

Occurrence of legacy and novel fluorochemicals in aquatic and terrestrial chains around a fluoropolymer manufacturing plant

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1. Introduction

It is well known that the fluorochemical plants, where poly- and perfluoroalkyl substances (PFAS) are synthesized or used, are relevant sources of PFAS for the surrounding environment. The soil, the rivers that receive the discharge of this industry and the groundwaters below the industrial plants often showed high levels of PFAS. Most of the industrial sites located in developed countries and in China have been characterised for the presence of legacy PFAS. However, the whole characterisation of the environmental release is hindered because information on the unknown PFAS that have been using for many years or that have recently replaced the banned PFAS (and so potentially released into the environment) is often covered by patents and industrial confidentiality. Besides, to comprehensively evaluate the environmental risks posed by an industrial activity, it is crucial to track the possible transfer of the emitted pollutants through terrestrial and aquatic trophic chains of the ecosystems neighboring the production sites.

After a preliminary work on PFAS in eggs of sedentary birds around the fluorochemical plant [2], a comprehensive study to assess the environmental PFAS contamination due to legacy and novel PFAS deriving from a fluorochemical industrial site that has been releasing large amounts of PFAS in the Po River valley (Northern Italy) over the past decades, have been carried out, analysing both abiotic (wastewater, river water and soil) and biotic (vegetable, invertebrates, fish, and wild bird eggs) matrices.

2. Materials and methods

Abiotic and biotic samples were collected within 5 km from the fluorochemical plant (PFS). The same matrices were collected 20 km far from the industrial site, within the plume of air emissions. Additionally, wild bird eggs from clutches laid in a rural site (RS) far from any known point source of PFAS were also collected.

Liquid and solid samples for the determination of legacy and novel PFAS were extracted and analysed according to previous methods developed for PFCA and PFSA [3,4]. Water samples were concentrated on a Waters WAX SPE cartridge whereas solid samples were extracted by acidified acetonitrile and purified on HybridSPE® cartridges. PFAS in the evaporated extracts were determined by liquid chromatography tandem mass spectrometry (UHPLC-MS/MS) operating in electrospray ionization (ESI) negative mode.

3. Results and discussion

The occurrence of nine perfluorocarboxylic acids (from C6 to C14), four perfluorosulfonic acids (C4, C6, C8 and C10), two fluorotelomer sulfonates (6:2 and 8:2 FTS), the perfluorooctane sulfonamide (FOSA) and, some novel fluorochemicals was investigated. Quantification with analytical standard was carried out for two novel perfluoro ether carboxylic acids (Figure 1 and 2): C6O4 (C6HF9O6; 2,2-difluoro-2-((2,2,4,5-tetrafluoro-5-(trifluoromethoxy)-1,3-dioxolan-4-yl)oxy)-acetic acid; CAS No. 1190931-41-9) [5], and the mixture of Cl-PFPECA also known as ADV (C3F6ClO-[CF(CF3)O]_e-[CF2CF(CF3)O]_p-CF2COOH, e=0-4, p=0-4, CAS No. 329238-24-6) [6]. Other novel PFAS were only revealed, since no analytical standards were available.

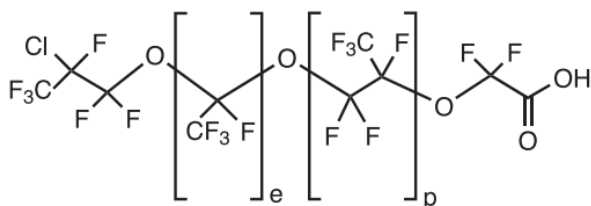


Figure 1: Structure of chloro perfluoro polyether carboxylic acids Cl-PFPECA e=0-4, p=0-4)

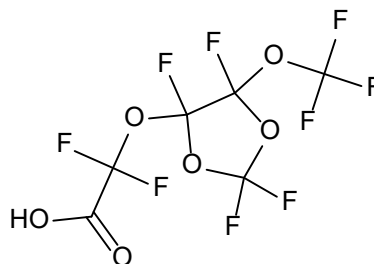


Figure 2: structure of C6O4 Acid

Legacy and novel PFAS were detected in the wastewaters and in the river downstream of the discharges, as well as in all the environmental samples collected around the industrial site. Among the quantified PFAS, the

components of the ADV mixture were largely the predominant PFAS accumulated both in the aquatic and terrestrial food chain (Figure 3), with levels similar or even greater than those of PFOA (previously used for many years). A similar pattern of contamination, although at lower concentrations, has been detected in the samples collected kilometers far from the fluorochemical plant. This suggests that PFAS were not only emitted into the river water but also to the air and they contaminated the area around and far away the productive facility via atmospheric deposition.

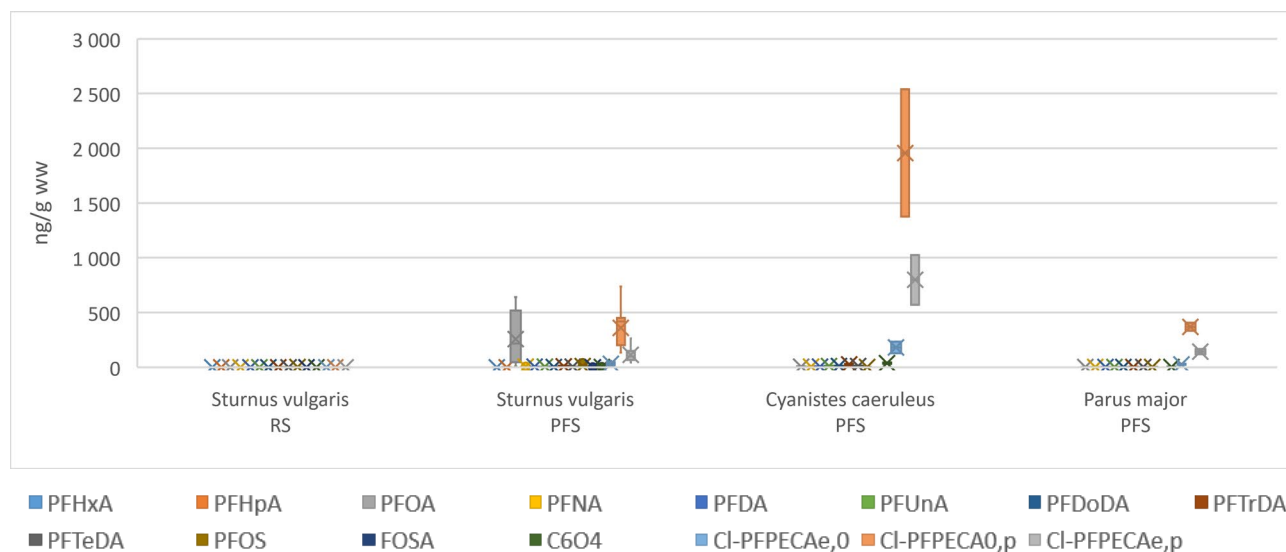


Figure 3: PFAS concentration in whole eggs of three wild bird species grouped according to the sampling sites. PFS, perfluoropolymer factory site; RS, rural site. Cl-PFPECA e,0 (variable number of perfluoroethyl units and zero fluoropropyl units) Cl-PFPECA 0,p (zero perfluoroethyl units and variable number of fluoropropyl units); Cl-PFPECA e,p (variable number of perfluoroethyl and fluoropropyl units).

4. Conclusions

The analysis of the collected samples revealed high contamination of the fluorochemical plant surrounding area, raising environmental concern. The contamination is not confined to few kilometers far the industrial site but atmospheric transport of emitted PFAS probably occurs. The detection of novel PFAS drives further investigations focused to quantify and assess the ecological and health risks of that newly identified substances.

5. References

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Acknowledgement - The authors thank Mark Strynar and James McCord (USEPA Office of Research and Development Center for Environmental Measurements and Modeling), Anna Robuck (Graduate School of Oceanography, University of Rhode Island, Narragansett, RI 02882, USA) and Gloria Post (New Jersey Department of Environmental Protection, Trenton, New Jersey, USA) for their help in supporting the study.