

AXE 3 - Sustainable pollution control, emerging contaminants and prevention towards zero pollution

Improvement of the global quantification of PFAS through TF, AOF and EOF measurements: Application to complex environmental matrices (sludge and compost) from wastewater treatment plants

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ABSTRACT

More than 4000 Per- and polyfluoroalkyl substances (PFAS) also called forever chemicals are attracting the warning of scientists and public authorities [1]. The application of ion chromatography to environmental matrices allows the global analysis of different halogens including fluorine thanks to initial sample combustion using CIC instrument [2].

Depending on the sample preparation, different fractions of the sample can be analysed by CIC [5]: TF (total fluorine), EOF (extractable organic fluorine) or AOF (adsorbable organic fluorine). Removal of inorganic fluorine (IF) is needed for discrimination of organic fluorine from TF content.

Even though the analytical principle is relatively simple, different methodological issues may arise. Differences in analytical responses related to the forms (inorganic or organic) or chemical structure (easily or not incinerated during combustion step), and mismatch with standards used for calibration could lead either to under- or over-estimation of the fluorine content [3]. Due to the large range of polarity among PFAS, recoveries during solid phase extraction step both on activated carbon or other polymeric cartridges should be assessed to avoid underestimation of OF content. Effect of complex matrices such as compost or sludges for solid samples, or WWTP effluent for liquid samples need to be investigated to validate the robustness of the method.

For this study, our objective is to propose validated robust and reliable methods for measuring global organic fluorine based on CIC measurements for TF and EOF for complex solids and AOF, SPE-AOF, EOF and TF for liquid samples. Methods will be applied on biosolids and recovered fertilizers to evaluate the capacity of PFAS release to the environment through spreading of these materials.

Methodology

The first it was determined whether the TF measured is in line with the expected quantity from a known added quantity of IF and/or OF. Impact of potential incomplete combustion of some specific chemical structures has been particularly studied. For AOF, the retention efficiency was assessed for PFAS compounds ranging in polarity. The proportion of polar PFAS retained on activated carbon was determined and compared to the proportion removed by the rinsing solution.

A similar approach was implemented with SPE in order to optimize the recovery of polar PFAS. AOF, SPE-AOF and EOF were finally assessed as the potential effects of complex matrices, in particular the organic carbon and suspended particulate matter content during combustion.

For solid samples, different protocols were tested on complex matrices (sludge and composts) to determine the best conditions to remove IF for EOF measurements. In parallel, the estimation of the IF content has been done on several biosolids samples (sludges, fertilizer, compost) to determine the mass balance gap between TF and calculated TOF measurements.

Conclusion

This work has led to a better understanding of the factors influencing the quantification of TF in complex matrices that can contain both IF and OF. It allows for better characterisation of the chemical groups among PFAS considered in the determination of AOF, EOF and TOF.

Significance / contributions of the study

These results allow a more reliable determination of the mass balance and the fate of PFAS during the wastewater treatment steps and a better understanding on how to limit the transfer of PFAS during fertilizers recovery from sewage sludge. The final goal is to provide a more reliable sustainable remediation of emerging contaminants and prevent spreading of PFAS in the environment towards zero pollution objectives.

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