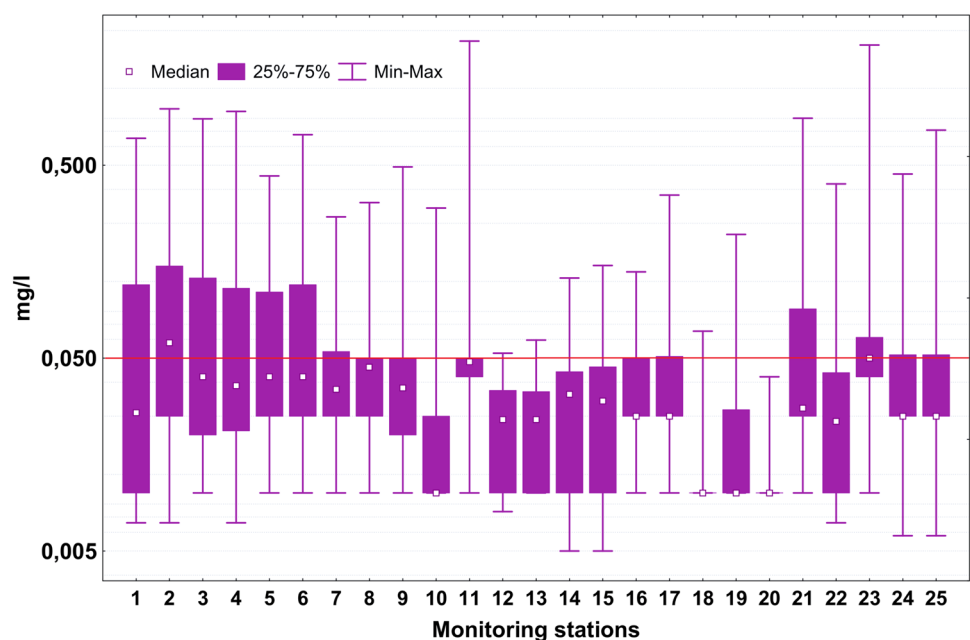
As shown in Fig. 4, more than 25% of the total number of samples had excessive concentrations of TPH within the oil fields with over 1000 development wells at densities more than 2 wells/km². It is established that in most cases the TPH come from diffuse sources of pollution, primarily, from local spills confined mostly to groups of oil wells and the main oil

pipeline (Khoroshavin and Moiseenko 2014). Even in the course of a normal, accident-free operation of oil production facilities, a weak contamination can occur due to the migration and diffusion processes of TPH that originate from the wellhead, mud pits and fuel storages (Panicheva et al. 2012).

Metal contents varied greatly due to significant differences in geological and ecosystem conditions within the ARC. In comparison with the Russian WQL, concentrations of Fe, Mn and Cu in most samples exceeded the standards for fisheries (Table 3). An extremely high concentration of Fe and Mn is one of the main hydrochemical characteristics of rivers in the north of West Siberia (Uvarova 2000). Iron concentrations ranged from 0.05 to 9.6 mg/l, with a median concentration of 1.7 mg/l. About 99% of the water samples had Fe values that exceeded the 0.1 mg/l threshold. The concentration ranges of Mn were 0.01–2.06 mg/l and exceeded the standards for fisheries in more than 88% of samples (Table 3). The concentrations of Fe and Mn were much higher than their world average values of 0.04 and 0.0082 mg/l, respectively (Martin and Meybeck 1979). The high content of Fe and Mn is caused by natural factors. It is established that Fe originates from soils in the area of northern peatlands (Muller and Tankere-Muller 2012). The behavior of Fe and Mn in soil is controlled by pH–Eh conditions (Kabata-Pendias 2011). Acid leaching of metals (Fe and Mn) is enhanced in surface waters of the West Siberia with waterlogged catchments owing to gleying processes (Moiseenko et al. 2013).

In addition to the reductive and acidic mobilization of Fe and Mn, dissolved organic matter originating from soils and peat may act as ligand and keep metals in solution. Regarding metals in general, seasonally changing saturation of soils

Fig. 3 Box–whisker plot of TPH levels (1993–2017). The maximal TPH concentration of 0.05 mg/l is set by the Russian fishery-related standards (List 1999)



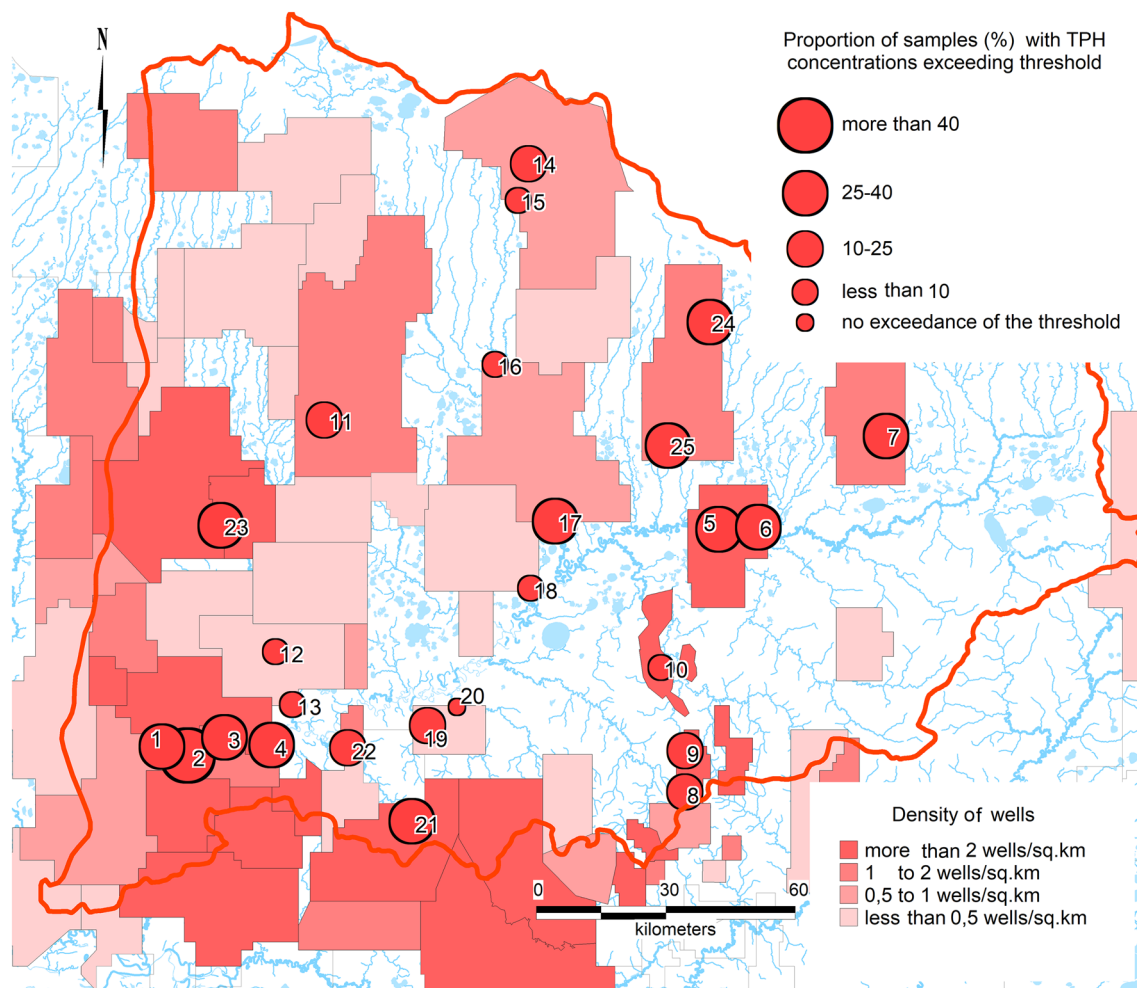


Fig. 4 The spatial distribution of TPH values higher than the threshold (0.05 mg/l)

with water often support mobilization of metals. The highest median Fe and Mn content (3.2–3.3 and 0.25–0.29 mg/l, respectively) was recorded at MS 5 and 6 (Agan River, Var'yoganskoe oil field). The maximum contents of Fe and Mn were observed in sub-basins, where the proportion of forests in the landscape structure was great and the proportion of bogs was relatively small (Table 1). Perhaps, the main reason for the intense influx of Fe and Mn into rivers in these sub-basins is a more intense interaction of precipitation with mineral matter of soils, while in sub-basins where bogs predominate, spring runoff occurs on the upper surface of thawed ombrotrophic peat without interaction with the mineral layers of the soil.

Concentrations of Pb and Ni were higher than the world average values (0.001 and 0.0022 mg/l respectively, according to Martin and Meybeck (1979) (Tab. 3). These data suggest that soils within the ARC undergo intense chemical weathering due to high concentrations of organic acids and low pH. Despite the low temperatures that inhibit the process of chemical weathering, the high content of organic

acids makes the metals highly mobile. Concentrations of Hg were below the detection limit (0.01 $\mu\text{g/l}$) in 50% of samples. An increase in Hg concentration was not observed in the oil fields with a high level of disturbance.

Many chemical parameters showed distinct seasonal patterns. Seasonal variations in precipitation, surface runoff, groundwater flow, interception and abstraction strongly affect river discharge and consequently the concentrations of chemical compositions of river water (Vega et al. 1998; Pejman et al. 2009; Garizi et al. 2011). As it can be seen in Fig. 5, higher values of ammonium, TPH chlorides, phosphates, Fe, Mn, Cu and Zn were observed in the ice season and lower values in the meltflow season. The dilution due to snowmelt is caused by a low content of major ions and metals in the snow as evident from the monitoring data collected in the region (Moskovchenko and Babushkin 2012). Seasonal changes in the concentration of chemical components were less pronounced than runoff fluctuations. So, in the Agan River, water discharge in the period from April to June increased by 7.7 times from 95 to 730 m^3/s (Resources

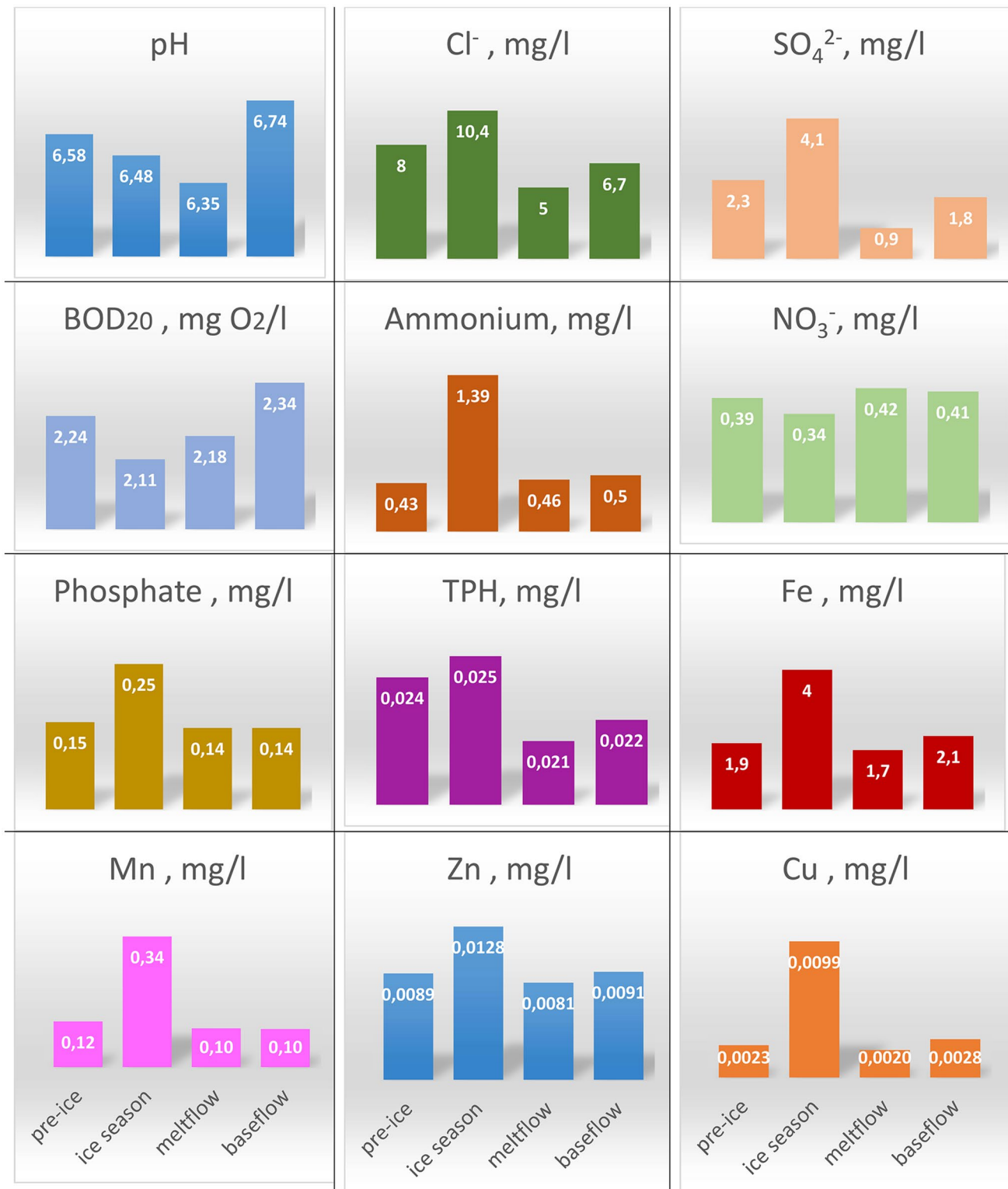


Fig. 5 Seasonal water quality parameters (median values)

1972), whereas the chloride content dropped by 1.9 times, from 13 to 7 mg/l. In meltwater, chloride has a mean concentration of 2.2 mg/l (Moskovchenko and Babushkin 2012).

Differences between meltwater and river water composition are explained by an intensive leaching during the thaw period as result of interaction between meltwater and soils.

High concentrations in winter can be attributed to the groundwater flow. As a result of the long contact time with the mineral substrate, groundwater contains significantly more soluble components. It was previously noted that the groundwater in West Siberia has a high concentration of metals (Slinko and Chernyanskii 2007). Conversely, nitrate concentrations were minimal in winter and maximal during the meltflow season. In the boreal river systems, a significant correlation usually exists between the $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ concentrations and discharge (Arvola et al. 2006, 2015), and highest concentrations of nutrients are found when the flow is increasing (Arheimer et al. 1996). In the Agan River and its tributaries, the maximal concentration of nitrates was also recorded during the meltflow season. The concentration of ammonium nitrogen was minimal during the meltflow season and maximal—under the ice. The lower 25% quartile of ammonium content exceeds the established standard for fisheries during the ice period. In winter, rivers have only influxes of groundwater from acidic reductive conditions that favor denitrification. In acid media, denitrification proceeds as a spontaneous result of purely chemical reactions, i.e., nitrates are reduced because of their unstable nature, i.e., high degree of oxidation (Gashkina 2011).

Minimum pH values were observed during snowmelt. This is attributed to the chemical properties of the snow cover in the region, particularly, weakly acidic reaction ($\text{pH}=5.4$) (Moskovchenko and Babushkin 2012). The pH level rises during the summer and autumn and then declines during the pre-ice, ice and meltflow seasons. The activation of biotic functions in the warm period causes an increase in pH values due to a decrease in the content of CO_2 spent for photosynthesis. The BOD_{20} values are minimal when the river is covered with ice and reach maximum values in the summer that is associated with the activation of aquatic biota.

Water Quality Index and the influence of oil development

Water quality along ARC streams was assessed using the CCME WQI. The values of the computed CCME WQI are presented in Table 5 which shows that during the study period the water quality was observed to vary between “poor” and “marginal” levels. It is evident that the low quality of surface water is caused, principally, by an extremely high content of Fe and Mn (Table 3). One of the processes which influences the water quality is the interaction between groundwater and soil minerals in the vadose zone. The concentration of dissolved metals is mainly controlled by factors resulting from the weathering, leaching and solubility of metal ions in groundwater, i.e., non-anthropogenic factors. However, a comparison of the CCME WQI values with

Table 5 Results of the calculated CCME WQI of the sampling point

MS	Level of disturbance (as in Table 1)	CCME WQI	Water quality according to CCME WQI
1	High	45	Marginal
2	High	33	Poor
3	High	41	Poor
4	High	38	Poor
5	High	40	Poor
6	High	37	Poor
7	High	47	Marginal
8	Moderate	48	Marginal
9	Moderate	47	Marginal
10	Moderate	47	Marginal
11	Extreme	40	Poor
12	Extreme	52	Marginal
13	Extreme	48	Marginal
14	Moderate	55	Marginal
15	Moderate	50	Marginal
16	Moderate	49	Marginal
17	Moderate	46	Marginal
18	Moderate	50	Marginal
19	High	45	Poor
20	Moderate	41	Poor
21	Extreme	43	Poor
22	Extreme	39	Poor
23	Extreme	38	Poor
24	Extreme	44	Poor
25	Extreme	45	Marginal

the level of disturbance showed evidence of anthropogenic contamination. MSs with “extreme” levels of disturbance in most cases demonstrate “poor” quality, whereas MSs with “moderate” levels of disturbance showed “marginal” water quality, with the exception of MS 20.

To assess the dependence of water quality parameters on disturbance indicators, a correlation analysis was performed. According to Table 6, there are statistically significant high positive correlations between TPH and Cl⁻ concentrations and the indices of anthropogenic disturbances. The other parameters (trace metals, nitrogen and phosphorus compounds, sulfates, pH values) did not show any statistically significant correlation.

Positively and significantly correlated values were found between TPH median annual values and the number or density of wells ($r=0.69$ and 0.70 respectively, $\alpha=0.05$), and between TPH median annual values and percentage of contaminated lands ($r=0.75$; $\alpha=0.05$). This indicates that the flow of oil into the rivers occurs both as a result of major accidents as well as minor spills at the drilling sites that were not considered by nature protection services. So, it was

Table 6 Statistical relationship between land disturbances and water chemistry in sub-basins of the ARC (Spearman's rank correlations)

Parameter	TPH median				Cl ⁻ median				TPH > WQL		CCME WQI	
	All seasons		Pre-ice		All seasons		Pre-ice		Meltflow	Baseflow		
	Ice	Meltflow	Ice	Meltflow	Ice	Meltflow	Ice	Meltflow				
Area of disturbed lands, %	0.28	0.19	0.26	0.27	0.61	0.55	0.56	0.77**	0.55	0.64*	0.29	-0.44
Number of wells in the sub-basin	0.70*	0.58	0.77**	0.62	0.82**	0.63*	0.62	0.79**	0.63*	0.57	0.44	-0.33
Density of wells in the sub-basin, wells / km ²	0.69*	0.62	0.72*	0.60	0.77**	0.72*	0.73*	0.89**	0.72*	0.83**	0.44	-0.35
Number of accidents	0.63	0.41	0.41	0.36	0.75*	0.77**	0.60	0.67*	0.77**	0.60	0.68*	-0.04
Density of accidents, acc/km ²	0.60	0.27	0.17	0.27	0.61	0.64*	0.55	0.47	0.64*	0.57	0.78**	-0.09
Area of contaminated lands	0.71*	0.48	0.58	0.48	0.75**	0.54	0.35	0.65*	0.54	0.39	0.53	-0.14
Percentage of oil-/brine-contaminated lands, ha/km ²	0.75*	0.38	0.31	0.38	0.73*	0.54	0.33	0.65*	0.54	0.39	0.76*	-0.26

TPH > WQL—percentage proportion of samples exceeding water quality limits value
 Correlation is significant: *at the 0.05 level; ** at the 0.01 level

noted (Soromotin 2011) that in Western Siberia 50% of oil drilling sites are polluted with oil at varying degrees. The proportion of samples exceeding TPH water quality limit values depends mainly on density of accidents ($r=0.78$; $\alpha=0.01$) and percentage of contaminated lands ($r=0.76$; $\alpha=0.05$). Obviously, accidents often lead to values exceeding the threshold for the concentration of TPH in surface waters and are extremely dangerous for aquatic organisms. The dependence of the content of petroleum hydrocarbons on the indicators of anthropogenic effects becomes apparent in the ice season probably, due to the fact that during this season the water flow in the rivers is at its lowest level.

The salt pollution of surface water (annual Cl⁻ values) was closely associated with the number of drill wells ($r=0.82$; $\alpha=0.01$), with the number of accidents at producing wells and pipelines ($r=0.75$; $\alpha=0.05$) and with the percentage of contaminated lands ($r=0.75$; $\alpha=0.05$). Chloride is a highly mobile anion that originates mainly from mining activities and from sewage from towns and villages; therefore, it can be used as an indicator for human activities in the ARC.

The dependence of the chloride content on the indicators of anthropogenic impact in the ice period was the most pronounced one (Table 6). For example, a close to linear correlation ($r=0.89$) was observed between the Cl⁻ concentration and the oil-well density within the sub-basin during ice season, which indicates the influx of salts into groundwater from non-point sources of pollution. At the same time, the effect of accidental spills on the chloride content was more pronounced during the flood period, when polluted meltwater entered the river network ($r=0.64$ and 0.77). On the basis of analysis of Cl⁻ concentrations and correlations in each season, it was revealed that besides geochemical aspects, salinization is controlled by three hydrological/anthropogenic processes: (1) concentration due to the baseflow effect, during the ice season; (2) dilution, during springtime, when river discharge reaches its maximum value; and (3) impact of non-point sources of pollution due to flushing of soil salts, which is dominant during the summer season.

The closest, but not statistically significant, correlation occurred between CCME WQI values and disturbed land areas ($r=-0.44$). This weak correlation of WQI with parameters of land disturbance suggests that water quality depends mainly on the environmental features of the catchment area that predetermine an intensive influx of metals into river waters.

Assessments of pollution sources and distribution require a detailed analysis of the impacts of accidents on hydrochemical parameters. It can, however, be difficult to link cases of increased pollutant concentrations with accidents for several reasons. Firstly, precise data on accidents in oil fields were classified and, therefore, unavailable until only relatively recently. Open access to

data on accident locations and causes, amounts of pollutants and areas of contaminated lands have only been available since 2014 (Service 2020). Before that time, it was only possible to obtain generalized information about the number of accidents without any details of their specific locations and amounts of pollutants. Secondly, according to the regular monitoring protocol, it is permitted to take only 3–4 samples per year, i.e., the time interval between sampling occasions is too long, which makes it impossible to identify direct impacts of most of the accidents on the river water composition. Only in cases of larger accidents that occur without mitigation measures being applied for localization of spillages, it is possible to detect impacts after several weeks and sometimes after several months. In other cases of accidents, where the ecological services of oil companies are available to immediately apply measures for spillage localization and remediation of contaminated lands, the duration of direct impact of pollutants on water quality is very short and does not result in significant contamination of water. According to the open-access data (Service 2020), such mitigation measures have recently been implemented in most cases.

It is only possible to identify impacts of accidents on river water quality in those cases where water sampling intervals are short and accurate information about the accidents is available. We have chosen the data set obtained in the course of monthly water tests at MS 24 and 25 in 2011, when all accidents were accurately recorded including locations, dates, pollutant types (e.g., crude oil or brine) and quantities spilled. MSs 24 and 25 were both located by the river Lagrn'egan, but in different positions in terms of exposure to pollution. MS 24 was located in the upper reaches of the river, where the influence of pollution sources was not very strong. MS 25 was located in the river's middle reaches, which accumulated the runoff from the industrial zone. All accident sites were located close to water courses (Fig. 6).

Monthly measured concentrations of chlorides in the Lagrn'egan River and dates of accidents are shown in Fig. 7. Throughout the year, MS 25 (which collected all the runoff from the oil field) was characterized by many times higher Cl^- concentrations as compared to MS 24 (in the upper reaches). Chloride concentrations at MS 24 varied from 0.9 to 9.5 mg/l, which was comparable with the Cl^- background levels from 0.5 to 15 mg/dm³ in rivers of the KHMAO (Moskovchenko et al. 2017). Chloride concentrations at MS 25 were significantly increased and varied from 6.7 to 62 mg/l, i.e., they continuously stayed above the background levels, which was indicative of the presence of diffuse pollution sources. Only in May, due to the influx of meltwaters into the river, differences between MS 25 and background levels were relatively small. After the Lagrn'egan River had crossed the oil field, Cl^- concentrations in water increased on average by 3.6 times, i.e., from 7.4 to 26.4 mg/l (Table 4).

During the year of 2011, there were two concentration peaks, which coincided with accidents (Fig. 7). In February, there was an accident involving the spillage of 3 tons of brine, which was followed by an increase in the Cl^- concentration at MS 25. In March, there was a pipeline rupture resulting with the leakage of 2 tons of pollutants and, due to the lowest water flow at that time of year, Cl^- concentrations peaked (at both MS 25 and 24). Following dilution with meltwaters, Cl^- concentrations dramatically decreased, but then increased again following of a series of accidents in June–July. It should be noted that during the summer–autumn period, when river discharge is much higher than that in winter, accidents did not cause such a sharp increase in Cl^- concentrations as during winter. That was the case, for example, with several small accidents occurring in August, October and November. However, those small accidents created diffuse pollution sources with long-lasting impacts in terms of increasing mean concentration of chlorides.

Changes in concentrations of TPH over the year of 2011 did not show a close relationship with the timing of accidents (Fig. 8). Only in March, there was a small TPH peak following the accident. A particularly prominent increase in TPH concentrations was observed during the flood period (May–June). We believe that such an increase was caused rather by an inflow of meltwaters, which carried TPH from earlier spillages, than by the accident that happened in May 2011. During the summer–autumn period, there were numerous accidents, which did not result in increases in TPH concentrations in water samples, and differences between TPH levels detected at MSs 25 and 24 were insignificant. Therefore, there was a time lag between an accident and its impact to a water body. This could be explained by the high buffer capacity of peat bogs, which are widespread within the oil field area and capable of accumulating pollutants. Peat bogs perform a role of natural traps that can adsorb and retain many substances and create barriers to the migration of chemical compounds of technogenic origin.

To assess long-time trends of contamination by brines and TPH, we created the time series plots, examples of which are shown in Fig. 9. The selected monitoring stations were characterized by different degrees of anthropogenic impact as follows: moderate (MSs 9 and 17), high (MSs 1, 2, 4, 5 and 7) and extreme (MS 21). The majority of the MSs were characterized by similar long-term variations in TPH and Cl^- . As shown in Fig. 9, higher values of TPH and Cl^- were observed in the 1990s. Particularly, TPH limit of 0.05 mg/l was consistently exceeded by 4–8 times at MSs 1–6 (Agan River) between 1993 and 1999. Such intense contamination of surface waters in the 1990s can be attributed to a high frequency of oil production accidents, insufficient land remediation efforts and drilling too many wells too close to the rivers. According to the open data

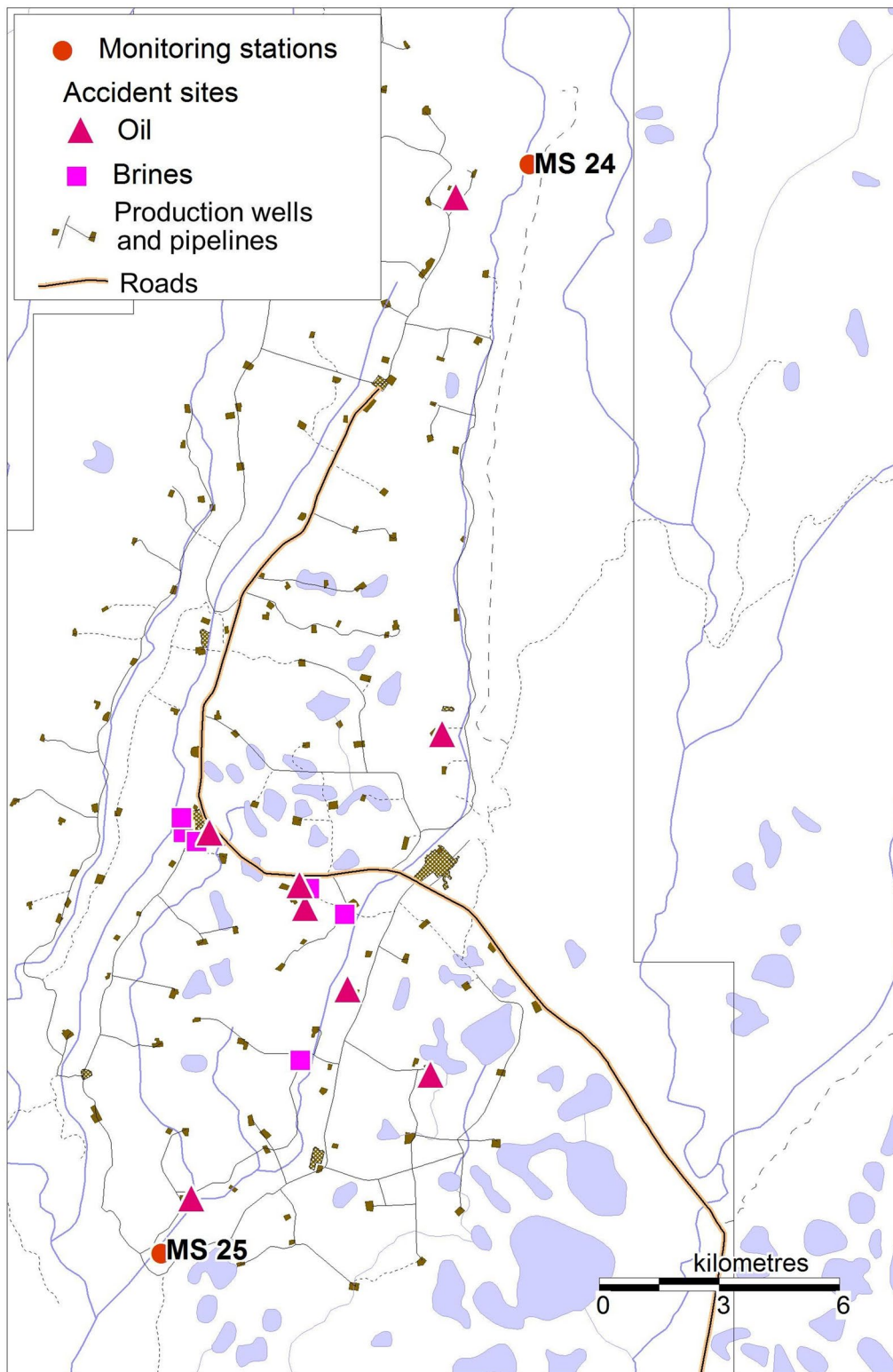


Fig. 6 Map showing the location of accidents in the vicinity of monitoring stations 24 and 25 (January–December 2011)

Fig. 7 Time series plot of monthly chloride concentration. 1-MS 25, 2-MS 24. Dates of accidents are marked by arrows and pollutant mass (tons) – by numbers

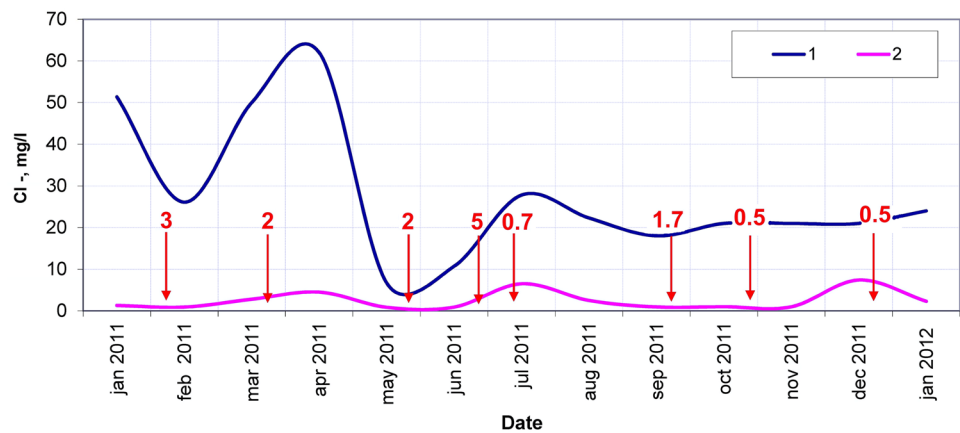
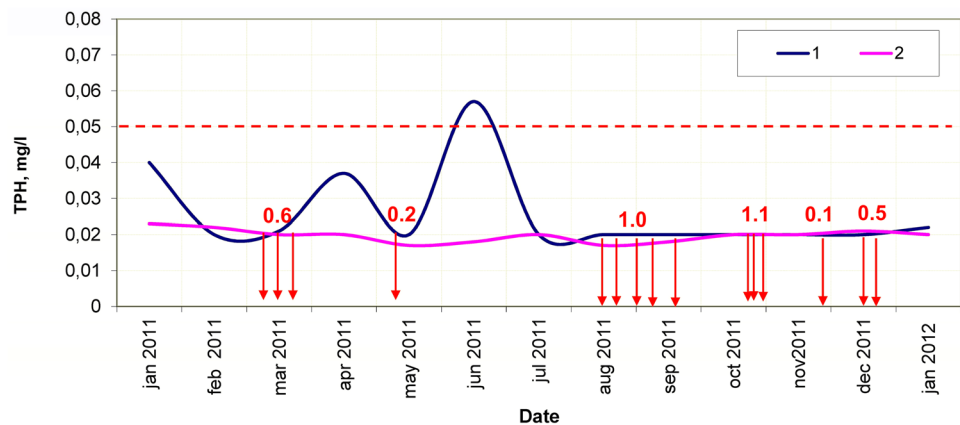


Fig. 8 Time series plot of monthly TPH concentration. 1-MS 25, 2-MS 24. Dates of accidents are marked by arrows and pollutant mass (tons)—by numbers. Russian water quality standard delineated as dotted line



source (Situation 2000), in 1995 the peak of accidents (2327 in total) is registered in the Nizhneartovsk administrative region that includes the ARC area. Later, the accident rate decreased, down to 743 accidents in 1999, and stayed at the same level until recent years, e.g., 635, 492 and 515 accidents happened in 2016, 2017 and 2018, respectively. In the 1990s, there were not only higher accident rates, but also greater volumes of spilled oil due to the use of out-of-date technologies. For example, an accident on a high-pressure pipeline within the Aganskoye oil field in 1995 caused the release of 520 tons of oil (IWAKO 2001), which apparently accounts for a high content of TPH recorded that year at MS 21 (Fig. 8). Another major accident occurred due to management mistakes on a high-pressure pipeline connecting the North Varieganskoye oil field (MSs 24 and 25, see Fig. 1) and the Samotlor oil field in the mid-1990s, when oil was spouting from the pipe for several weeks resulting in the oil spill of 3500 tons over the area of 2.2 ha (ibid).

High pollution rates in the early 1990s were also connected with the former strategies of well positioning. Until the mid-1980s, exploratory and development wells were positioned, as a rule, close to the rivers that were used as transport routes for deliveries of drilling equipment. Later,

as the water-protective legislation improved, drilling on river banks was officially forbidden. However, contamination of the rivers by oil spillages and saline solutions from existing wells continued in the 1990s. An intensive cleaning and remediation of oil-contaminated lands started from the mid-1990s. For example, in the Nizhneartovsk administrative region, the area of remediated lands increased from 253.5 to 665.5 ha over a period from 1995 to 1999 (Situation 2000).

Oilfields with moderate anthropogenic impact (e.g., MS 17) were characterized by relatively stable TPH concentrations in surface waters between the mid-2000s and the present time (Fig. 9). A small increase in TPH concentration (up to 0.25 mg/l) at MS 17 after snowmelt in 2011, which was followed by a decrease to 0.05 mg/l by the end of the year, could be connected with an accident that occurred in 2010 and was followed by oil leakage into the river network.

The volume of spillages had significantly decreased since the mid-2000s, when systems for automatic pressure control within pipelines were implemented on a large scale. Average quantities of pollutants released into the environment as a result of accidents decreased from 16 tons in the early 2000s to less than 1 ton at the present time (Fig. 10). In the event of a pipeline rupture, the oil

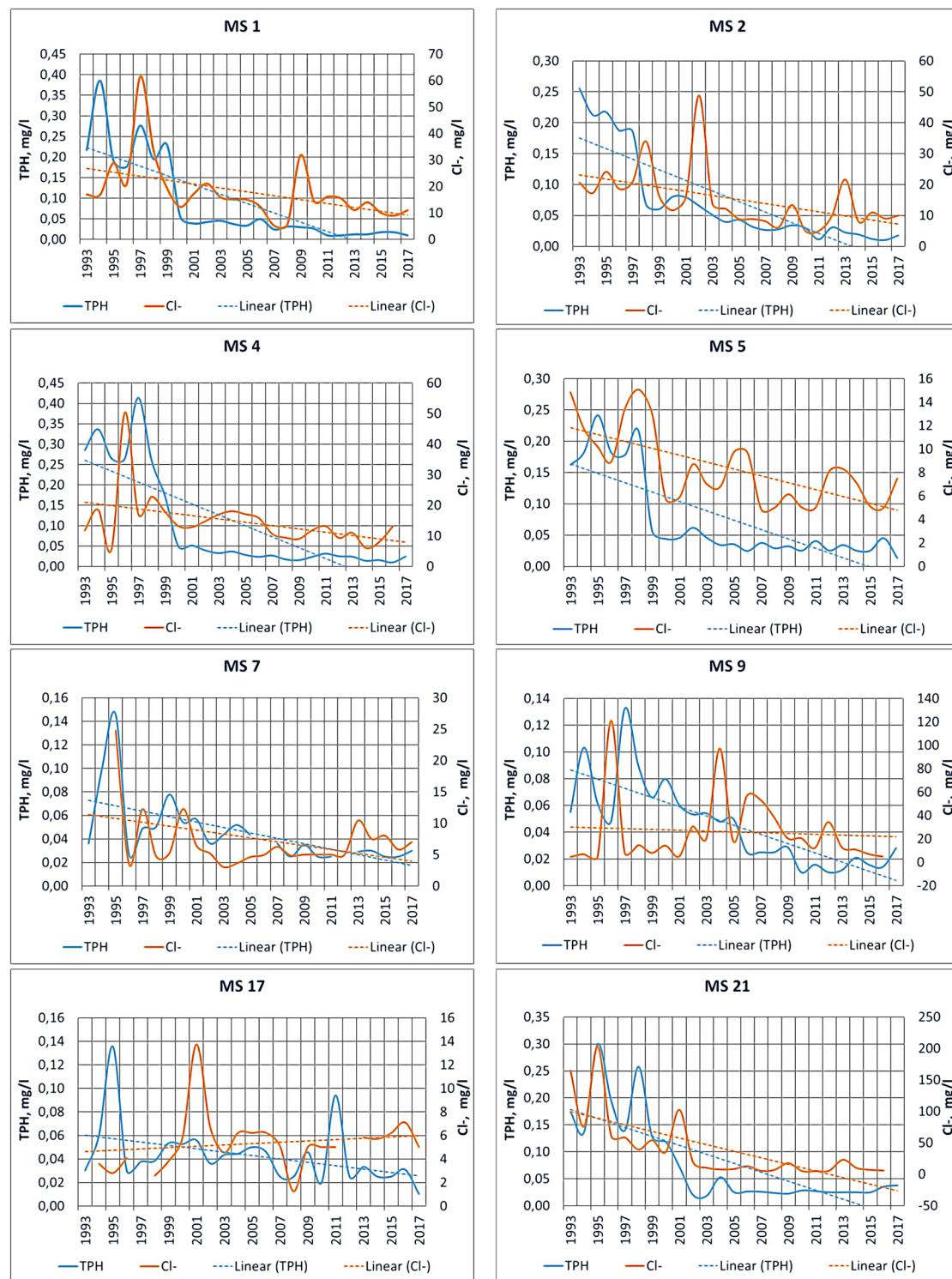


Fig. 9 Time series of mean annual concentrations (mg/l) of TPH and Cl^- in surface waters

supply is interrupted, which helps to prevent a significant amount of oil leakage and to limit the spillage area to less than 1 ha and the spilled oil mass to less than 1 ton in 97% of cases.

Conclusion

The results from the present study demonstrate that the quality of surface waters is relatively poor with respect to the

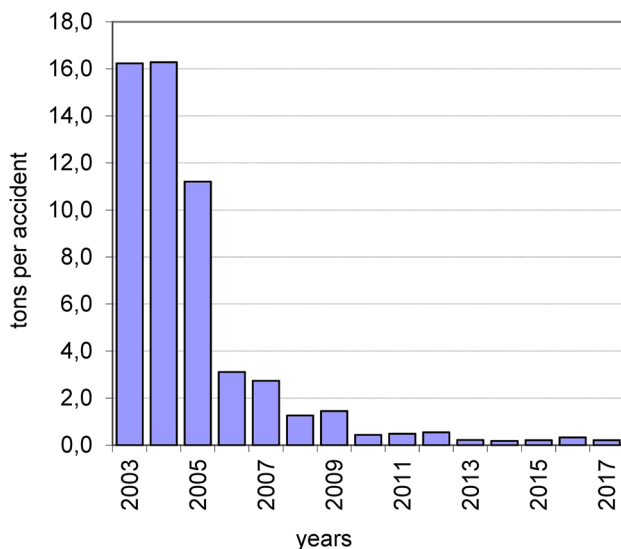


Fig. 10 The average quantity of pollutants (crude oil and brines) per accident in oil fields within the Agan River catchment over the period of 2003–2017

Russian standards. Trace metal (Ni, Hg, Pb, Zn, Cu, Mn) concentrations exceeded the standards for fisheries at 10.8%, 14.5%, 22.3%, 24.7%, 54.7% and 88.6% of samples, respectively. Concentrations of Fe were above the threshold at all the surveyed monitoring stations. High concentrations of Fe, Mn and Cu were caused mainly by natural factors such as intensive leaching of rocks and soils under the influence of organic acids, which is typical for the region. The Agan River and its tributaries had excessive concentrations of ammonium, especially, near towns and villages during the ice season. Median values of NO_3^- , BOD_{20} , SO_4^{2-} were mainly found within their standard limits. The CCME WQI showed that the water quality ranged between “poor” and “marginal.”

Seasonal variations reflect the dilution effect during meltflow as well as the effect of groundwater during the ice season. Most variables (Cl^- , Fe, Mn, Cu, Zn, TPH) reached their lowest values during the meltflow season, when thaw waters move through the system. The ice season was characterized by elevated concentrations of almost all variables except BOD_{20} , NO_3^- and pH.

Concentrations of TPH were high enough to raise concern about the negative impacts of oil development. During 1993–2017, 34.6% of the samples fell into the “polluted” category (TPH > threshold 0.05 mg/l). Cases of strong pollution were most often noted in the 1990s. The results indicated that the input of TPH was largely due to leakages from oil production wells and by the runoff from large oil spills. Stream water quality varied depending on level of disturbance caused by the oil development. The results of correlation analyses revealed that there was a significant

relationship between the parameters of land disturbance and some water quality variables (petroleum hydrocarbons and chlorides). TPH and Cl^- displayed a strong correlation with the density of wells, the frequency of accidents and with the percentage of oil or brine contaminated lands. Concentrations of Cl^- sharply increased as a result of accidents in a close proximity to water bodies and regularly increased much later as a consequence of diffuse pollution following spillages. The number of cases when TPH concentrations exceeded the Russian water quality standards for fisheries has greatly decreased since the mid-2000s. Despite the fact that accidents at oil pipelines do occur nowadays, large spills are avoided thanks to an automated system of monitoring of the pressure level in pipelines.

The monitoring program for oil fields within the KHMAO is very complex and costly and, probably, requires some amendments. Such parameters of monitoring as Fe, Mn and pH only indicate that conditions are unfavorable, but provide little information on oil industry impact. However, monitoring has undoubtedly positive effects on oil production management. In our opinion, it would be useful to make the results of monitoring accessible for the general public online, so that a wide circle of scientific and public organizations could objectively assess the environmental impact of the Russian oil industry.

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References

- Alekin OA (1970) The foundations of hydrochemistry. *Gidrometeoizdat, Leningrad (in Russian)*
- Arheimer B, Andersson L, Lepisto A (1996) Variation of nitrogen concentration in forest streams—influences of flow, seasonality and catchment characteristics. *J Hydrol* 179:281–304
- Arvola L, Einola E, Jarvinen M (2015) Landscape properties and precipitation as determinants for high summer nitrogen load from boreal catchments. *Landscape Ecol* 30:429–442. <https://doi.org/10.1007/s10980-015-0166->
- Arvola L, Jarvinen M, Hakala I (2006) Nutrient export from small boreal catchment areas: the influence of annual and seasonal hydrology. *Verh Int Verein Limnol* 9:2031–2034
- Bayley SE, Zoltek J, Herman AJ, Dolan TJ, Tortora L (1985) Experimental manipulation of nutrients and water in a freshwater marsh: effects on biomass, decomposition, and nutrient accumulation. *Limnol Oceanogr* 30:500–512
- Bilgin A (2018) Evaluation of surface water quality by using Canadian Council of Ministers of the Environment Water Quality Index (CCME WQI) method and discriminant analysis method:

- a case study Coruh River Basin. *Environ Monit Assess* 190:554. <https://doi.org/10.1007/s10661-018-6927-5>
- Bolan NS, Hedley MJ (1990) Dissolution of phosphate rocks in soils. 2. Effect of pH on the dissolution and plant availability of phosphate rock in soil with pH dependent charge. *Fertil Res* 24:125–134. <https://doi.org/10.1007/BF01073580>
- CCME (2001) Canadian environmental quality guidelines for the protection of aquatic life, CCME water quality index: technical report, 1.0. <https://www.ccme.ca/files/ceqg/en/137.pdf>. Accessed 17 April 2020
- Evans DM, Schoenholtz SH, Wigington PJ Jr, Griffith SM, Floyd WC (2014) Spatial and temporal patterns of dissolved nitrogen and phosphorus in surface waters of a multi-land use basin. *Environ Monit Assess* 186:873–888
- FAO (1988). Soil map of the world. Revised legend, by FAO–UNESCO–ISRIC. World Soil Resources Report No. 60. Rome.
- Fharnham IM, Singh AK, Stetzenbach KJ, Lohannesson KH (2002) Treatment of nondetects in multivariate analysis of groundwater geochemistry data. *Chemom Intell Lab Syst* 60(1–2):265–281. [https://doi.org/10.1016/S0169-7439\(01\)00201-5](https://doi.org/10.1016/S0169-7439(01)00201-5)
- Garizi AZ, Sheikh V, Sadoddin A (2011) Assessment of seasonal variations of chemical characteristics in surface water using multivariate statistical methods. *Int J Environ Sci Technol* 8:581–592. <https://doi.org/10.1007/BF03326244>
- Gashkina NA (2011) Zonal features of the distribution of biogenic elements and organic matter in small lakes. *Water Resour* 38(3):352–371
- Gorham E, Bayley SE, Schindler DW (1984) Ecological effects of acid deposition upon peatlands: a neglected field in ‘acid-rain’ research. *Can J Fish Aquat Sci* 41:1256–1268
- Grasby SE (1997) Controls on the chemistry of the Bow River, southern Alberta, Canada. Ph.D.thesis. University of Calgary, Calgary, AB. <https://doi.org/10.11575/PRISM/15509>
- GOST 17.1.2.04-77 (1977) State standard. Nature protection. Hydrosphere. Indicators of status and rules of taxation of fishery water bodies. The USSR State Committee for Standards, Moscow. https://allgosts.ru/13/020/gost_17.1.2.04-77. Accessed 11 Sep 2019 **(In Russian)**
- GOST R 51592-2000 (2000) State standard. Water. General requirements for sampling. Moscow: The USSR State Committee for Standards. <https://docs.cntd.ru/document/1200008006>. Accessed 17 April 2020 **(In Russian)**
- Groeschke M, Frommen T, Taute T et al (2017) The impact of sewage-contaminated river water on groundwater ammonium and arsenic concentrations at a riverbank filtration site in central Delhi. *India Hydrogeol J* 25:2185. <https://doi.org/10.1007/s10040-017-1605-1>
- Groisman PY, Gutman G, Shvidenko AZ, Bergen KM, Baklanov AA, Stackhouse PW (2013) Introduction: regional features of Siberia. In: Groisman P, Gutman G (eds) Regional environmental changes in siberia and their global consequences. Springer, Dordrecht
- Hese S, Schmullius C (2009) High spatial resolution image object classification for terrestrial oil spill contamination mapping in West Siberia. *Int J Appl Earth Obs Geoinf* 11:130–141. <https://doi.org/10.1016/j.jag.2008.12.002>
- IWACO Report (2001) West Siberia oil industry environmental and social profile. Final report, edited by Lodewijkx M, Ingram V, Willemse R, June 2001. <https://www.greenpeace.org/nl/klimaatverandering/4468/west-siberia-oil-industry-environmental-and-social-profile>. Accessed 17 April 2020
- Jamrah A, Al-Futaisi A, Hassan H, Al-Oraimi S (2007) Petroleum contaminated soil in Oman: evaluation of bioremediation treatment and potential for reuse in hot asphalt mix concrete. *Environ Monit Assess* 124:331–341. <https://doi.org/10.1007/s10661-006-9230-9>
- Kabata-Pendias A (2011) Trace elements in soils and plants. CRC Press, Boca Raton
- Kauffman GJ, Belden AC (2010) Water quality trends (1970 to 2005) along Delaware streams in the Delaware and Chesapeake Bay watersheds, USA. *Water Air Soil Pollut* 208:345–375. <https://doi.org/10.1007/s11270-009-0172-z>
- Khoroshavin VY, Moiseenko TI (2014) Petroleum hydrocarbon runoff in rivers flowing from oil and gas producing regions in Northwestern Siberia. *Water Resour* 41(5):532–542. <https://doi.org/10.1134/S0097807814050030>
- Lepistö A, Granlund K, Rankinen K (2004) Integrated nitrogen modeling in a boreal forestry dominated river basin: N fluxes and retention in lakes and peatlands. *Water Air Soil Pollut Focus* 4:113–123. <https://doi.org/10.1023/B:WAF0.0000028349.82505.39>
- List of Fishery Related Standards: Maximal Allowable Concentrations (MAC) and Safe Reference Levels of Impact (SRLI) for Hazardous Substances for Water Bodies Used for Fishery (1999) VNIRO, Moscow **(in Russian)**. <https://standartgost.ru/gpkey-1429383306.0>. Accessed 09 September 2019
- Ljozin VA (1999) Rivers of the Khanty-Mansi Autonomous Okrug: reference book. Vektor Book, Tyumen **(in Russian)**
- Lumb A, Halliwell D, Sharma T (2006) Application of CCME water quality index to monitor water quality: a case of the Mackenzie river basin, Canada. *Environ Monit Assess* 113:411–429. <https://doi.org/10.1007/s10661-005-9092-6>
- Martin JM, Meybeck M (1979) Elemental mass-balance of material carried by major world rivers. *Mar Chem* 7:173–206. [https://doi.org/10.1016/0304-4203\(79\)90039-2](https://doi.org/10.1016/0304-4203(79)90039-2)
- Meybeck M (1982) Carbon, nitrogen, and phosphorus transport by World rivers. *Am J Sci* 282(4):401–450
- Mikhailova LV, Uvarova VI, Barkhovich OA (1988) Water ionic composition and mineralization in the Ob River and some its tributaries. *Water Resour* 3:25–35 **(In Russian)**
- Moiseenko TI, Gashkina NA, Dinu MI, Kremleva TA, Khoroshavin VYu (2013) Aquatic geochemistry of small lakes: effects of environment change. *Geochem Int* 51(13):1031–1148. <https://doi.org/10.1134/S0016702913130028>
- Moiseenko TI, Gashkina NA, Dinu MI, Khoroshavin VY, Kremleva TA (2017) Influence of natural and anthropogenic factors on water acidification in humid regions. *Geochem Int* 55(1):84–97. <https://doi.org/10.1134/S0016702916120090>
- Moskovchenko DV, Babushkin AG, Artamonova GN (2009) Surface water quality assessment of the Vatinsky Egan River catchment, West Siberia. *Environ Monit Assess* 148:359–368. <https://doi.org/10.1007/s10661-008-0166-0>
- Moskovchenko DV, Babushkin AG (2012) Peculiarities of formation of chemical composition of snow waters (on example of Khanty-Mansi autonomous district). *Kriosfera Zemli* 16(1):71–81 **(in Russian)**
- Moskovchenko DV, Babushkin AG, Ubaidulaev AA (2017) Salt pollution of surface water in oil fields of Khanty-Mansi Autonomous Area-Yugra. *Water Resour* 44(1):128–138. <https://doi.org/10.1134/S0097807817010109>
- Moskovchenko DV, Babushkin AG (2017) Oil pollution of the ana-branches of the Ob river on the territory of Khanty-Mansi Autonomous Okrug-Yugra. *Geogr Nat Resour* 38(3):238–245. <https://doi.org/10.1134/S1875372817030040>
- Mueller L, Sheudshen AK, Syso A et al (2016) Land and water resources of Siberia, their functioning and ecological state. In: Mueller L, Sheudshen A, Eulenstein F (eds) Novel methods for monitoring and managing land and water resources in Siberia. Springer, Cham, pp 3–73. https://doi.org/10.1007/978-3-319-24409-9_1
- Muller FLL, Tankère-Muller SPC (2012) Seasonal variations in surface water chemistry at disturbed and pristine peatland sites in the flow country of northern Scotland. *Sci Total Environ* 435:351–362. <https://doi.org/10.1016/j.scitotenv.2012.06.048>

- Nikanorov AM, Smirnov MP, Klimenko OA (2010) Long-term trends in total and anthropogenic discharge of organic and biogenic substances by Russian rivers into the Arctic and Pacific seas. *Water Resour* 37:361–371. <https://doi.org/10.1134/S0097807810030103>
- Opekunova MG, Opekunov AY, Kukushkin SY, Arestova IY (2018) Evaluation of environmental transformation in areas of hydrocarbon deposits in the north of Western Siberia. *Contemp Probl Ecol* 11(1):99–110. <https://doi.org/10.1134/S1995425518010109>
- Panicheva LP, Moiseenko TI, Kremleva TA, Volkova SS (2012) Biochemical transformation of petroleum hydrocarbons in the waters of Western Siberia. *Tyumen State Univ Herald* 12:34–43
- Pejman AH, Bidhendi GRN, Karbassi AR et al (2009) Evaluation of spatial and seasonal variations in surface water quality using multivariate statistical techniques. *Int J Environ Sci Technol* 6(3):467–476. <https://doi.org/10.1007/BF03326086>
- Recommendations for development of oil and gas resources within important wildlife habitat (2010) Wyoming Game and Fish Department Cheyenne, Wyoming. <https://www.nrc.gov/docs/ML1108/ML110810642.pdf>. Accessed 17 April 2020
- Regulations on the organization of a local ecological monitoring within the boundaries of the license areas for the right to use mineral resources with the purpose of extracting oil and gas on the territory of Khanty-Mansi Autonomous Okrug–Yugra (2011). Decree of the Government of Khanty-Mansi Autonomous Okrug–Yugra of December 23, 2011 No. 485. <https://prirodnadzor.admhmao.ru/prirodopolzovatelyam/normativno-pravovye-akty>. Accessed 17 April 2020 **(In Russian)**
- Resolution of the government of Khanty-Mansi Autonomous Okrug No. 302-p “On approval of requirements for identifying the source of contamination of environmental components, designing and conducting local environmental monitoring within the boundaries of the licensed areas of oil and gas development in the Khanty-Mansiysk Autonomous Okrug—Ugra (2003) <https://zakon-regio.n.ru/1/48679>. Accessed 17 April 2020 **(In Russian)**
- Resources of a surface water of the USSR. Vol. 15. Altai and West Siberia. Issue 2. Middle Ob (1972) *Gidrometeoizdat Publ, Leningrad* **(In Russian)**
- Scientific and applied guide to the climate of the USSR. Series 3. Issue 17. Tyumen and Omsk regions (1998) *Gidrometeoizdat Publ, S-Petersburg* **(In Russian)**
- Service for supervision and control for environmental protection of the Khanty-Mansiysk Autonomous district (2020) Accident rate. <https://prirodnadzor.admhmao.ru/doklady-i-otchyety/regionalny-e-otchyety/avariynosti/>. Accessed 17 April 2020
- Shchur LA, Bazhina LV, Volkova NI, Trofimova MA (2003) Water quality of small rivers in the zone of influence of gold-mining facilities in Krasnoyarsk Region. *Water Resour* 30(1):72–80. <https://doi.org/10.1023/A:1022007919097>
- Shvartsev SL, Savichev OG, Frizen LF et al (1996) The ecological and geochemical state of the water in the middle course of the Ob River. *Water Resour* 23(6):723–731
- Shvartsev SL, Serebrennikova OV, Zdvizhkova M, Savichev OG, Naimushin OS (2012) Geochemistry of wetland waters from the lower Tom Basin, southern Tomsk Oblast. *Geochem Int* 50(4):367–380. <https://doi.org/10.1134/S0016702912040076>
- Shvidenko AZ, Gustafson E, McGuire AD et al (2013) Terrestrial ecosystems and their change. In: Groisman PJ, Gutman G (eds) *Regional environmental changes in Siberia and their global consequences*, chapter 6. Springer, Berlin, pp 171–249
- Sikora LJ, Keeney DR (1983) Further aspects of soil chemistry under anaerobic conditions. In: Gore AJP (ed) *Ecosystems of the World 4A, Mires: Swamp, Bog, Fen and Moor: general studies*. Elsevier, Amsterdam, pp 247–256
- Situation of the Environment and Natural Resources in the Nizhnevartovsk Region (2000). *Regional Environmental Committee Nizhnevartovsk Publ.* **(In Russian)**
- Slinko OV, Chernyanskii SS (2007) Engineering–geological substantiation of water resource protection in the zones of oil and gas fields. *Water Resour* 34(1):75–87. <https://doi.org/10.1134/S0097807807010083>
- Soromotin AV (2011) Ecological consequences of different stages of the development of oil and gas deposits in the taiga zone of the Tyumen’ oblast. *Contemp Probl Ecol* 4:600–607. <https://doi.org/10.1134/S1995425511060063>
- Tortorelli RL, Pickup BE (2006) Phosphorus concentrations, loads, and yields in the Illinois River basin, Arkansas and Oklahoma, 2000–2004: US Geological Survey Scientific Investigations Report 2006–5175. <https://doi.org/10.3133/sir20065175>
- Tsuzuki Y (2013) Explanation of 47-year BOD alternation in a Japanese River Basin by BOD generation and discharge. *Water Air Soil Pollut* 224:1517. <https://doi.org/10.1007/s11270-013-1517-1>
- Tyagi S, Sharma B, Singh P, Dobhal R (2013) Water quality assessment in terms of water quality index. *Am J Water Resour* 1(3):34–38. <https://doi.org/10.12691/ajwr-1-3-3>
- Uvarova VI (2000) Contemporary status of the water quality in the Ob River within Tymen’ Oblast. *Vestn Ekologii Lesovedeniya i Landshaftovedeniya* 1:18–26 **(In Russian)**
- Varanka S, Hjort J (2017) Spatio-temporal aspects of the environmental factors affecting water quality in boreal rivers. *Environ Earth Sci* 76:21. <https://doi.org/10.1007/s12665-016-6338-2>
- Vega M, Pardo R, Barrado E, Deban L (1998) Assessment of seasonal and polluting effects on the quality of river water by exploratory data analysis. *Water Res* 32(12):3581–3592
- WHO (2011). *Guidelines for drinking-water quality*. 4th edition. https://www.who.int/water_sanitation_health/publications/2011/dwq_guidelines/en. Accessed 17 April 2020.
- Vuorenmaa J, Rekolainen S, Lepistö A et al (1990s) Losses of nitrogen and phosphorus from agricultural and forest areas in Finland during the 1980s and 1990s. *Environ Monit Assess* 76:213. <https://doi.org/10.1023/A:10155840144171990s>
- Zhang L, Shi K, Yue L (2007) Chemical characteristics and pollution sources of petroleum hydrocarbons and PAHs in sediments from the Beiluohe River, Northern China. *Environ Geol* 53:307–315. <https://doi.org/10.1007/s00254-007-0645-6>

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