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Citation: AIP Conference Proceedings **2051**, 020322 (2018); doi: 10.1063/1.5083565
View online: https://doi.org/10.1063/1.5083565
View Table of Contents: http://aip.scitation.org/toc/apc/2051/1
Published by the American Institute of Physics

Water Chemical Composition in a Petroleum-Contaminated Swamp Forest within the Malaya Icha River Basin, Great Vasyugan Mire, Western Siberia

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Abstract. In recent decades, oil exploration and production has caused the wetlands of Western Siberia to become polluted. As a result of oil spills, the genetic type of water has changed in connection with the receipt of oil and associated mineralised waters. The water of a petroleum-contaminated swamp forest was found to be characterised by high levels of TDS, Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+} and HCO_3^- in comparison with its background territory, as well as significant contents of organic substances and hydrocarbons. The most representative group of hydrocarbons in the water comprised alkanes, including steranes and hopanes. In July 2016 year, three years after oil spill, a decline in the overall level of water pollution by mineral substances and petroleum products was noted.

INTRODUCTION

Today, the volume of oil produced in Western Siberia exceeds 10 billion tons. The hydrocarbon reserves explored amount to approximately 60 billion tons of equivalent fuel. Intensive exploitation of the region's natural resources in conditions of high waterlogging (approximately 50%) has instigated a large range of environmental problems, including the pollution of the natural environment by oil and oil products as a result of spills [1]. Therefore, assessment of ecological conditions in areas of oil production has become an urgent issue. This study investigates water chemical composition in a swamp forest that has suffered from an oil spill in the southwestern part of the Great Vasyugan Mire in Western Siberia.

MATERIALS AND METHODS OF RESEARCH

The study area is located within the southeast West Siberian Plain, the alluvial plain formed following the destruction of the ice sheets and retreat of the sea as a result of the extensive meandering of large rivers (Fig. 1). The climate is continental, with long, cold winters and short, hot summers, and an average annual temperature of 1.8°C. The oil spill site is located in the area of the Maloichsky oil field in the Novosibirsk region of Russia (N56°48'43.4" E78°28'54.7"), in the basin of the Malaya Icha River (right tributary of the Tara River, Irtish River watershed, southwestern spurs of the Great Vasyugan Mire). The oil spill area, which measures approximately 1,000 m^2, occurred at the end of 2013 following the breakdown of the oil pipeline.

The oil spill site is located within a birch and aspen-birch swamp forest, with a tree height of 15 m. The shrub layer is represented by willow. The maximum thickness of the peat is 40 cm. Water samples were taken at the oil spill in a birch and aspen-birch swamp forest, as well as 100 m beyond the oil spill, in a similar area. The swamp forest contains birch, aspen, Siberian cedar and spruce, and is situated between the rivers Bakchar and Iksa (northeastern part of the Great Vasyugan Mire, N56°58'8.6"E82°35'58.8"). The area is remote and largely separate from anthropogenic impact and transport infrastructure [2].

Proceedings of the Advanced Materials with Hierarchical Structure for New Technologies and Reliable Structures
AIP Conf. Proc. 2051, 020322-1–020322-4; https://doi.org/10.1063/1.5083565
Published by AIP Publishing. 978-0-7354-1777-9/$30.00

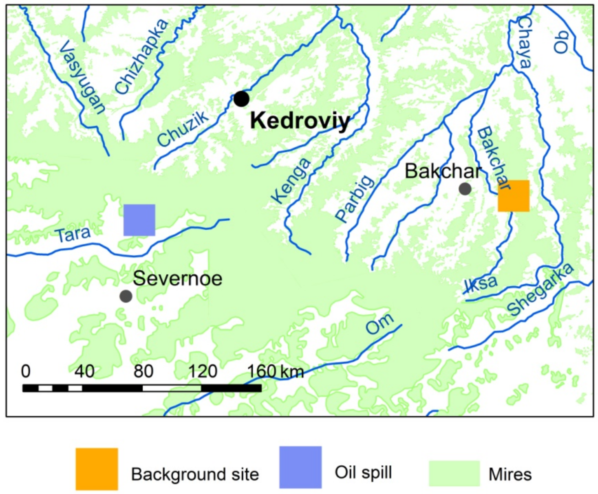

FIGURE 1. Map of sampling points

Samples of water were taken at depths of 20 cm using specially prepared glass and plastic bottles. The pH, Eh (PH200, ORP200 HM Digital, South Korea), water temperature, O_2 (WTW, Oxi 3205, Germany) and CO_2 were determined immediately after sampling. The samples were subsequently preserved. Prior to analysis, the samples were stored at a temperature of +4 to +6°C and filtered through a filter with a pore diameter of 1–2.5 µm. The concentrations of Ca^{2+}, Mg^{2+}, CO_2, HCO_3^- and Cl^- in the water were determined using the titrimetric method, the F_{etotal}, NH^+_4, NO^-_3, SO_4^{2-} and DOC were determined using the spectrophotometry method (Specol-1300, Analytik Jena, Germany), and the chemical oxygen demand (COD) was estimated with potassium dichromate. Determination of the concentrations of K^+ and Na^+ ions was undertaken using the method of flame photometry (PFA-378, Russia), and the Pb, Cu and Zn concentrations were determined using inversion voltammetry (STA, Russia). Total dissolved solids (TDS) were estimated as the sum of the concentrations of all ions in the chemical composition of the water. The content of hydrocarbons was determined via the fluorimetric method. The individual composition of hydrocarbons was determined by chromatography-mass spectrometry using a DFS magnetic-mass spectrometer from ThermoScientific (Germany), provided by the collective use centre of TomTsKP SB RAS. CPI-2 was calculated based on the composition of n-alkanes data in order to determine the nature of hydrocarbons in the water [3]: $CPI\text{-}2=2*(C_{21}+C_{23}+C_{25}+C_{27}+C_{29}+C_{31})/((C_{20}+C_{22}+C_{24}+C_{26}+C_{28}+C_{30})+(C_{22}+C_{24}+C_{26}+C_{28}+C_{30}+C_{32}))$.

RESULTS AND THEIR DISCUSSION

The data revealed that the water at the oil spill site was neutral, Na-Cl-type, with significant levels of CO_2 and low O_2 (Table 1). A distinctive feature of the chemical composition of the waters is their complex composition of organic compounds of biogenic and petroleum origin. It is important to consider changes in the chemical composition of the waters at the oil spill site from 2014–2016. In October 2014, a year following the development of the oil pipeline, the waters were characterised as $Cl^{Na9}_{III1,4}$ (O.A. Alekin classification [4]), neutral with a mineralisation of 1418 mg/L:

$$M_{1,4}\frac{Cl45HCO_3 5}{Na24Ca13Mg5K5}.$$

Comparison of the water chemical composition with the background indices indicates a transformation in ion-salt composition from HCO_3^--Ca to Na-Cl, with a significant (more than 10 times) increase in mineralisation and contamination with petroleum hydrocarbons. The COD of the water was 78.2 mg/L and the hydrocarbon content was 0.98 mg/L, in excess of the maximum allowable concentrations (MAC) for use as domestic and drinking water. The water also contained high levels of NH_4^+ and Fe_{total} (3.24 and 0.19 mg/l, respectively). Furthermore, in comparison with the background area, an increase in the concentrations of K^+, Ca^{2+}, Mg^{2+} and HCO_3^- can be identified. The content of Zn, Cd and Pb did not exceed background values. Higher concentrations were determined for Cu (0.0052 mg/L).

TABLE 1. Water chemistry composition 2014–2016 years

Component	Sampling points						MAC[1]
	Petroleum-contaminated swamp forest				Pristine swamp forest 100 m outside from oil spill	Pristine swamp forest interfluve of Bakchar and Iksa River	
	25.10.14	14.05.15	28.07.15	27.07.16	27.07.16	28.07.14	
pH	7.02	7.44	7	8.34	7.80	6.74	6.5–8.5
Eh, mV	–60	–73	–118	71	34	–76	
K^+, mg/L	103.5	1.70	87.5	5.5	2.1	4.2	
Na^+, mg/L	**270.9**	12.8	**436**	11.2	3.6	1.4	200
Ca^{2+}, mg/L	125.41	17.7	108.22	29.2	35.11	9.17	
Mg^{2+}, mg/L	31.14	5.70	**110.8**	11.67	7.87	3.92	50
NH_4^+, mg/L	3.24	5.00	–	4.95	3.08	6.96	1.93
Fe_{total}, mg/L	0.19	0.92	2.86	5.46	4.50	1.8	0.3
$CL^–$, mg/L	**786.56**	17.7	**2506.80**	16.48	8.86	4.49	350
$SO_4^{2–}$, mg/L	6.85	2.69	28.7	4.48	0.75	6.55	500
$NO_3^–$, mg/L	0.10	0.91	**145.2**	1.39	0.38	3.08	45
$HCO_3^–$, mg/L	192.2	58.60	404	118.6	116.85	54.9	
COD, mg/L	**78.2**	**99.45**	**127.84**	**151.6**	**117.20**	**142**	15
CO_2, mg/L	–	14.96	185.5	35.9	32.9	–	
O_2, mg/L	–	2.03	0.81	0.12	0.10	2.33	>4
Zn, mg/L	0.012			0.05	0.02605	0.03	1
Cd, mg/L	<0.0002			<0.0002	<0.0002	0.0002	0.001
Pb, mg/L	0.0052			0.00074	0.00188	0.005	0.03
Cu, mg/L	0.0052			0.00154	<0.0005	<0.0005	1
Hydrocarbons, mg/L	**0.98**	**4.6**	**50**	**5.64**	0.026	–	0.3
EC, μCm/cm	2370	192	7860	231	193	96	
TDS, mg/L	**1418**	123.9	**4121**	209.1	183.1	96.5	1000

[1] MAC—maximum allowable concentrations of domestic and drinking water use Hygienic standards 2.1.5.1315-03. SanPiN 2.1.5.980-00.

Mineralisation changes in the oil spill site during 2014–2016 years were of a sharp and abrupt nature, owing to the dynamics of groundwater levels, processes of dilution and the concentration of mineral substances contained in the water and soil (Fig. 2). For comparison, within the pristine swamp forest changes in the sum of ions in different periods of water were smooth and the sum of ions did not exceed 100 mg/L. Within the oil-contaminated area the maximum values of the sum of ions (TDS) in July 2015 were 4121 mg/L, whereas in May 2015 (snowmelt period) and July 2016 (rainfall) the TDS reduced to 123.9 and 209.1 mg/L respectively. The content of $Cl^–$ and Na^+ changed synchronously, reaching maximum values in October 2014 and July 2015 (Fig. 3). During periods of snowmelt and rainfall the content of $Cl^–$ and Na^+ in the waters of the oil spill site sharply decreased, while the predominant ions comprised $HCO_3^–$ and Ca^{2+}. COD of contaminated waters in the period 2014–2016 years gradually increased, reaching maximum values in July 2016, due to an increase in dissolved organic compounds and transformation of oil pollution. The content of hydrocarbons at the water sampling points varied widely from 0.23 to 36.2 mg/L. The maximum content of hydrocarbons was determined in July 2015 as 50 mg/L. A major influence on the content of hydrocarbons is the migration of petroleum hydrocarbons within the oil spill site. Therefore, in July 2016 changes in the configuration and size of the oil spill at a high water level were seen with oil products moving southwards. In general, a decrease in the overall level of water pollution was identified in July 2016 (Fig. 4).

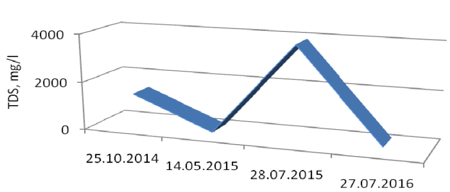

FIGURE 2. TDS dynamics 2014–2016

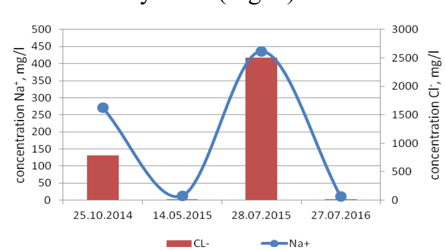

FIGURE 3. Na^+ and $Cl^–$ water content dynamics 2014–2016

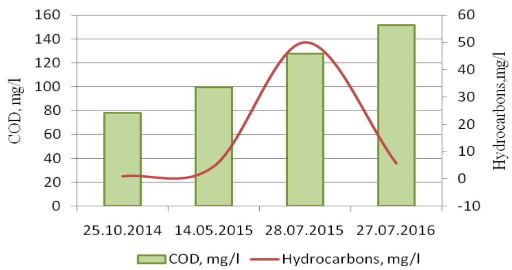

FIGURE 4. COD of water and hydrocarbons content dynamics 2014–2016

The most representative group of hydrocarbons in the waters were alkanes, constituting approximately 80% of all hydrocarbons. The maximum molecular weight distribution of the alkanes in water taken from the oil spill was C_{17} with a smooth distribution curve, indicating the presence of light oil in the water. The CPI-2 for the waters at the oil spill site was 1.1, confirming oil pollution. In the waters at the oil spill site sterols and hopanes of the oil series were found, representing a wide range of compounds. In the water sample of the pristine swamp forest, no steranes and hopanes were identified and the distribution of alkanes was typical of bog waters and the predominance of homologues of C_{25} and C_{27} alkanes was also characteristic. Among the aromatic compounds mono-, bi-, tri- and tetraaromatic were found in the investigated waters. Most samples contained naphthalenes and phenanthrenes. The highest content of arenas was observed in the waters of the oil spill site and the lowest in the pristine swamp forest at a distance of 100 m. Pyrenes were only contained in the waters of the oil spill site (Table 2).

TABLE 2. Main groups of organic compounds in waters of the oil spill site, μg/L

Component	Petroleum-contaminated swamp forest	Pristine swamp forest 100 m	Component	Petroleum-contaminated swamp forest	Pristine swamp forest 100 m
Acyclic			Cyclic		
n-Alkanes	23.72	0.93	Tocopherols	0.01	0.00
Squalene	0.00	0.00	Dibenzofurans	0.17	0.007
Methyl esters of QC	0.02	0.04	Sesquiterpenoids	0.00	0.00
Ethyl esters of QC	0.09	0.01	Diterpenoids	0.01	0.004
Isopropyl esters of QC	0.02	0.02	Triterpenoids	0.02	0.00
Long-chain esters of QC	0.50	0.03	Steroids	0.09	0.02
Phytol	0.00	0.00	Aromatic hydrocarbons	2.87	0.01
Phytone	0.02	0.01	Cyclohexanes	1.29	0.00
n-Alkan-2-ones	0.00	0.01	Dibenzothiophenes	0.17	0.00
n-Aldehydes	0.01	0.01	Oil hopanes	0.18	0.00
			Oil steranes	0.05	0.00

CONCLUSIONS

As a result of the oil spill, a change in the genetic type of waters occurred, connected with the receipt of oil and associated (reservoir) mineralised waters. Thus, the water of the petroleum-contaminated swamp forest was characterized by high contents of TDS. Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+} and HCO_3^- in comparison with the background territory, as well as high levels of organic substances and hydrocarbons. The mineralisation of water increased to 1424 mg/L (the maximal mineralisation was determined in July 2015 at 3918.2 mg/L) and the concentrations of Cl^- at 977 mg/L and Na^+ at 250 mg/L, 15–20 times in excess of the background values. In the water of the petroleum-contaminated area, the average content of hydrocarbons was 18.5 mg/L with a maximum of 50 mg/L 166 times in excess of the MAC. The most representative group of hydrocarbons in the water comprised alkanes, although in the waters of the oil series steranes and hopanes were also found. In July 2016 a decrease in the overall level of water pollution by mineral substances and petroleum products was noted due to dilution processes. However, the overall level of water pollution with oil products remains high and their migration beyond the oil spill has been noted.

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