ANNUAL REPORT ON GEOTRACES ACTIVITIES IN RUSSIA

April 1st, 2018 to March 31st, 2019

New scientific results

Arctic Ocean Basin

- "The White Sea Environment" monograph was published in book series of "The Handbook of Environmental Chemistry", Springer, 2018: part 1 "Biogeochemistry of the Atmosphere, Ice and Water of the White Sea", A.P. Lisitsyn and V.V. Gordeev (eds.); part 2 "Sedimentation Processes in the White Sea", A.P. Lisitsyn and L.L. Demina (eds.). The results of multidisciplinary researches in the White Sea basin (subarctic) from 2000 to 2016 were summarized in the monograph. We should note that most of the data presented in the volumes is directly related to the goals and objectives of the GEOTRACES.

- The large (size up to 51×40×10 cm) randomly distributed single blocks (massive crusts) and small crusts micrite-cemented by Mg-calcite were found for the first time on the surface of the modern shelf sediments of the Siberian Arctic seas. The researches were carried out at a cold methane seep site in the Laptev Sea (depth of 63 m) (Figure 8). Microbial mats, methane gas bubbles and carbonate blocks were also visually observed. The composition, morphology, macro- and microstructure of carbonate blocks and crusts have been studied. We guess the carbonate blocks and crusts were developed earlier (not in recent conditions), and evidently not at the site they were sampled. The involvement of methane in the carbonate formation has been proven. We suggested that the methane is predominantly thermogenic. It participated in the formation of carbonate blocks and crusts during the dissociation of gas hydrates during the warming period in the Arctic, which occurred in the Holocene, about 10.5–8.5 ka. Further task of studying authigenic carbonates on the East Siberian shelf should be a detailed study of their U-Th carbonate age to determine carbonate precipitation rates and to provide new insights on the intensity of methane-containing fluids in the Arctic (Kravchishina et al., in preparation).

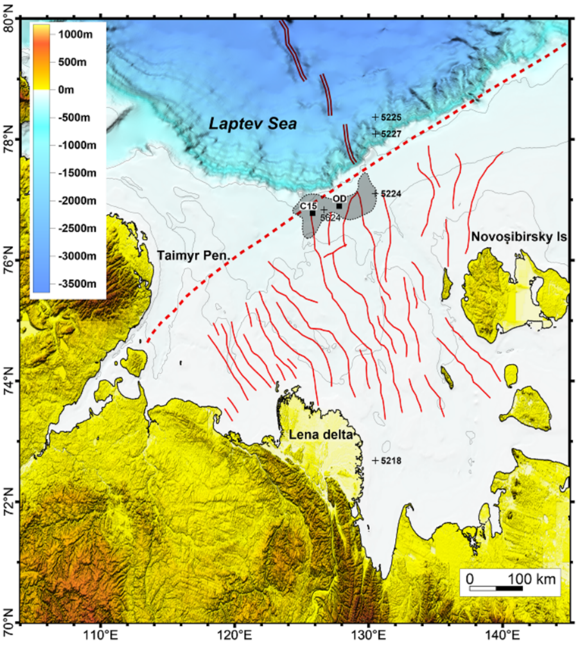

Figure 8. Map of the study area in the Laptev Sea, grid is from IBCAO V.3 (Jakobsson et al. 2012). Filled squares mark two studied sites, crosses indicate sampling sites. Gray color shows the domain of cold methane seep fields according to data from (Shakhova et al., 2015). The double red line is the axis of the Gakkel Ridge, the dashed red line is the Khatanga-Lomonosov Fault Zone, and the red lines are the faults of the Laptev Sea Rift System (Drachev, 2000).

- The isotopic characteristics (εNd, $^{207}Pb/^{206}Pb$, and $^{87}Sr/^{86}Sr$) of the modern bottom sediments sampled in the Barents Sea during the 67th cruise of the R/V *Akademik Mstislav Keldysh* were studied. The major contribution to the formation of the isotopic Nd and Sr composition of bottom sediments in the Barents Sea is made of rocks from the northern European continental margin. The material from the island uplifts (Franz Josef Land, Novaya Zemlya Archipelago), which are composed mainly of basic magmatic rocks, is delivered to the northern Barents Sea along with the Arctic currents, being accumulated within the first few tens of kilometers from their shores. However, this material does not significantly influence the isotopic characteristics of bottom sediments in the central areas of the sea. It is interesting to note that the values of εNd and $^{87}Sr/^{86}Sr$ in the bottom sediments of the central Barents Sea are markedly lower than the corresponding characteristics of sedimentary material incorporated in the ice and carried by the Transpolar Drift Stream (Figure 9). This suggests that ice rafting did not contribute much to the formation of the bottom sediments in the Barents Sea (*Maslov et al., 2019*).

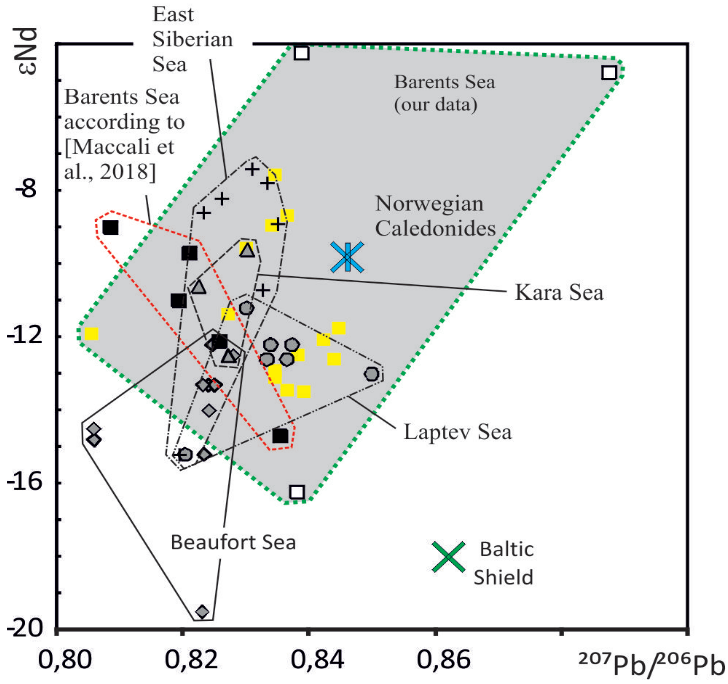

***Figure 9**. Distribution of points of bottom sediments from the Eurasian region of the Arctic Sea and the Beaufort Sea (according to (Maccali et al., 2018) and our data) in the $^{207}Pb/^{206}Pb$–εNd diagram (Maslov et al., 2019).*

- In the central part of the Arctic Ocean, sea ice actively accumulates sedimentary material from the atmosphere (in snow) in its top layer and from the hydrosphere (under new ice formation). The snow – ice – water system in the region of the North Pole is characterized by high values of the biogenic matter (from 65 to 85%) even in winter. The participation of the lithogenic component is small (from 15 to 35%) and is mainly related to aeolian transportation. Sea ice fluxes of sedimentary material at the North Pole in April are characterized by a total flux of 37 mg/(m^2 day) and a flux of organic carbon of 7.4 mg C/(m^2 day) (*Novigatsky, Lisitzin, 2018*).

- The fluorescence quantum yield (FQY) as a function of excitation wavelength within 240–500 nm range for a variety of the Arctic shelf waters was determined for the first time in order to identify the characteristic chromophoric dissolved organic matter (CDOM) peculiar to different regions of the Arctic basin affected by freshwater runoff. The surface water samples were collected during several cruises in 2015–2017 in the Laptev Sea, White Sea, Kara Sea and East Siberian Sea influenced by freshwaters river runoff, as well the shelf areas of those seas not affected by terrigenous runoff. To characterize DOM, conventional optical indices SR, HIX, and BIX were calculated. In most cases, important humic character of DOM was established, while the contribution of autochthonous organic matter varied from low to intermediate level. For the samples with terrestrial impact, the FQY decreased from excitation at 240 nm to 270–280 nm and then increased, demonstrating two peaks at 340 and 380 nm, with constant decrease towards longer excitation wavelengths; at λ_{ex} = 380 nm FQY varied from 1.4% to 3.1%. In some cases, additional maximum at 270 nm of FQY-excitation dependency was observed as an indicator of autochthonous nature of biological material. Minimal FQY was measured for the White Sea surface waters, the maximal for the Laptev and East Siberian seas (*Drozdova et al., 2018*).

- The fluxes of anthropogenic heavy metals (Pb, Cd, As, Zn, Ni, Cr, Cu) to the surface of four Russian Arctic seas (the White, Pechora, Kara, and Laptev seas) were estimated using previously calculated concentrations of these elements in the surface atmosphere at some island and continental points. Comparison of the obtained values with the flows of the same components carried by the big rivers into the sea has been carried out. We included the amendments for Pb and Cd atmospheric fluxes to the waters of the White Sea and Pechora Sea, taking into account the contribution of Europe, as well as the contribution of wind raising dust and soil particles in these fluxes, according to EMER reports. The contribution of the atmosphere is comparable with rivers ones for Pb, Ni, Cu and Cr in the White Sea. The contribution of atmospheric transport of heavy metals to the waters of the Kara Sea and Laptev Sea are small, but may be important for those parts of the seas where the roles of large Siberian rivers (Ob', Yenisei, and Lena) are negligible (*Vinogradova, Kotova, 2019*).

Atlantic Ocean Basin

- Distribution of platinum group elements (Ru, Pd, Pt, and Ir) and gold in hydrogenous ferromanganese deposits from the southern part of the Atlantic Ocean (Brazil Basin and Cape Basin) has been studied. The presented samples were the surface and buried Fe–Mn hydrogenous nodules, biomorphous nodules containing predatory fish teeth in their nuclei, and crusts. Platinum content varied from 47 to 247 ng/g, Ru from 5 to 26 ng/g, Pd from 1.1 to 2.8 ng/g, Ir from 1.2 to 4.6 ng/g, and Au from less than 0.2 to 1.2 ng/g. In the studied Fe–Mn crusts and nodules, Pt, Ir, and Ru are significantly correlated with some redox-sensitive trace metals (Co, Ce, and Tl). Similar to cobalt and cerium behaviour, ruthenium, platinum, and iridium are scavenged from seawater by suspended ferromanganese oxyhydroxides (Figure 10). The most likely mechanism of PGE accumulation can be sorption and oxidation on δ-MnO_2 surfaces. The obtained platinum fluxes to ferromanganese crusts and to nodules are close and vary from 35 to 65 ng×cm^{-2}×Ma^{-1} (*Berezhnaya et al., 2018*).

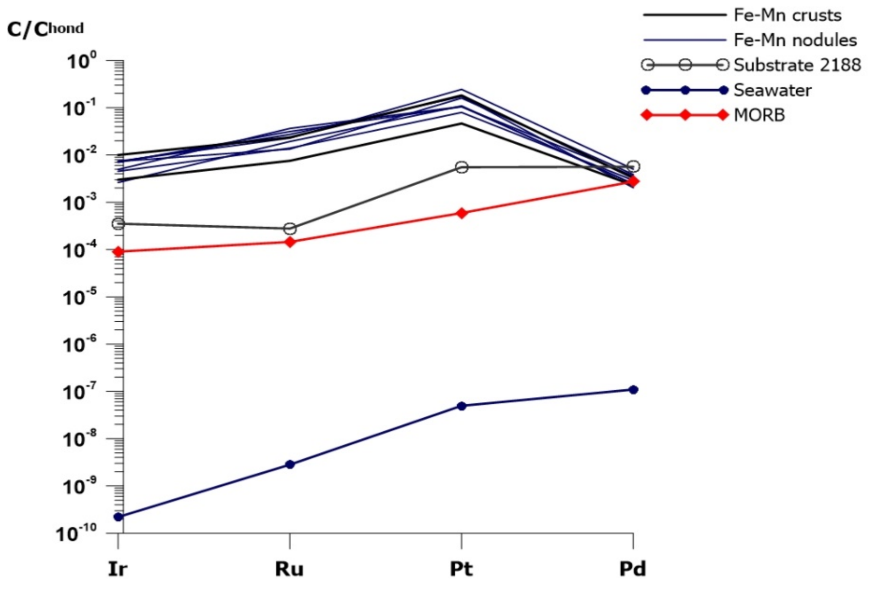

Figure 10. *CI Chondrite-normalized platinum group elements patterns in studied nodules, crust and substrate. For comparison MORB and seawater PGE pattern is shown (Berezhnaya et al., 2018).*

- Investigation of the sinking particles' fluxes using sediment traps at five depths on a latitudinal transect along 59°30'N in the North Atlantic during 2015–2017 was carried out. A seasonal, inter-annual, and vertical change of the total particle flux was revealed, whose values varied between 10 and 145 mg/m^2/day, the latter was measured in July, 2016.The Fe speciation in the deep-sea particle flux at 3 stations were examined by use of sequential leaching procedure. Our data exhibit that at station 3580 (2192 m depth), located above the Snorry Drift, the total Fe content increased strongly with the water depth, while proportion of the Fe main geochemical phases did not remain significantly: the lithogenic form varied within the limits of 55–70%, and Fe in form of authigenic oxy-hydroxides from 20 to 30% of total Fe content (Figure 11). Portion of Fe bound to organic matter did not exceed 20% of total Fe content throughout the water column investigated (*Demina, Klyuvitkin, in press*).

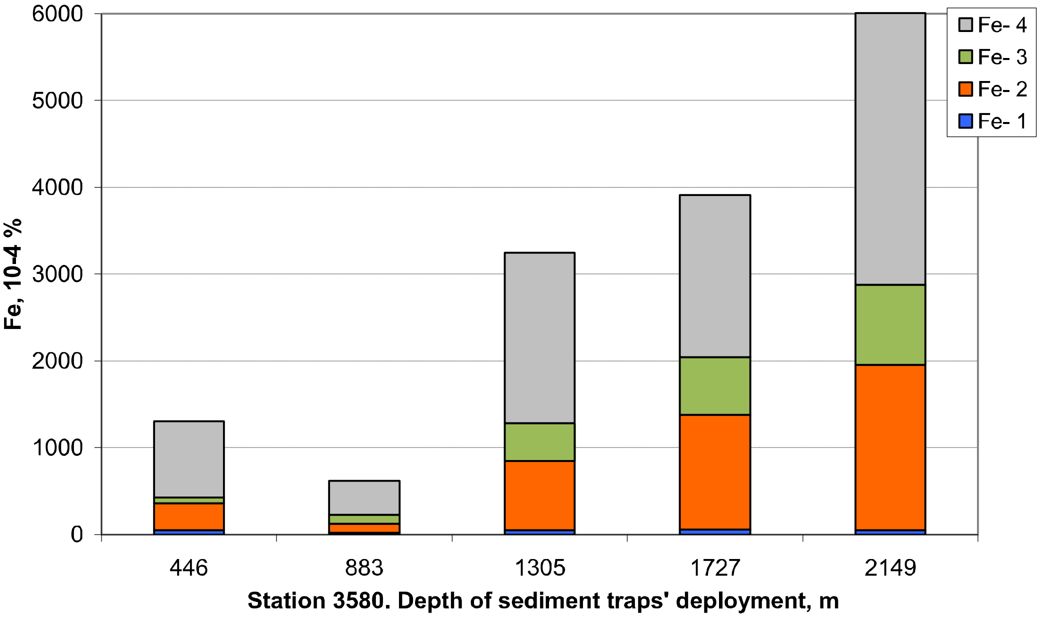

Figure 11*. Concentration of Fe in the 4 different occurrence forms in particle fluxes at station 3580 (59°29.977 N; 32°50.533 W) in the North Atlantic. Speciation of Fe: Fe-1 – adsorbed/bound to carbonates [Luoma, Bryan, 1981], Fe-2 – oxy-hydroxides [Chester, Hoges, 1967], Fe-3 – bound to organic matter [Kitano, Fujiyoshi, 1980], Fe-4 – lithogenic form (total digestion with concentrated HNO_3, HCl and HF) (Demina, Klyuvitkin, in press).*

Cruises GEOTRACES-related

- The researches of aerosols, suspended particulate matter (including vertical fluxes of trapped sedimentary material) and bottom sediments in the North Atlantic and the Barents Sea were carried out during the 71th cruise of RV Akademik Mstislav Keldysh, July–August 2018 (Figure 12). Principal Scientist – Sergey V. Gladyshev, Shirshov Institute of Oceanology, Russian Academy of Sciences.
- The researches of suspended particulate matter and vertical fluxes of trapped sedimentary material in the Siberian Arctic seas were carried out during 72th cruise of RV Akademik Mstislav Keldysh, August–September 2018 (Figure 13). Principal Scientist – Mikhail V. Flint, Shirshov Institute of Oceanology, Russian Academy of Sciences.

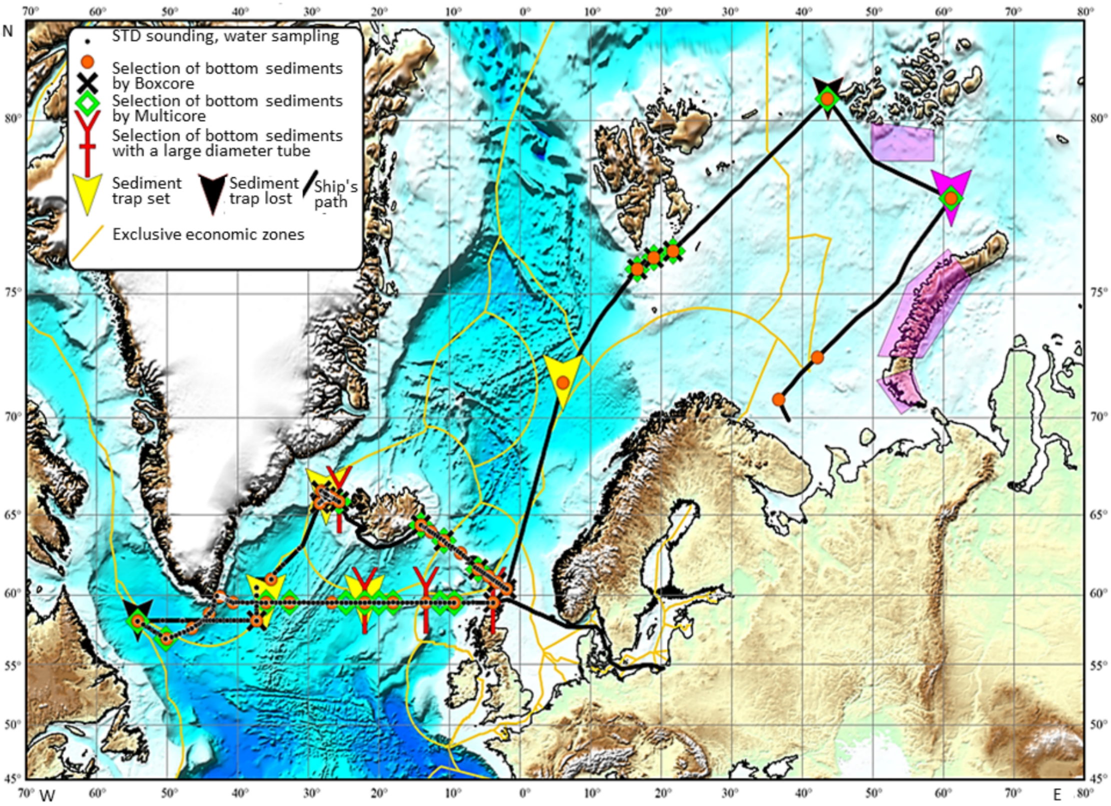

***Figure 12**. The rout and sampling sites in the 71th cruise of RV Akademik Mstislav Keldysh.*

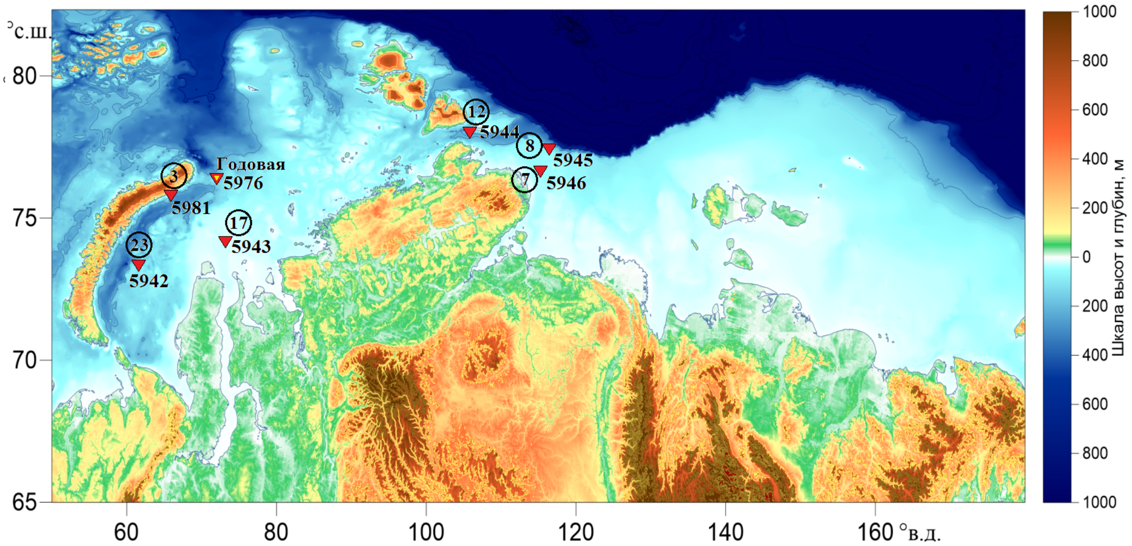

***Figure 13**. The location of moorings (with sediment traps) deployed in the Kara and Laptev seas, 72th cruise of RV Akademik Mstislav Keldysh. The circles indicate the number of days of exposure.*

New projects and/or funding

- Project of the Russian Science Foundation, No. 19-17-00234 “Biogeochemistry of organic compounds, heavy metals, and radionuclides in the ecosystems of the Arctic Seas (by example of the White, Barents, Laptev and East Siberian Seas)”, 2019–2021.
- Project of the Russian Foundation for Basic Research, No. 19-05-007-87 “Formation, transformation and transport of dispersed sedimentary matter under the influence of the

constant movement of water masses in the dynamic hydrological structure of the Atlantic branch of the Great Ocean Conveyor Belt", 2019–2021.

New GEOTRACES-related publications (published or in press)

- Berezhnaya E., Dubinin A., Rimskaya-Korsakova M., Safin T., 2018. Accumulation of Platinum Group Elements in Hydrogenous Fe–Mn Crust and Nodules from the Southern Atlantic Ocean. Minerals. 2018. 8(7). 275.
- Chernov I., Lazzari P., Tolstikov A., Kravchishina M., Iakovlev N., 2018. Hydrodynamical and biogeochemical spatiotemporal variability in the White Sea: A modeling study. Journal of Marine Systems. V. 187. P. 23–35. doi: 10.1016/j.jmarsys.2018.06.006.
- Demina L.L., Budko D.F., Novigatsky A.N., Alexeeva T.N., Kochenkova A.I., 2018. Occurrence forms of heavy metals in the bottom sediments of the White Sea. Sedimentation Processes in the White Sea: The White Sea Environment Part II / A.P. Lisitsyn, L.L. Demina (eds.). The Handbook of Environmental Chemistry. Springer, Berlin, Heidelberg. P. 241–270.
- Drozdova A.N., Kravchishina M.D., Khundzhua D.A., Freidkin M.P., Patsaeva S.V., 2018. Fluorescence quantum yield of CDOM in coastal zones of the Arctic seas. International Journal of Remote Sensing. P. 1–24. https://doi.org/10.1080/01431161.2018.1506187.
- Klyuvitkin A.A., Kravchishina M.D., Dara O.M., Rusanov I.I., Lisitzin A.P., 2018. Seasonal variability of vertical fluxes of dispersed sedimentary matter in the Black Sea. Doklady Earth Sciences. V. 483. Part 2. P. 1558–1563. doi: 10.1134/S1028334X18120139
- Kravchishina M.D., Klyuvitkin A.A., Lukashin V.N., Politova N.V., Novigatsky A.N., Lisitsyn A.P., 2018. Distribution of suspended particulate matter in the Caspian Sea. Russian Meteorology and Hydrology. V. 43. No. 10. P. 697–705.
- Kravchishina M.D., Lein A.Yu., Flint M.V., Baranov B.V., Miroshnikov A.Yu., Dara O.M., Dubinina E.O., Boev A.G., Savvichev A.S., in preparation. Newly discovered methane-derived antigenic carbonates on the Laptev Sea shelf.
- Kravchishina M.D., Lisitsyn A.P., Klyuvitkin A.A., Novigatsky A.N., Politova N.V., Shevchenko V.P., 2018. Suspended particulate matter as a main source and proxy of the sedimentation processes. The White Sea Environment Part II / A.P. Lisitsyn, L.L. Demina (eds.). The Handbook of Environmental Chemistry. Springer, Berlin, Heidelberg. P. 13–48.
- Kravchishina M.D., Novigatskii A.N., Savvichev A.S., Pautova L.A., Lisitsyn A.P., 2019. Studies on sedimentary system in the Barents Sea and Norwegian-Greenland Basin during cruise 68th of the R/V Akademik Mstislav Keldysh. Oceanology. V. 59(1). P. 158–160.
- Lein A.Y., Dara O.M., Bogdanova O.Y., Novikov G.V., Ulyanova N.V., Lisitsyn A.P., 2018. Sources of minor and rare-earth elements in hydrothermal edifices of near-continental rifts with sedimentary cover: evidence from the Guaymas Basin, Southern Trough. Oceanology. V. 58. No. 2. P. 250–265.
- Lisitzin A.P., Gordeev V.V. (eds.), 2018. Biogeochemistry of the Atmosphere, Ice and Water of the White Sea. The White Sea Environment. Part I. In: The Handbook of Environmental Chemistry. Springer, Berlin, Heidelberg, 327 pp.

- Maslov A.V., Kuznetsov A.B., Politova N.V., Kozina N.V., Novigatsky A.N., Shevchenko V.P., 2019. Isotopic composition of Nd, Pb, and Sr in modern bottom sediments of the Barents Sea. Doklady Earth Sciences. V. 485. Part 1. P. 268–272.
- Maslov A.V., Shevchenko V.P., Kuznetsov A.B., Stein R., 2018. Geochemical and Sr–Nd–Pb-isotope characteristics of ice-rafted sediments of the Arctic Ocean. Geochemical International. V. 56. No. 8. P. 751–765.
- Novigatsky A.N., Klyuvitkin A.A., Lisitsyn A.P., 2018. Vertical fluxes of dispersed sedimentary matter, absolute masses of the bottom sediments, and rates of modern sedimentation. The White Sea Environment. Part II / A.P. Lisitsyn, L.L. Demina (eds.). The Handbook of Environmental Chemistry. Springer, Berlin, Heidelberg. P. 49–66.
- Novigatsky A.N., Lisitzin A.P., 2018. The North Pole Region: First Data on the Snow–Sea Ice–Ice Water Sedimentation System. Doklady Earth Sciences. V. 483(2), P. 1534–1538. DOI: 10.1134/S1028334X18120085.
- Politova N.V., Novigatsky A.N., Kozina N.V., Terpugova S.A., 2018. Multidisciplinary research in the Barents Sea on cruise 67 of the R/V Akademik Mstislav Keldysh. Oceanology. V. 58(3). P. 499–501.
- Shevchenko V.P., Lisitsyn A.P., Vinogradova A.A., Starodymova D.P., Korobov V.B., Novigatsky A.N., Kokryatskaya N.M., Pokrovsky O.S., 2018. Dispersed sedimentary matter of the atmosphere. The White Sea Environment. Part I / A.P. Lisitsyn, V.V. Gordeev (eds.). The Handbook of Environmental Chemistry. Springer, Berlin, Heidelberg.
- Vinogradova A.A., Kotova E.I., 2019. Pollution of Russian northern seas by heavy metals: comparison of atmospheric flux and rivers inflow. Izvestiya, Atmospheric and Oceanic Physics. V. 55. Iss. 7. https://link.springer.com/journal/volumesAndIssues/11485

Completed GEOTRACES-related PhD theses

- Dina P. Starodymova defended PhD thesis in December 2018 (Shirshov Institute of Oceanology, Russian Academy of Sciences). Based on mean airborne metal concentration their fluxes on the surface water of the White Sea were estimated. Since different heavy metals are related to different size fraction of aerosols they are defined by different dry deposition rates (Milford, Davidson, 1985). Pb, Cd, Sb and Bi fluxes were considered to be on the same level over the area of the White Sea. Ni and Cu fluxes were calculated separately for different areas of the sea. Annual input of particulate Ni, Cu Cd and Bi with aerosols were 22–58% of annual input of these metals by the Severnaya Dvina River runoff (Pokrovsky et al., 2010), while estimates of annual atmospheric input of Pb and Sb exceed their inflow from the Severnaya Dvina River beyond the marginal filter (Figure 14).

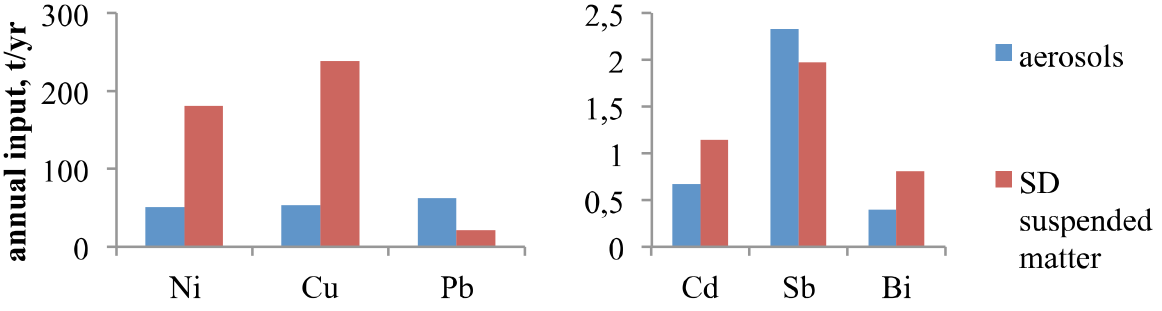

Figure 14. *Annual particulate heavy metals input to the White Sea from atmosphere and with Severnaya Dvina (SD) River runoff (Starodymova, 2018).*

- Dmitry F. Budko defended PhD thesis in December 2018 (Shirshov Institute of Oceanology, Russian Academy of Sciences). The geochemical speciation of Al, Fe, Mn and trace metals in the vertical fluxes of trapped sedimentary matter and in bottom sediments of the White Sea were studied. He evaluated the contribution of some geochemical processes at various stages of sedimentation in the White Sea.

Submitted by Marina Kravchishina (kravchishina@ocean.ru).