Dynamics of legacy and emerging pollutants in fjord ecosystems of the high Arctic: Svalbard (Norway) and NE Greenland

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Introduction:

Recent climate changes are much faster than previous long-term ones, causing stress on polar marine ecosystems resulting in changes in atmosphere/ocean exchanges, ocean properties, sea ice cover and thickness. These phenomena, associated to anthropogenic emissions, are triggering shifts in global biogeochemical cycles and marine ecosystem (Guldberg, 2010). Consequently, ecosystems are rapidly changing. The polar oceans are the final sink for many semi-volatile organic contaminants, which thanks to the atmospheric transport and to the cold condensation concentrate in these areas. The decrease of sea ice, as well as the presence of snow and the mechanism of ice formation/melting, can have a big impact on the carbon cycle, on the mobility of contaminants and on biodiversity loss (VandenBrink, 2011). Moreover, the list of chemicals found in arctic ecosystems continuous to grow and increasing temporal trends have been reported for some current-use chemicals (NCP, 2013). The study of the composition of Dissolved Organic Carbon (DOC) and the occurrence of organic contaminants together with the biodegradation capability of natural microbial communities, is of strategic importance to describe the circulation of nutrients and the impact of allochthones sources on the marine ecosystem. Anthropogenic impacts can change the quality of the natural DOC, with repercussions on the spread, persistence and bioavailability of allochthonous organic matter, including the fate and the toxic effects exerted by some persistent organic pollutants (POPs). Contaminant global transport (POP, http://chm.pops.int) could also be affected by climate change and it is essential adding new elements to study potential biotic repercussions of synergistic effects between long-slow global stressors (e.g. increasing temperature due to climate change) and short-rapid local stressors (e.g. contaminants and coastal hypoxia). The aim of this study was: 1) evaluating the dynamics of contaminants in the high Artic fjord ecosystem. The concentration of pollutants of environmental concern (PAHs, NPs and BPA, POPs, PCBs, CUPs, PFAs, others) will be studied in sediment and seawater. 2) Characterizing the DOC in the water column by ultrafiltration tangential-flow techniques according to the size fractions (colloidal and truly dissolved) to evaluate if the transport of contaminants is affected by DOC dimensions. 3) Investigating the potential links occurring between ecosystem contamination and metabolic processes mediated by the resident microbial communities.

Materials and methods

Three campaigns were carried out in Arctic fjord ecosystems: two in the Kongsfjorden (Svalbard) (June 2016, March 2017) and one in the Bessel Fjord (NE Greenland) (September 2017) during the international TUNU Programme on board the R/V Helmer Hanssen. The Kongsfjorden Bay ecosystem is a high –latitude (sub)-Arctic fjord. Its waters are influenced by both the Atlantic water masses of the WSC as well as the Arctic-type coastal waters, and a glacial input of melt water (Svendsen et al., 2002). North-East Greenland is a polar area of high scientific interest and value due to biological, ecological, eco-toxicological features of organisms. It is likely the last remote region of the Northern hemisphere, poorly known and understudied due to the limited access (it is a National Park controlled by the Government of Greenland and Denmark). However, the Greenland Government has allowed minerals and petroleum prospections (http://licence-map.bmp.gl/) for resource exploitation. For these reasons it is crucial to increase our understanding of how NE Greenland ecosystems cope with global change, thereby it deserves further ecological and ecotoxicological investigations. In addition, reports by Arctic Monitoring and Assessment Programme (AMAP, www.amap.no) show an informational gap dealing with contamination in this area. The experimental design was drawn up to sample seawater (50 L surface and bottom) and sediment along a transect in order to determinate the dynamics of persistent and emerging contaminants: PCBs, PAHs, NPs, BPA, CUPs, PFAs. At the same time, with the ultrafiltration tangential-flow technique, dissolved organic matter (DOM) was characterized for colloidal and truly dissolved fractions. The degree of contamination was evaluated together with microbial community biomass (first link in the heterotrophic food web) with flow cytometry technique.

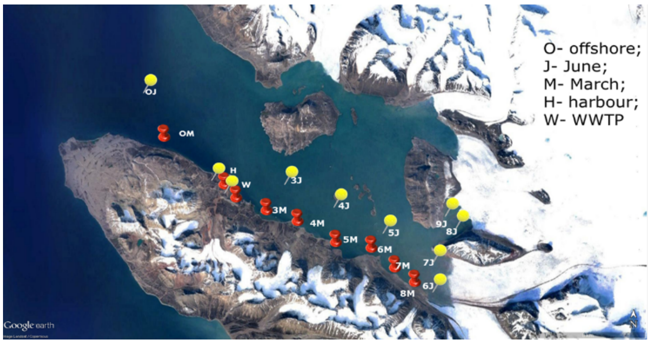

Figure 1. Map of the Kongsfjorden (Svalbard, Norway) sampling sites.

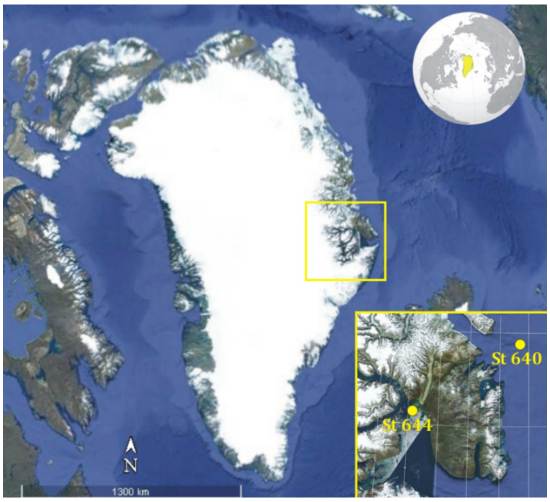

Figure 2. Map of the NE Greenland sampling sites.

The extraction/clean-up of microorganic pollutants from aqueous samples was performed by solid-phase extraction (SPE), performed by different cartridges (i.e.: Supelco C18 sorbent, Bellefonte, USA), previously conditioned with the suitable solvents depending on the target compounds. Samples were then passed through the cartridges under vacuum, and the cartridges were vacuum-dried for 5 min. Elution was made with 3 mL of an opportune solvent (methanol, hexane, acetone or dichloromethane), depending on the target pollutants. Extraction from sediment was performed by using a Pressurized Liquid Extraction system (PLE), followed by an analytical determination with RP-HPLC interfaced with an UV detector and LC-MS/MS. All the final extracts were dried under a nitrogen stream. Analysis of PFAs, PAHs, NPs and BPA were performed using HPLC/MS–MS, while concentrations of CUPs and PCBs were determined by GC-ECD with confirmations in GC/MS-MS (Patrolecco et al., 2010; Valsecchi et al., 2015; Corsolini et al., 2017; Ademollo et al., 2018).

Results and discussion

Statistical evaluation of microorganic contaminants, DOC, DOM and the biomass of the microbial community was performed. The PAH concentrations measured in the Kongsfjorden whole water in the summer period varied from 2.9 to 40.4 ng/L, the minimum value was found in the offshore points while the maximum in the Ny-Ålesund harbor. Along the transect from the harbor to the glaciers the PAH levels were quite similar although we observed an upward trend moving to the glaciers. This finding was consistent also with the change in the composition of DOC due to the material given by the snow/ice melting. The pattern showed the predominance of petrogenic PAHs, likely due to coal, crude oil and atmospheric dust. Unexpectedly, values founded at the end of the polar winter (8-20 March 2017) were slightly lower than in summer, with a maximum of 37.3 ng/L in the harbor and a minimum of 1.9 ng/L offshore, while PAH concentrations ranged from 13.1 to 17.7 ng/L in the sampling points versus the glacier. As expected, the concentrations of NPs showed higher values (23.42 and 10.42 ng/L in June and March, respectively) in the seawater sampled near the wastewater treatment plant. No significant differences were found in the BPA levels along the transect in both the sampling periods (0.71 and 0.45 ng/L in June and March, respectively).

Figure 3: Concentration levels (ng/L) and seasonal variations of DOC (mg/L), C/N, PAHs, NPs and BPA in the seawaters along the transect in Kongsfjorden (Svalbard) in June 2016 and March 2017.

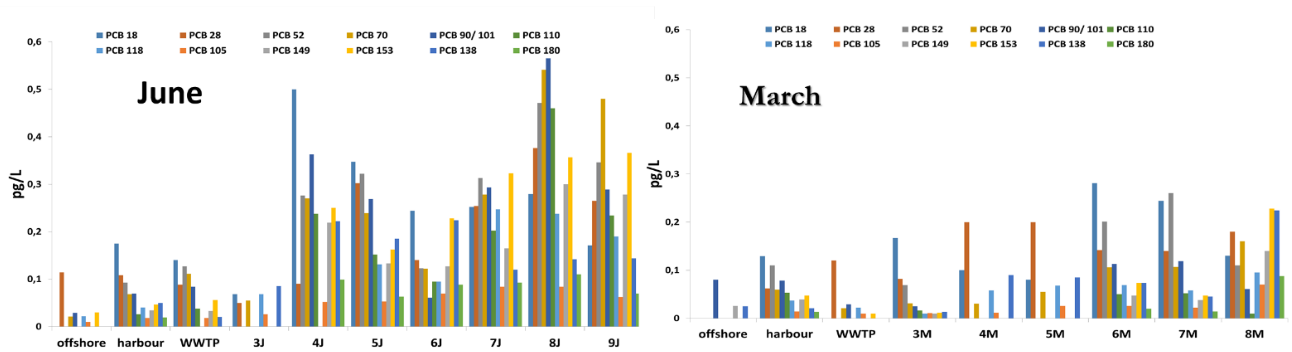

Figure 4: Concentration levels (pg/L) and seasonal variations of PCBs in the seawater along the transect in Kongsfjorden (Svalbard) in June 2016 and March 2017.

The PCBs transport occurs through the atmosphere and ocean currents. Data showed the release of POPs from melting glaciers highlighting the relevance of the snow/ice as secondary source of legacy pollutants. The PFAs are widely distributed in marine waters. In June, the pattern observed were: PFHxA>PFOA>PFBS>PFDA>FOSA.

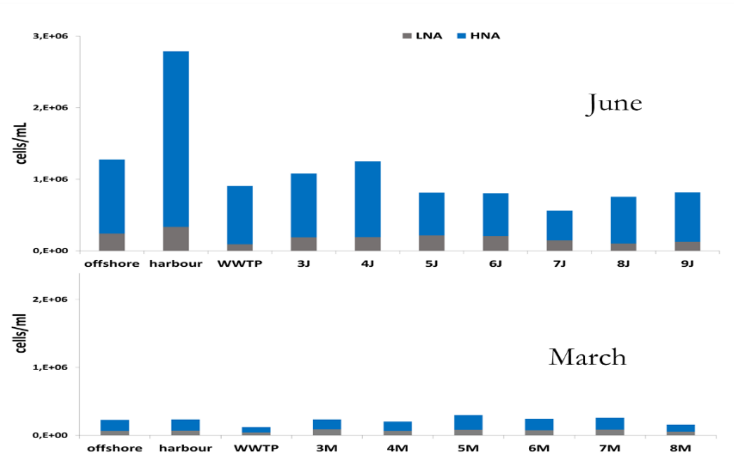

Figure 5: Differences in the microbial abundance between June and March in the seawater of the Kongsfjorden.

Overall, along the transect we observed an upward trend moving to the glaciers for all the contaminants except for the BPA. This trend is particularly evident in June due to glacial mass balance and the run off from the snow/ice melting. This finding is consistent with the observed change in the composition of DOC and in the C/N ratio, due to freshwater run off that means a significantly amount of organic material of terrestrial origin. The fate of this organic material has a significant impact on the global carbon cycle. Values at the end of the polar winter were slightly lower than those found in summer. The absence of solar irradiation and the lower temperature of seawater, factors inhibiting the biotic and abiotic degradation of these xenobiotics, competed with the greater anthropogenic pressure and the sea/ice melting, typical factors of the spring-summer period. Bacterial degradation of allochthonous organic matter in the Arctic Ocean is slow, also due to the fact that the weak photochemical alteration may restrict the formation of biologically labile DOM (Paulsen et al., 2017; Nizzetto et al., 2012). A comparison with a not anthropized environment like the Bessel Fjord has been performed.

Understanding the interactions between the ecological effects of climate change and anthropogenic pressures, it is a priority for the identification of possible alterations and long-term effects of these vulnerable marine ecosystems, by correlating the presence of contaminants, the characteristics of organic matter and the impact on carbon fluxes.

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