Regional Monitoring of Hydrocarbon Levels (Grönfjord, the Greenland Sea)

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Key Points:

- Based on the results of multi-year state monitoring programme some local concentrations maxima for THC in the surface horizon may be a sign of a marked anthropogenic impact on the water area along the coastline though no exclusively anthropogenic impact on the water body was depicted in this study.
- In some areas of the sea, local sources of natural origin contribute to elevated levels of PAHs in bottom sediments. The results confirm that further research is needed to study the volatility of hydrocarbon content in the waters of Grönfjord.

Abstract

This study assessed total hydrocarbon content and polycyclic aromatic hydrocarbon content in Grönfjord (the Greenland Sea, Svalbard). The field study was held in marine expeditions of research vessel “Barentsburg” by the North-Western Branch of the Federal State Budget Institution, Research and Production Associaton «Typhoon» in summer periods of 2012 to 2022. In the framework of the field works simultaneous measurements of hydrological and hydrochemical characteristics of the water column were done. The data was analyzed using standard procedure in purpose to gather new information about the levels of hydrocarbons (measured as total hydrocarbon contents), polycyclic aromatic hydrocarbons. The results showed pronounced interannual variations of total hydrocarbon contents and polycyclic aromatic hydrocarbons concentrations. Supposed that local natural sources contribute to elevated polycyclic aromatic hydrocarbons and total hydrocarbon content levels both in water and in sediments, the levels of contamination do not signify exclusively anthropogenic influence on the sea-body. At the same time, some local elevated petroleum hydrocarbons concentrations, which were detected in the surface water layer, may be a sign of existing industrial activity affecting the waters of the fjord. Continuity of tasks starting from earlier expeditions indicates that many processes in the Norwegian Sea, Greenland Sea require further research.

Plain Language Summary

The long-term trends in the concentration of petroleum hydrocarbons in surface and bottom layers have been identified, and the values of their total and average content are given. The results showed that Grönfjord is a fairly representative area allowing to obtain assessments of the influence of economic activity on the state of the natural environment. The trends in the values of long-term monitoring are suggested for consideration in planning and taking any economic and environmental measures.

1 Introduction

The article presents long-term studies of the content of petroleum hydrocarbons in the waters of Grönfjord where the assessment of seasonal fluctuations in concentrations is very complicated due to the short period of open water.

The fjords of southwestern Spitsbergen (European Arctic) are a climatically sensitive area, where warm Atlantic water-masses meet cold Arctic Water. There are sufficient long-term series of reliable observations of physical characteristics of seawaters and only some fragmentary data on hydrochemical parameters of the aquatic environment, in par-ticular, in regards to the content of oil hydrocarbons in seawater/bottom sediments. For the purpose of environmental monitoring and assessment of the levels of pollution it is very important that the specialized hydrochemical data banks should be created and updated. It has been repeatedly demonstrated that in environmental damage assessments it is very useful to have information about sources of hydrocarbons present in the affected area before accidents or any human activities (Peterson et al, 2002; Yunker, 2015). Together with volumes of water, rivers carry mineral and organic suspensions, dissolved mineral substances. All this geoflow, regulated primarily by the magnitude and regime of water runoff, has a powerful direct and indirect impact on the natural situation of the coastal, hydrophysical processes and ecological conditions of the Arctic seas (Alekseev, 1989). Identification of environmental factors of a cyclic nature makes it possible to conduct a comparative analysis of transformations and substantiate the effect of a polluting factor. The main objective of the study is to receive new information on the concentration of contaminants of anthropogenic origin such as oil hydrocarbons (in measures of total hydrocarbon contents (THC) and polycyclic aromatic hydrocarbons (PAHs).

The results of the study are supposed to present a comprehensive assessment of degree of anthropogenic impact, accounting to oil pollution and can possibly help to identify the processes between ongoing changes and influencing factors.

2 Materials and Methods of the research are based on data collected on the Svalbard archipelago located in the high Arctic (76°-80°N) within the northernmost reach of the West Spitsbergen Current (WSC), in this specific setting close to the Polar Front, where even small variations in the system of flows are expected to give large and distinct signals in paleoceanographic parameters (S´lubowska et al, 2005).

2.1 Work area

The study area covers Grönfjord, which is located on the Western Svalbard Island, the fjord is a part of the bigger Isfjord. Spitsbergen archipelago, Greenland Sea). Isfjord, cutting into Western Svalbard near Barentsburg at the point where the main coal mining areas are located, is of the greatest importance for navigation. Grönfjord is the southwestern arm of the Isfjord. Grönfjord is located between 77°07´ and 77°58´ N. latitude and 13°56´ and 14°20´ E. longtitude in the western part of the archipelago and extends meridionally to the South-South-East (Figure 1).

Figure 1. Field detachments at the base of the Spitsbergen party in Barentsburg (Photo courtesy of Stock Venture "PMGE". Source: http:// http://pmge.ru/index.php?id=666&lang=RUS).

It constitutes the Southwestern branch of the East Fjord, goes far into the land, its southern coast borders on relatively large glaciers while the water area of the gulf is open to the Arctic basin. It extends southward for 17 km with the maximum depth – 155 m. The North European Basin (NEB), including the Norwegian and Green-land Seas, plays a key role in exchange between the Arctic Basin (AB) and the North At-lantic (NA). The total area is more than 193 km^2, and 60 km^2 of it – a subject to glaciation. Due to its geographical position, Grönfjord is a significant energy-active zone

(Alekseev, 1989; Korshenko, 2020). In the central part of the Greenland Sea, which is the deepest sea of the Arctic Ocean (maximum depth is about 4800 – 5527 m) WSC forms powerful cyclonic eddies. The formation of the hydrological regime of the fjords of the West Spitsbergen Island occurs un-der the influence of several factors: the inflow of warm saline Atlantic waters, the inflow of relatively desalinated cold Arctic waters, river runoff and the processes of ice formation and ice melting (Clear Seas Related Reports; Svendsen et al. 2002). To the north and west the coastline has fjords formed along fault lines, portions of marine terraces on the coast are evidence of recent uplifts.

The main volume (from the horizon of 40 m to the bottom) of Grönfjord is occupied by slightly warmer intermediate waters of 34.0-34.7 ‰. Owing to reasonably high accumulation rates, these settings are especially suitable for providing high resolution sedimentary records of regional hydrological and environmental changes. There is also a considerable number of watercourses in the area, which contribute to the accelerated rate of sedimentation in the basin (Knies at al., 2011). Sedimentation then also undergoes spatial and temporal changes associated with the dynamics of the aquatic environment. More fine-grained material is carried out seaward, the bulk of the terrigenous material comes in the form of a solid runoff of rivers due to the transfer from land, providing the supply of pollutants, including oil products. Bottom sediments, having a high sorption capacity, accumulate petroleum hydrocarbons, which in cold arctic conditions can be stored for a long time due to extremely slow bio-degradation processes. The Svalbard archipelago is located in the high Arctic (76°-80°N) within the northernmost reach of the West Spitsbergen Current (WSC), which is the continuation of the North Atlantic Current. In these specific settings close to the Polar Front, even small variations in the system of flows are expected to give large and distinct signals in paleoceanographic parameters (S´lubowska et al, 2005).

2.2 Methods

All the chemical analyses of sediments have been carried out using the accredited methods used by FSBI RPA «Typhoon» for PAH/THC analyses. THC has been analysed by gas chromatography with flame ionization detector. A method of infrared spectroscopy allowed to measure the content of non-polar and low-polar petroleum hydrocarbons by the use of column chromatography. PAH contcentrations were analysed with application of a high performance liquid chromatography method, measurings range from 0.005 μg/dm^3 for some PAH including benzo(a)pyrene and was done according to the methodology described by regulatory documents (RD 52.18.800-2013, RD 52.10.243-92). The onboard works were conducted as a part of the ongoing state monitoring programme. Background observations were carried out in order to study interannual variability at stations, located in the areas with lower levels of pollution, or in the clean waters. In general, samples of local monitoring were taken at stations adjacent to the territory of Barentsburg in the eastern part of Grönfjord. The location of the stations was chosen according to geomorphological characteristics of the bottom and the configuration features of Grönfjord coastline (Figure 1). Sea water samples were taken onboard with the use of Niskin bathometer with a volume of 5-10 *l* for two horizons (surface and bottom). Bottom sediment samples were taken by a Van Veen grab, an instrument to sample (disturbed) sediment up to a depth of 15 cm in the seafloor. All samples were collected in accordance guidance documents (GOST R 51592-2000, GOST 17.1.5.01-80). Sampling, preservation and chemical analysis was carried out in accordance with GOST 17.1.3.07-82.

3 Data

In this study in order to determine the levels of pollutants, including petroleum hydrocarbons, the North-Western Branch of Research and Production Association “Typhoon” (NW RPA“Typhoon”) took samples of water in the surface and in the near-bottom layers. All samples are assessed for the values of total hydrocarbon content (THC) and the values of polycyclic aromatic hydrocarbons (PAH) contents.

The article is based on data collected in field surveys in the period 2012 – 2022 presenting concentrations of THC and PAH (μg/dm^3) in the area of Svalbard. A series of samplings was carried out in surface and in near-bottom sea waters. The sampling surveys were performed in the period of transition from the summer warming phase with the maximum influence river runoff to the autumn cooling phase with a reduced river runoff.

In total 362 water samples were collected in surface and bottom layers of the water column and analyzed for petroleum hydrocarbons and polyaromatic hydrocarbons (PAH) content. In particular, 24 seawater samples were collected annually for PAH analysis. Water samples were taken from the surface and bottom horizons at ten stations in the eastern part of the waters of Grenfjord, adjacent to the territory of Barentsburg, where the sea depth reaches 110 m, with an average depth of 49 m and at two stations in the western part of the waters of Billefjord Bay, adjacent to the territory of Pyramid at depths ranging from 7 to 11 m (Figure 2).

4. Results

4.1. Results of THC study in the surface layer

For the study area, the mean and elevated THC were annually determined. The levels of THC in the surface and in the near-bottom horizons (2012- 2021) are presented in the Table 1. THC plots (Figures 2, 3) depict sampling results for the surface and the near-bottom horizons.
The results of THC study (μg/dm^3) in the surface layer showed average concentrations ranging from 5 to 22 μg/dm^3 with a local maximum of 86 μg/dm^3 (station 14) at the mouth of Grenfjord. THC levels are also depicted in figures 2, 3. An increase in the content of hydrocarbons in the surface layer is determined in the range of 33 – 70 μg/dm^3 (at stations 28, 26) in the coastal areas of Grönfjord.
In recent years elevated values declined and reached 3 μg/dm^3 (in 2021). Earlier, in 2016 average concentrations were approximately at the levels of 2015 and lower than those of 2014, 2015 (averaged to 29-38 μg/dm^3) reaching up to 42 μg/dm^3 at the western margin of Grönfjord.

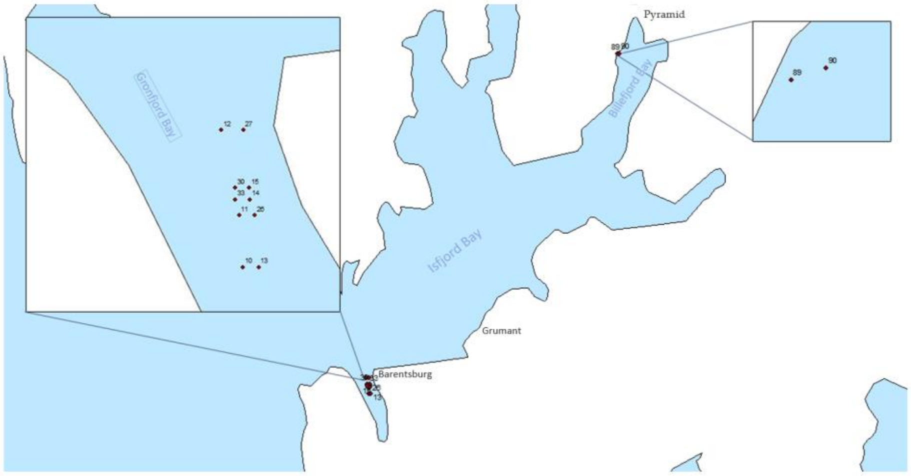

Figure 2. Region map and observation area in the waters of Grönfjord (Korshenko, 2022).

In the surface water layer hydrocarbon content varies on a broad range: from 5 to 22 $\mu g/dm^3$ with a local maximum up to 86 $\mu g/dm^3$.
In 2012 THC ranges at lower levels than concentrations in 2013 (from 9 to 39 $\mu g/dm^3$ at average of 19 $\mu g/dm^3$). In the waters of the eastern part of Grönfjord THC varies from 2 to 86 $\mu g/dm^3$ (starting from the outer area towards the area of the confluence of the stream flowing through Barentsburg). In 2014, 2015 THC varied mainly within 2 - 70 $\mu g/dm^3$ (beginning from the northern part of Grönfjord to the area of confluence of the stream flowing through Barentsburg),at average 26 $\mu g/dm^3$.
In 2016 THC concentrations ranged from 5 to 42 $\mu g/dm^3$, in 2017 THC varies at levels from 0.6 to 5 $\mu g/dm^3$. In 2018 concentrations range from 7 to 23 $\mu g/dm^3$ raising in direction from the adjacent water area of Billefjorden to the north of Barentsburg. In 2019 THC varied from 1 to 32 $\mu g/dm^3$ northward of Barentsburg at average value of 15 $\mu g/dm^3$. In 2021 THC concentrations ranged from 3 to 5 $\mu g/dm^3$ at average about 4 $\mu g/dm^3$. For different areas of the sea, the average THC in the study area decreased starting from station 14 (22 $\mu g/dm^3$) to the water area north from Barentsburg (station 27 (9) and further to the of Grönfjord outlet (station 33 (5) (Western part < Central part). In 2019 the highest values of THC (70-86) were observed. Maximum values of THC varied from 2012 to 2022 in different areas of Grönfjord in the range 11 - 86 $\mu g/dm^3$ (from the open part to the area at the mouth of Grönfjord near Barentsburg (station 14). The range of values in surface layer is somewhat broader than in near-bottom layer, the results of which are discussed below (see also Table 1).

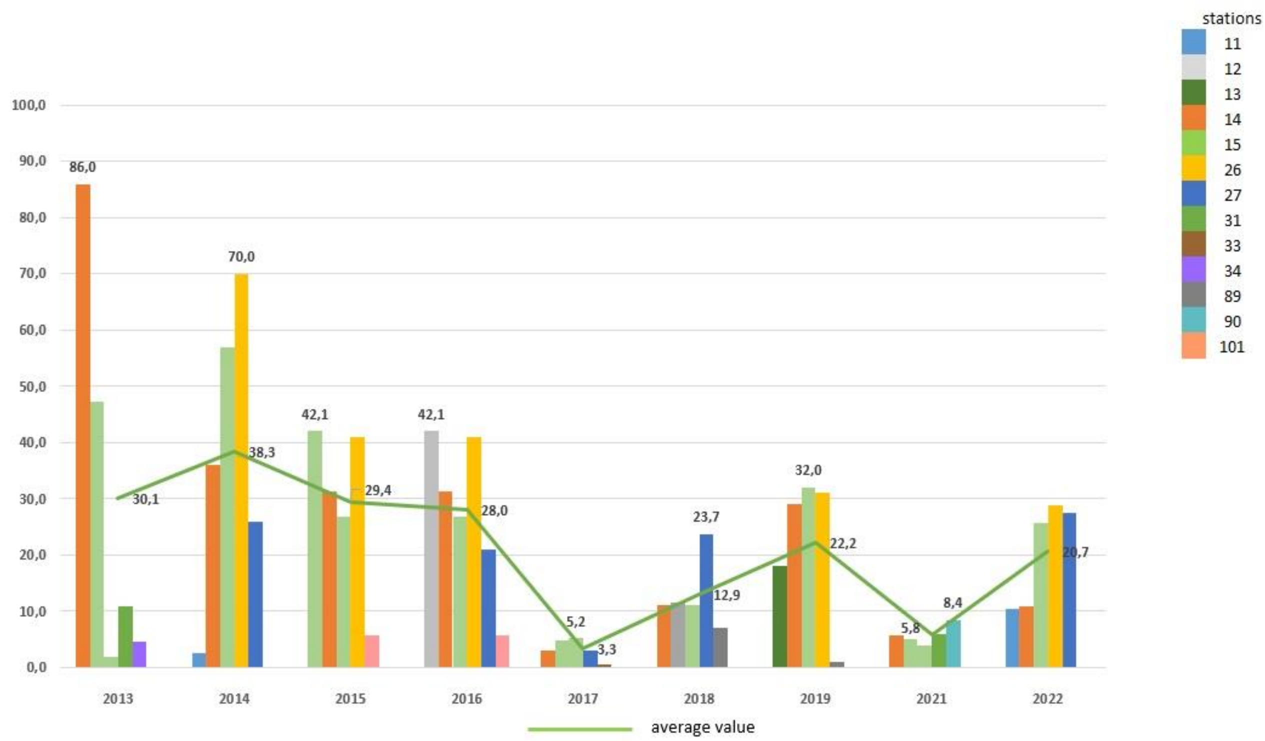

Figure 3. Long-term changes in maximum and average concentrations of THC, µg/dm^3, in the surface water layer (by stations) (2012-2022).

4.2. Results of THC study in the near-bottom horizon

In 2016 the results of the study of THC (µg/dm^3) in the near-bottom water layer are detected at maxima of 35 µg/dm^3 in the main parts of the gulf; in 2018 concentrations – 38 µg/dm^3 (in the area north of Barentsburg); in 2019 – 42 µg/dm^3 in the area at the mouth of the stream flowing through Barentsburg (in total – 10 µg/dm^3). In 2017 in the gulf outlet concentrations turned out to be lower than in previous years, their content in 2016 averaged to 21 µg/dm^3.

The average THC concentrations decreased for different areas in sequence: from the station 14, located in the area at the mouth (22 µg/dm^3) – to the station 27 in the direction to the north of Barentsburg (9 µg/dm^3) and to the open part of the gulf (5 µg/dm^3)(Figure 3).

The results revealed pronounced interannual variations of THC concentrations near the bottom in the study period. Basically, in the near-bottom layer, the THC content at almost all stations is lower than in the surface layer with some exceptions at 2 stations – 27 and 12 µg/dm^3.

Rapid sea-level drops, tectonic uplift, and re-activitation of faults during the late Miocene may be responsible for the leakage of hydrocarbons during the late Miocene (AMAP, 2007). In 2019 among all controlled areas of the gulf, the highest value of the average concentration of petroleum hydrocarbons reached 42 µg/dm^3 in the near-bottom layer.

Table 1. General long-term dynamics of the average and maximum concentration of THC, µg/dm^3, in the surface and the near-bottom horizons in various parts of Grönfjord (Svalbard) (2012-2022).

Stations (№)														
10	**11**	**12**	**13**	**28**	**29**	**30**	**31**	**32**	**33**	**34**	**14**	**15**	**26**	**27**
The Surface Horizon														
7/24	6/27	7/42	10/36	10/33	13/28	7/19	11/36	9/37	**5**/19	9/23	**22**/**86**	18/57	17/70	9/26
The Near-Bottom Horizon														
5/22	7/22	8/**42**	8/24	8/22	7/21	7/21	10/24	7/35	5/26	6/16	10/27	13/36	12/39	9/38

Herein, THC content in the near-bottom horizon is 1.5–3.6 times higher than in the surface layer. Such features in the distribution of hydrocarbons in the near-bottom layer can be explained by water dynamics in the near-bottom layer (Novikov, Draganov, 2021) contributing to resuspension of sediments and formation of elevated amount of suspended matter and higher concentrations of hydrocarbons. Besides, at some stations elevated levels of hydrocarbon concentrations can be associated with HC fluid flows from the sedimentary layer suggesting migration of hydrocarbons from deeper sediment layers.

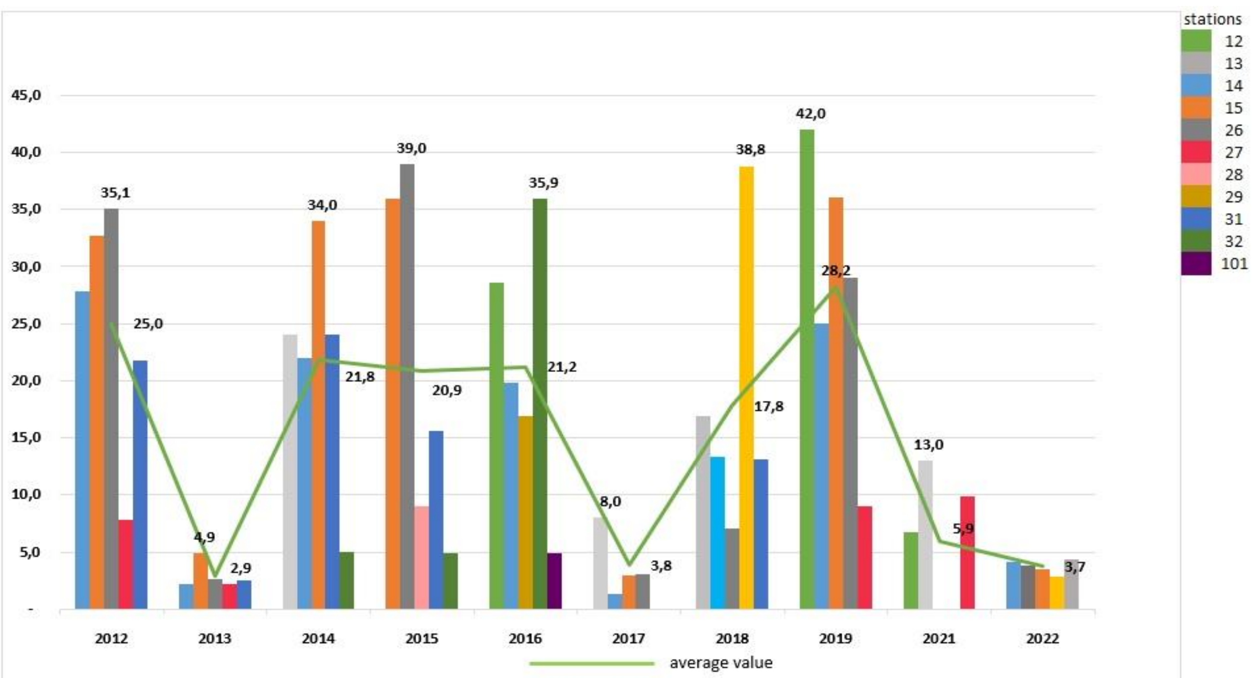

Figure 4. Long-term changes in maximum and average concentrations of petroleum hydrocarbons THC, µg/dm^3, in near-bottom layer (by stations) in Grönfjord (Svalbard) (2012-2022).

The results showed that THC had substantial reduction the last years (2021, 2022) supposing a reduction in revenue from natural sources and transport of contamination in the near-bottom layer but still affecting more the surface water layers.

4.3. Results of PAH

The term polycyclic aromatic hydrocarbons (PAHs) refers to a group of several hundred chemically related, environmentally persistent organic compounds of various structures and varied toxicity. PAHs are known by a high level of chemical stability, therefore, in environmental monitoring PAHs are considered to be the priority pollutants and subject to control in monitoring of the state of the environment (Lee et al., 2015, Clear Seas Related Reports, 2017). PAHs enter the environment through oil spills, fuel combustion, forest fires, and industrial releases. These pollutants are mostly formed during the incomplete combustion and pyrolysis of fossil fuels or wood, and from the release of petroleum products (Manahan, 1994).

Other sources of PAHs include petroleum spills, oil seepage, and diagenesis of organic matter in anoxic sediments. PAHs are also found in coal tar, crude oil, creosote, and roofing tar, and a few are used in medicine or to make dyes, plastics, and pesticides. PAHs produced for commercial use, include naphthalene, fluorene, anthracene, phenanthrene, fluoranthene, and pyrene (Franck, Stadelhofer, 1987). State monitoring system makes records of PAHs in Grönfjord annually. Some of the 16 controlled compounds as priority PAH constituents (ΣPAH) are as follows: (naphthalene (Naph); acenaphthylene (Ace); fluorene (Flu); acenaphthene (Acen); phenanthrene (Phe); anthracene (Ant); fluoranthene (Fluo); pyrene (Pyr); benzo(a)anthracene (BaA); chrysene (Chry); benzo(b)fluoranthene (benzo(b)); benzo(k)fluoranthene (benzo(k)); benzo(a)pyrene (BaP); dibenzo(a,h)anthracene (Diben); indeno(1,2,3cd) pyrene (Ind); benzo(g,h,i)perylene (BghiP)) are not detected every year but more than half out of 16 compounds are always observed in the sea water [Korshenko, 2021]. Since 2015, there has been a decrease in the concentration of PAHs in the study area. In 2016, PAHs were not determined in sea waters. In 2017-2018 there is a slight increase, but since 2019, the downward trend of this indicator over a ten-year period has again been maintained, compared to 2012 and 2014 (Figure 5).

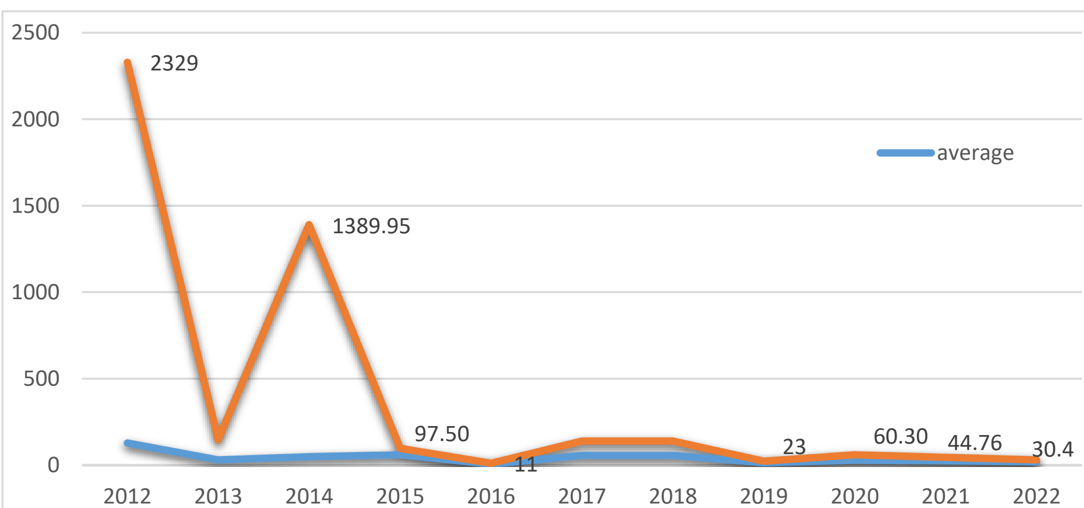

Figure 5. Dynamics of PAH, in Grönfjord (2012-2022).

Last years (2019-2022) the average values of the amount of PAHs were as follows: in 2019 - 13.35 ng/dm^3, in 2020 - 29.30 ng/dm^3, in 2021 - 24.20 ng/dm^3; maximum - 23, 60.30 ng/dm^{3}and 44.76 ng/dm^3, respectively. The trend towards decreasing PAH concentrations in 2022 remains. The average total content of priority compounds of the PAH group in the waters of Grenfjord in July 2022 reached 19.75, the maximum – 30.40, which is 1.5 times lower than the extreme values in 2021. The presence of annually predominant PAH in marine waters was assessed in the diagram (Figure 6). The diagram shows the most part of naphthalene, the next predominant PAH is phenanthrene, the next highest concentration observed annually is chrysene, and the lowest concentrations – pyrene and, the last – benzo(a)pyrene. In 2022 naphthalene content was below detection limit.

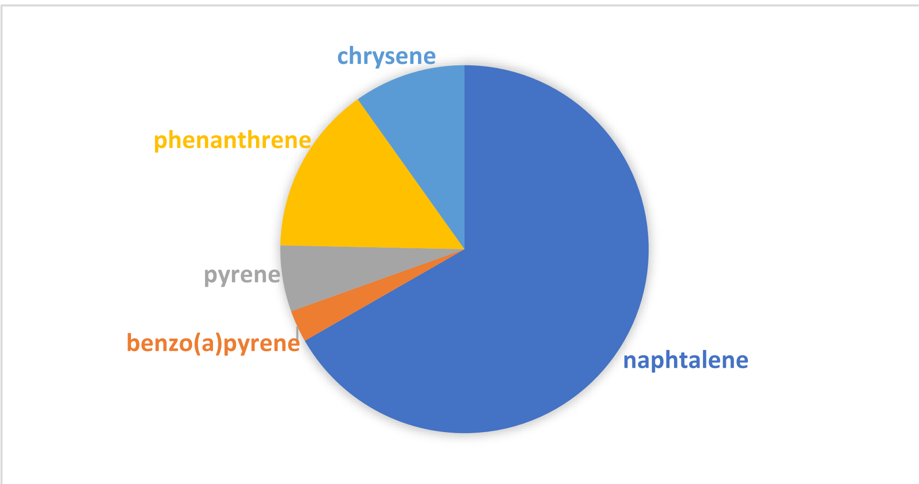

Figure 6. Diagram of the content of the most common and cancerogenic PAHs, in the waters of Grönfjord, ng/dm^3 (based on the average values of each compound (2012 – 2022).

The results showed that the predominance of naphthalene and phenanthrene was detected. Various studies showed that similar PAH concentrations and the predominance of naphthalene and phenanthrene was detected off the coast of Svalbard and in the fjords of the archipelago for decades. Thus, it has been suggested that the source of PAHs in bottom sediments and in marine waters comes from the process of erosion of carbonaceous deposits in the western part of Svalbard (Dahle, 2009).

Local sources of natural origin contribute to elevated PAH levels in some areas. High concentrations of pyrogenic PAHs are determined by low-temperature processes of natural formation. As the earlier surveys showed, relatively high concentrations of PAHs are grouped along the coast of Svalbard and near its southern tip (3000–7000 ng/g) in bottom sediments (Nemirovskaya at al, 2020).

Data on studies of PAHs in bottom sediments is more prolific than that in the seawater. Thus, sea bottom sediments are characterized by a “significant” degree of benzo/a/pyrene contamination (27–47 ng/g in Grönfjord) (Korshenko, 2020), which may be associated with sampling directly during the period of ice melting. However, increased concentrations can also be associated with the flow of petroleum hydrocarbons in shipping areas. Offshore, in open sea areas within the Svalbard-Medvezhinsky section of the shelf, PAH concentrations in sediments are significantly higher than in the central parts of the sea, and significantly decrease eastward to the levels proper to those in the central parts of the Barents Sea.

In the composition of PAHs, along with anthropogenic polyarenes: pyrene, fluoranthene (Fluo), benzo(k)fluoranthene (benzo(k)), PAHs were also present, which are predominantly of natural origin - naphthalene, phenanthrene, chrysene.

Most likely, it reflects the leading role of weathering and abrasion of coal-bearing rocks of the archipelago (for instance, naphthalene, a benzene hydrocarbon obtained originally from distillation of coal tar) and the part of air distribution of dust material in background formation of PAH in sediments. As stated in previous studies a relatively high concentration of naphthalene and methylnaphthalenes, the presence of short-chain alkanes in sediments indicates another source of pollution - the invasion of PAHs together with petroleum hydrocarbons from the sedimentary cover (Ilyin at al, 1997).

Analysis of PAHs based on collation of the concentrations in the surface and in the bottom water layers of the relevant periods showed no significant differentiation in the values.

Only surface concentrations exhibit elevated levels of some PAHs, probably as a result of higher amounts of organic particles in this layer.

In the surface layer PAH concentrations of 59.18 ng/g were detected on station 12 (85 m depth), where the values in the bottom layer were about 51.45 ng/g. In 2017 at the same station PAH concentrations in the surface layer were about 10 ng/g and in the bottom layer - 5 ng/g. In the remainder of the studied area, the observed PAH levels are supposed mostly due to complex sedimentation processes, influenced by biotic activities, long-range atmospheric transport, or sea currents.

In the Greenland Sea and in the Grönfjord major sources of contaminants include: natural processes; long-distance transport of atmospheric deposition; accidental releases from local industrial activities; and vessel fuel emissions. As the Barents Sea is among the most intensive vessel transits region in the Arctic fishing vessels accounted for a large majority of logged vessel transits in 2015-2017 (62,1 %), followed by general cargo ships (7,2 %), research vessels (2,9 %) and ships associated with the oil industry (2,6 %). Fishing vessels also accounted for a large majority of the logged operating hours in the region during 2015–2017 and this amount continues to rise.

Thus, elevated THC concentrations can also be associated with the flow of petroleum hydrocarbons in shipping areas.

Results from the Norwegian-Russian joint ecosystem surveys (BESS 2018, ICES, 2019, MAREANO (2006-2022) showed no elevated concentrations of THC or PAH (public domain) in the entire open waters of the Barents Sea. Also the maps of excessive background levels were applied to consider the issues related to the containment of technogenic pollution in the Barents and the Norwegian sea bottom sediments. Thus, the problem of localization of technogenic pollution in bottom sediments is considered by the Polar Branch of «VNIRO» in the integrated maps (THC, PAH) (Novikov, Draganov, 2021).

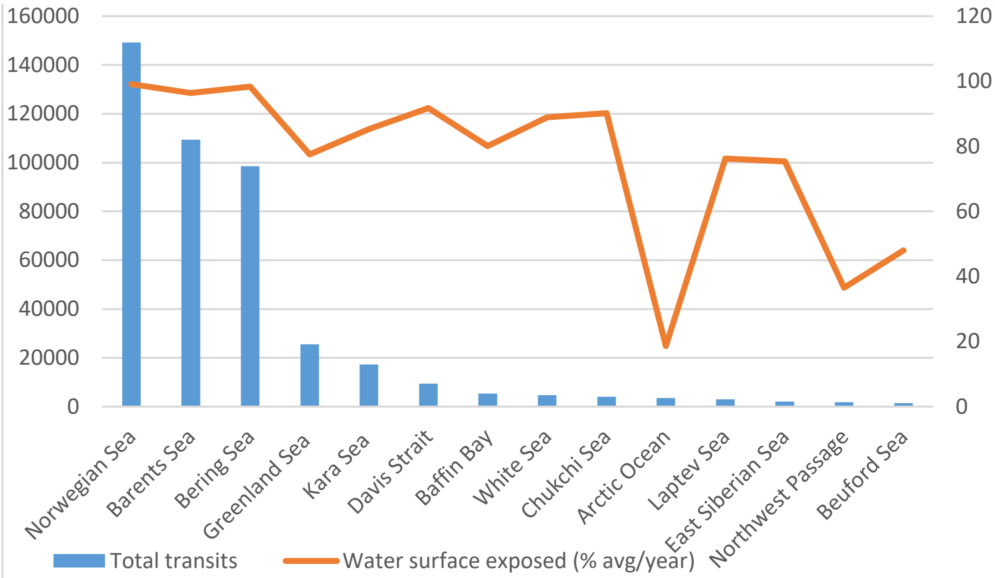

Figure 7. Total number of vessel transits operating in Arctic waters and average water surface exposed to vessel traffic (% year) during 2015–2017. Data courtesy of Silber & Adams, 2019 (Silber, Adams, 2019).

Comparative analysis of THC and PAH levels in different years reveals that actual concentrations of THC and PAH have become lower than those of the previous years starting from 2005. Concentrations of most of the pollutants in the waters of Grönfjord showed values typical for the coastal waters of the Norwegian Sea and the North Sea. According to water quality requirements for fishery reservoirs the waters of Grönfjord are classified as «moderately polluted» (quality class III) with an insignificant level of impact of coastal sources of pollution in summer periods of 2019, 2020 (Korshenko, 2020, 2021, 2022), the classification is consistent with the Norwegian classification (moderat, klasse III) (www.mareano.no).

Nevertheless, any economic activity entails certain pressures on territories and ecosystems and does not exclude the risk of environmental pollution. Along with escalating oil and gas activities near Svalbard the type of oil spilled in marine ecosystems as well as the unique environmental conditions in which an oil spill takes place are both important for the evaluation of an impact of spilled oil on the characteristics and conditions of a spill site, especially in marine environments covered in ice. Research is needed to better understand what happens to oil spilled into the cold, icy, yet ecologically sensitive waters of the fjord and even the Arctic, where interest in oil exploration, production and shipping is on the rise.

The evaluation of PAH sources present in the waters of Grönfjord depicted the predominance of mixed pyrogenic activities such as biomass and coal combustion, which may have resulted because of vehicular emissions. Svalbard is the area with large coal reservoirs, and where coal-mining activities have been in progress for decades. Comparative studies of bottom sediments collected in the Svalbard offshore area and soils from West Spitsbergen Island have demonstrated the predominant source of PAHs to be the erosion of coal-bearing bedrock in Svalbard (Boitsov, 2009).

With the concentration of various nature users in a small coastal area, in order to avoid conflicts of interest and preserve the unique ecosystem of the archipelago, it is highly recommended to apply the sustainable management tools in the region. At present, the region of the Norwegian and the

Greenland Seas remains the object of intensive field research and this paper is also devoted to continue and develop the previous studies.

5 Conclusions

This study assessed THC and PAH in Grönfjord – a navigable area, which is due to escalating economic activities exposed to a risk of oil spill. The results of the study also made it possible to clarify the distribution of elevated hydrocarbon levels.

Maximum concentrations of hydrocarbons (THC) were determined in the surface water layer. The average total content of petroleum hydrocarbons in the surface waters of the surveyed area is observed in the range from 5 to 22 (83 μg/dm^3). The maximum content of THC was recorded at station 14 in the surface layer at a depth of 87 m in the area north of Barentsburg, closer to the central part of of Grönfjord.

For surface waters it should be noted that during the five years since 2017 there was a reducing tendency in the degree of pollution (THC). In 2021, 2022 lower concentrations if compared to previous years may result in a decrease in oil pollution and the increased protection and supervisory measures, control of emissions resulting on the less glacier pollution. Findings showed that THC had substantial reduction suggesting reduction in revenue.

The maximum concentrations at the near-bottom layer were at a depth of 85.5 m at the station in the southern part of Grönfjord (42 μg/dm^3), elevated THC concentrations at horizons of 20.5-110.0 meters are typical for areas with high oil and gas generation poten-tial. However, increased concentrations can also be associated with sampling time during the period of ice melting or supplies of petroleum hydrocarbons in navigable areas.

Approximately similar values of the average and maximum concentrations both in the surface and in the near-bottom layers are noted at the most remote offshore stations. Since 2017 in the following five years there was a tendency to reduce the degree of pollu-tion.Since the beginning of research in Grönfjord (in 2012) according to the state observational network data PAHs have been recorded every year, and their concentrations are well-corresponded to those in other studies and the open data. Until 2015 the maximum content of total PAHs could reach 1390 ng/dm^3. Since 2015 there has been a decrease in the concentration of PAHs in the study area. Naphthalene, phenanthrene, and chrysene predominate annually among the most cancenogenic PAHs and pyrene and benzo(a)pyrene have the lowest concentrations.The levels of individual PAHs can be associated with their origin sources through the use of specific PAH species which provide more unique markers for the sources. In some areas of the sea, local sources of natural origin contribute to elevated levels of PAHs in bottom sediments, in particular near Svalbard. In the study area, the observed levels of PAHs are mainly due to complex sedimentation processes, including those under the influence of nutrient activity, long range atmospheric transport or sea currents. The review highlights the need to further identify the variability of these parameters in continuous monitoring of the state of the waters of Grönfjord.

Thus, no exclusively anthropogenic impact on the water body was depicted in this study. At the same time, some local concentrations maxima for THC in the surface horizon may be an evidence of a marked anthropogenic impact on the water area along the coastline. It also indicates that many processes in the North European Basin require further continuous research. Currently, there is a number of approaches to identify vulnerable areas of the sea coastal areas (Wells et al, 2007; Shavykin, Ilyin, 2010) and the results of the work may be used in the aims of environmental monitoring, forecasting and development of measures for rehabilitation of water resources and their protection, also they can be applied in practice of interested companies. The study confirms that of Grönfjord is a fair representative area for conducting comprehensive observations in order to obtain estimates of the impact of economic activity on natural environment and the state of stability of hydrocarbon content and the level of pollution of sea bodies. In prospect, summer hydrochemical studies will make it possible also to measure the presence of WSC in the waters of Grönfjord and track the pollutant inflows into the Arctic Ocean.

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The authors declare no conflict of interest.

Open Research

Data Availability Statement:

1. Data published in the literature: Datasets and software for this research are included in this paper (in the part Methods and also figures and tables). Data available on request North-Western Branch of Scientific and Production Association “Typhoon”, on contact by e-mail: typhoon.ecol@mail.ru.
2. Datasets for this research are also described in these papers: [Marine Water Pollution. Annual Report 2019. – Editor Alexander Korshenko, Moscow, “Nauka”, 2020, p. 192-198. ISBN 978-5-9500646-7-8; Marine Water Pollution. Annual Report 2021/Editor Alexander Korshenko – Moscow: SOI, 2023, p.153-158. – ISBN 978-5-6045347-2-4 and in the reports given in yearbooks available by link: http://www.oceanography.ru/index.php/2020-11-08-17-54-32/2020-11-08-18-07-11

Software Availability Statement:
Software archived in a repository: Software for this research is available in these in-text data citation references. Such software must be findable and accessible (e.g. via URLs) and on access: https://www.rpatyphoon.ru/about/structure/units/szf.php

Software is stored in this in-text citation reference: Korshenko A.N. (ed.) (2019, 2020, 2021) [with these access restrictions if any]. The Annual Reports summarize routine observation data on the quality of the seawaters and bottom sediments conducted by regional chemical laboratories and the NW RPA “Typhoon”.

Research and Production Association “Typhoon” is the main research institution of Russian Federal Service for Hydrometeorology and Environmental Monitoring (Roshydromet) for environmental monitoring including persistent organic pollutants (all environmental components). The North-Western Branch of Research and Production Association “Typhoon” (NW RPA “Typhoon”) (Saint Petersburg, Russia) is an institution subordinate to the Roshydromet. NW RPA “Typhoon” is accredited by the Federal Agency for Technical Regulation and Metrology for competence and independence in the Accreditation System of Analytical Laboratories (Centers) and has the Roshydromet licenses necessary for the implementation of its activity profile in the areas: operational inspection of areas with extreme environmental pollution; development of projects for integrated environmental monitoring systems with varying degrees of spatial localization; hydrological and morphometric studies on water bodies; industrial environmental control; background and local monitoring of environmental pollution; environmental monitoring; assessment of pollution of natural environment components; carrying out serial chemical analytical works and expert analytical studies; creation of specialized environmental information data banks. NW RPA “Typhoon” is equipped by a chemical-analytical testing center and applies scanning spectrophotometers with PC-based data processing stations, filtration IR photometers, spectrofluorimeters, automatic titration installations, ionometric installations, gas-liquid chromatographs with various detector systems, atomic absorption systems with flame and non-flame atomization options and cold steam attachments for mercury determination, high-resolution ion chromatographs and other analytical equipment. The expedition team is equipped with highly efficient natural water sampling systems, modern autonomous aspiration units for sampling atmospheric air, bottom sediment and soil samplers with pneumatic reinforcement, sets of field laboratories for express determination of hydrochemical parameters, processing and concentration of samples for pollutant content and other equipment applied in hydrometeorological and hydrological studies.

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Figure 1. Field detachments at the base of the Spitsbergen party in Barentsburg (Photo courtesy of Stock Venture "PMGE". Source: http://http://pmge.ru/index.php?id=666&lang=RUS).

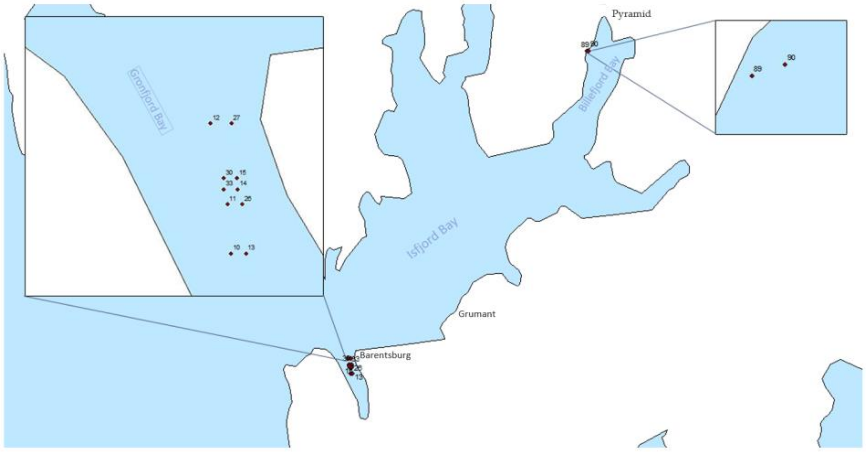


Figure 2. Region map and observation area in the waters of Grönfjord (Korshenko, 2022)].

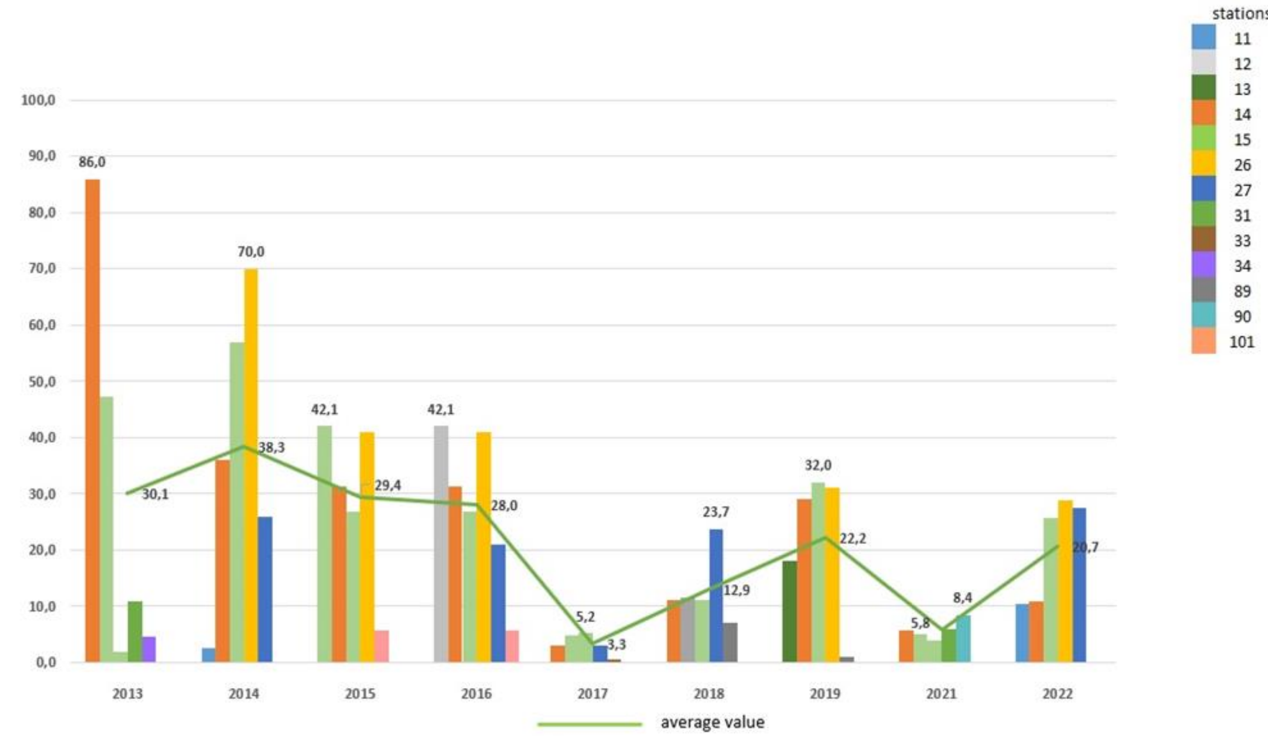


Figure 3. Long-term changes in the maximum and average concentrations of THC, µg/dm³, in the surface water layer (by stations) (2012 – 2022).

Table 1. General long-term dynamics of the average and maximum concentration of THC, µg/dm³, in the surface and near-bottom horizons in various parts of Grönfjord (Svalbard) (2012 – 2022).

Stations (№)

10	11	12	13	28	29	30	31	32	33	34	14	15	26	27
The Surface Horizon														
7 / 24	6 / 27	7 / 42	10 / 36	10 / 33	13 / 28	7 / 19	11 / 36	9 / 37	**5** / 19	9 / 23	**22** / **86**	18 / 57	17 / 70	9 / 26
The Near-Bottom Horizon														
5 / 22	7 / 22	8 / **42**	8 / 24	8 / 22	7 / 21	7 / 21	10 / 24	7 / 35	5 / 26	6 / 16	10 / 27	13 / 36	12 / 39	9 / 38

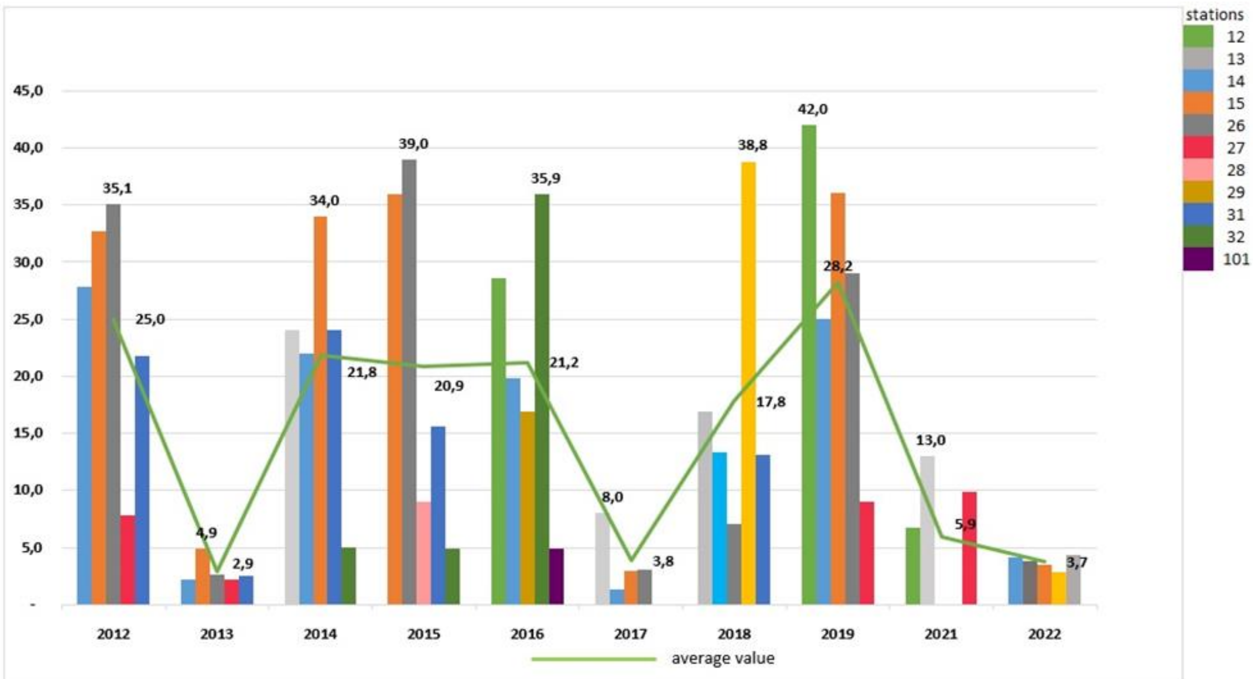


Figure 4. Long-term changes in maximum and average concentrations of petroleum hydrocarbons THC, µg/dm^3, in near-bottom layer (by stations) in Grönfjord (Svalbard) (2012-2022).

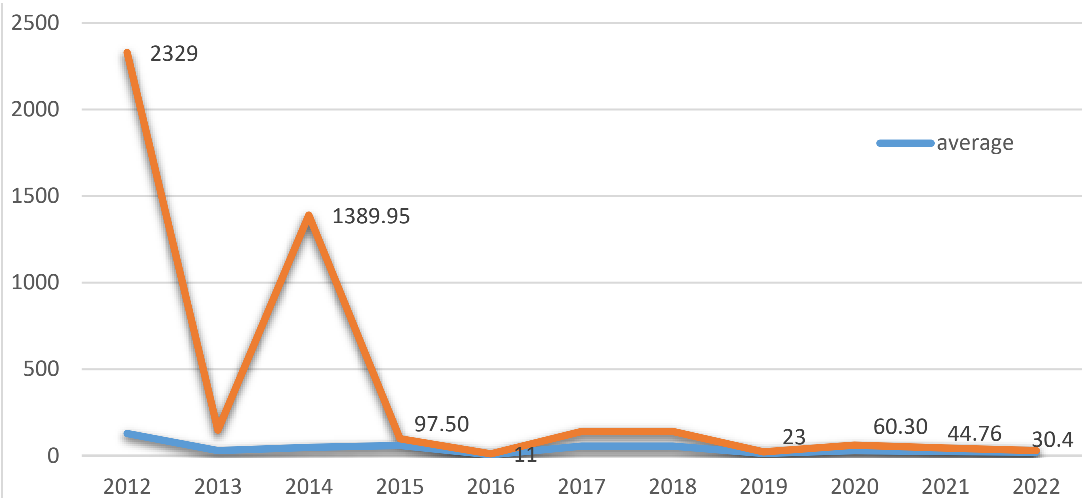


Figure 5. Dynamics of PAH, in Grönfjord (2012-2022).

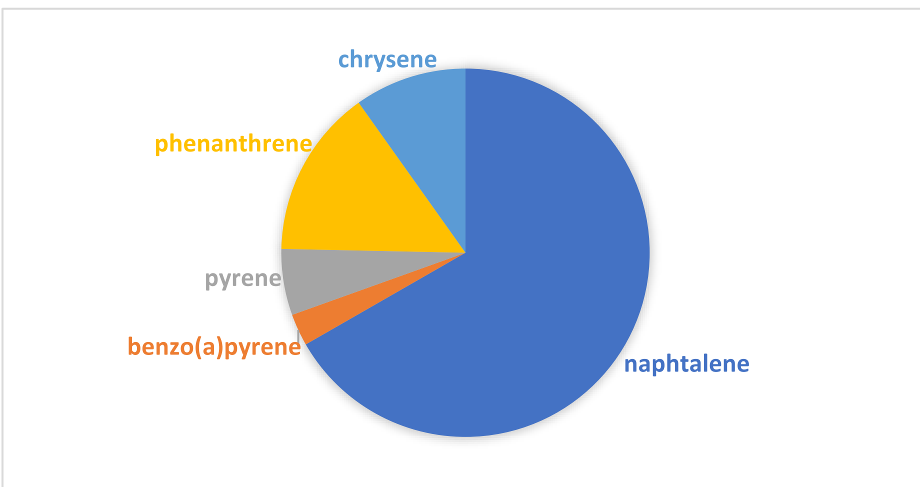
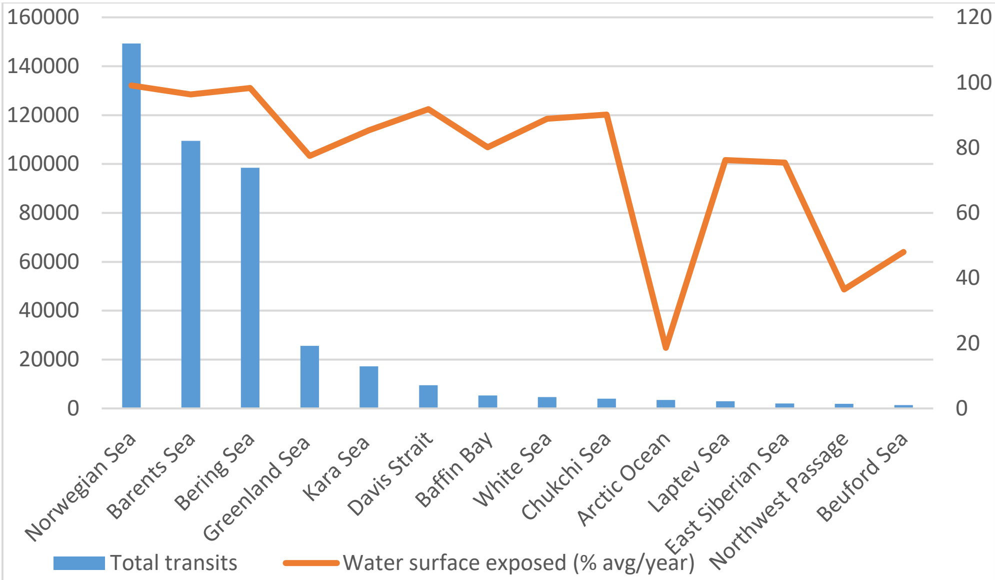


Figure 6. Diagram of the content of the most common and cancerogenic PAHs, in the waters of Grönfjord, ng/dm^3 (based on the average values of each compound (2012 – 2022).

564 

565 **Figure 7. Total number of vessel transits operating in Arctic waters and average water surface**
566 **exposed to vessel traffic (% year) during 2015–2017. Data courtesy of Silber & Adams, 2019**
567 **(Silber, Adams, 2019).**