

Distribution of lithium and fluorine containing compounds in the Hungarian section of the Danube River

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Abstract Due to the increasing production and recycling of lithium batteries over the world, we can calculate with increasing fluorine contamination in the aquatic environment and drinking water reservoirs. This study was conducted to qualification and quantification of five parameters; elemental lithium, inorganic fluoride, total adsorbable organic fluorine, and selected per- and polyfluoroalkyl substances - perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS) - along the Hungarian section of the Danube River. On the basis of these analytical data, the study aimed to assess the potential environmental risks posed by fluorine-containing compounds. These compounds are introduced into the river through tributaries and emissions from wastewater treatment plants, as well as factories producing lithium-ion batteries and wrapping paper along the Danube River banks. Concentrations were determined by applying the following analytical techniques: inductively coupled plasma mass spectrometer, combustion ion chromatography, ultra-high-performance liquid chromatograph mass spectrometer.

Considering the measured analytical data, it was established, that the total lithium level in the River varied in concentration range of 1-5 $\mu g/L$. Concentration of inorganic fluoride amounted to 28-76 $\mu g/L$, while the total adsorbable organofluorine was 0.22-12.5 $\mu g/L$. The PFOA and PFOS concentrations remained relatively stable, within a narrow range of 0.7-2.3 ng/L and 0.7-1.7 ng/L, respectively.

Keywords: Danube, lithium, fluoride, organofluorine, PFAS

1. Introduction

High number of fluorine containing chemicals e.g. pesticides, herbicides, pharmaceuticals, per- and polyfluorinated alkyl compounds (PFAS) belong to the group of organofluorines. The main sources of the extremely resistant and toxic PFAS compounds are the treated industrial wastewaters emitted by lithium-ion battery (LIB) and paper factories, as well as the communal

wastewater treatment plants located on the bank of the Danube River.

2. Materials and Methods

Along the Hungarian strech between Gönyű and Dunaföldvár, 12 sampling points were selected and water samples were collected monthly. Concentrations of lithium, organofluorines and PFAS (PFOA, PFOS) compounds were quantified by applying the following analytical techniques: inductively coupled plasma mass spectrometer, combustion ion chromatography and ultrahigh-performance liquid chromatograph mass spectrometer.

3. Results

Concentration changes of lithium in the Danube River varied within a relatively narrow range of 1.00–4.80 μg/L. The spatial and temporal distribution of inorganic fluoride concentrations varied in the range of 28-76 µg/L (mean value: 45.1±7.7 μg//L). Organofluorine concentrations of the Danube River during the sampling period amounted to $0.22-12.5 \mu g/L$ (mean value: $3.19 \pm 2.62 \mu g/L$) and it was approximately twice as high in September and November comparing with the other sampling months. This phenomenon can be attributed to increased precipitation and moderate flooding, which enhance the washout of chemicals from agricultural areas. It was demonstrated that PFOA and PFOS values along the Hungarian section of the river remained relatively stable, concentrations were changed within a narrow range of 0.7-2.3 ng/L and 0.7-1.7 ng/L, respectively.

4. Conclusions

It can be concluded that lithium, fluoride, AOF and PFOA compounds showed minimal fluctuation in the Danube River during the sampling period. We plan to expand our research to include new PFAS compounds used in LIB production, such as bis-perfluoroalkyl sulfonamides in

water and sediment samples as well and it has to be highlighted that in case of sediments, we have to calculate with a long-term memory effect resulting in a risk for the drinking water production based on bank filtration technology

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