Hydrophilic Organic Pollutants – A Threat to the Arctic?

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Introduction

Concerning organic chemicals, the focus is currently set on lipophilic persistent organic pollutants (POPs). Due to their propensity for long-range transport and bioaccumulation, they are an obvious problem for Arctic ecosystems. In contrast to the extensive research into POPs in the Arctic, hardly any attention has been paid so far to more hydrophilic compounds.

The majority of anthropogenic chemicals in the aquatic environment consist of moderately to highly polar organic compounds. Among them are surfactants such as nonylphenols and their ethoxylates, aromatic sulfonic acids, complexing agents (e.g., EDTA), and residues of pharmaceuticals. Through the improvement of analytical techniques many of these have become accessible to investigation during the last years. Of special importance are the development of suited solid-phase extraction (SPE) sorbents and the recent achievements in high performance liquid chromatography- mass spectrometry (LC-MS).

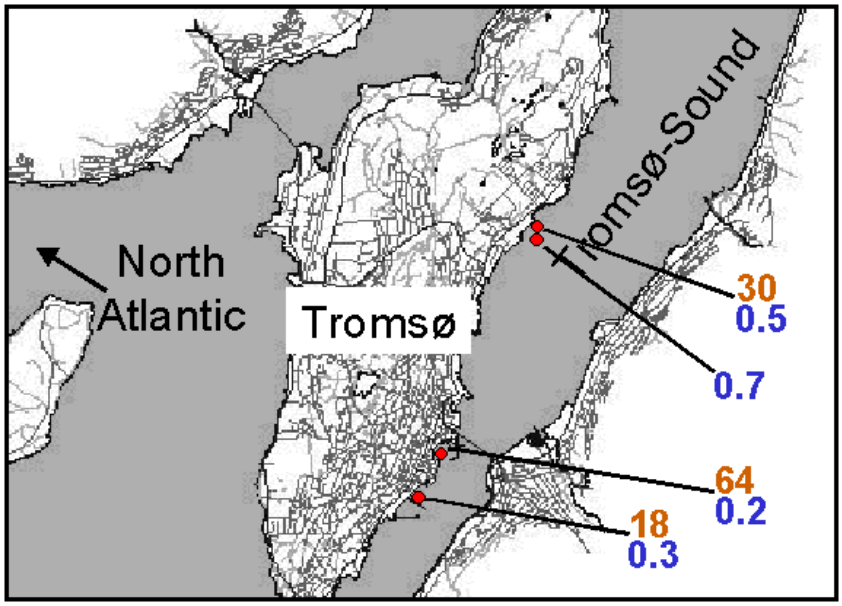
Pharmaceuticals are of special concern as they are designed to trigger a certain biological effect. Thus, they can be expected to interfere with the respective receptors, enzyme or hormonal systems of unintentionally exposed aquatic organisms. In contrast to other environmental pollutants like for example pesticides, which are released mainly seasonally, pharmaceutical drugs are introduced continuously into the receiving waters. Certain compounds exhibit a considerable persistence which in the case of clofibric acid leads to its distribution in surface and groundwater and even a widespread occurrence in the North Sea (Weigel et al., 2002). But even compounds of low persistence could act as if they were persistent due to perpetual life-cycle exposures for aquatic organisms (Daughton and Ternes, 1999). The main threats encountered so far from the presence of these compounds in the environment are: i) Development of antibiotic-resistant bacteria upon exposure to contaminated sewage effluent (Andersen and Sandaa, 1994); ii) Endocrine disruption. The therapeutic administration of both synthetic and natural hormones leads to concentrations in sewage effluents that might reach effective levels. Purdom et al. (1994) observed positive responses in fish down to 17-α-ethinylestradiol exposure levels of 0.1 to 0.5 ng/L, which is even below the concentrations of this substance typically found in sewage effluents; iii) Genotoxic effects. Many antineoplastic drugs act as alkylating agents. The therefrom arising genotoxic potential poses a high risk to exposed organisms; iv) Unexpected effects. For example, certain antidepressants were reported to induce spawning in mussels (Fong, 1998).

In the course of the project „Pharmaceutical residues as pollutants in North Norwegian contaminated and pristine aquatic ecosystems“, the occurrence and distribution of several classes of pharmaceutical drug residues in effluent and seawater from the Tromsø area is investigated. The project consists of mainly six parts: a) non-target screening of sample extracts for the occurrence of unexpected compounds of potential concern, b) determination of polar neutral drugs, including caffeine as a tracer for domestic sewage, c) determination of acidic drugs, mainly analgesics and their metabolites, also including the antibacterial triclosan, d) determination of basic drugs (β-blocker and antidepressants), e) determination of synthetic and natural estrogens, f) determination of antibiotics.

Methods
Water samples (1 L) were collected in the Tromsø-Sund using clean glass bottles in a specially constructed sampler. Sewage samples were either taken from a tap at a treatment plant or with a steel bucket from the sewer. After filtration (47 mm Whatman GF/A glassfibre filters) they were extracted using either Bakerbond SDB-1 (200 mg) cartridges (summer 2001) or glass cartridges packed with 500 mg Waters Oasis HLB (60 µm) (April 2002). Elution was carried out sequentially with a) *n*-hexane (removal of hydrophobic matrix), b) ethyl acetate (polar neutral analytes), c) methanol (acidic analytes). The methanolic eluate was derivatised with methyl chloroformate The qualitative and quantitative determination of the neutral and acidic compounds was then carried out by GC/MS. In case of the β-blockers and antidepressants, the cartridge was directly eluted with methanol and analysis performed by LC/MS.

Results
In a first survey, a small set of seawater samples from the Tromsø-Sund was taken in summer 2001. A limited non-target screening was performed on the obtained sample extracts in order to assess the relevance of the proposed target analytes and to search for further potentially important compounds. The sample composition was dominated by hydrocarbons (alkylbenzenes, aliphatic hydrocarbons, PAHs) presumably originating from shipping/port activities. Furthermore, a variety of benzoic acid derivatives were identified in the samples. Among them were parabenes which are used as preservatives in personal care products as well as 2,4-dichlorobenzoic acid. Besides a variety of miscellaneous compound several alkylphenols were detected.
The screening of the Sund-samples for a set of target analytes (neutral and acidic compounds) revealed the presence of caffeine and the analgesic ibuprofen in all of the samples. The estimated concentrations are given in figure 1.

Figure 1: Estimated concentrations of caffeine and ibuprofen in summer 2001



Concentrations [ng/L]
Upper value: caffeine
Lower value: ibuprofen

In a more extensive investigation in April 2002, several seawater samples were taken at different locations (area affected by hospital effluent, central harbour area, area affected by the central sewage outlet of the inner city). Simultaneously, water samples were taken from the contributing sewers. The poster presents detailed quantitative results from all locations. In brief, it can be stated that in sewage samples caffeine, diclofenac, ibuprofen and its two main metabolites hydroxy- and carboxy-ibuprofen, and triclosan were present in concentrations up to the µg/L – range. The β-blockers metoprolol and propranolol were detected in both sewage samples screened for these compounds, the anti-depressants

paroxetine and sertraline in one of them in the ng/L-range. Most of the seawater samples contained caffeine in the ng/L-range while ibuprofen and its metabolites were present in some samples at sub ng/L-concentrations.

Conclusions

Although most of the investigated compounds presumably are not prone to a strong bioaccumulation and the observed concentrations in seawater are rather low, the findings raise concern for some reasons. The presence of caffeine in most samples from Tromsø-Sund despite the strong tidal current indicates that this area is continuously exposed to human domestic effluents. While the impact of most pharmaceuticals on aquatic organisms is not investigated yet, some compounds are known to be active at very low concentrations in the environment: estrogens and certain anti-depressants (selective serotonine reuptake inhibitors). Furthermore, the specific arctic conditions (low temperatures, light conditions) strongly affect the biological, chemical and photolytic transformation behaviour of these compounds and might turn them more persistent compared to lower latitudes. Around human settlements, where pharmaceuticals are constantly released into the environment, they have to be regarded as a potential threat to the especially vulnerable Arctic ecosystems.

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