

Per- and polyfluoroalkyl substances (PFAS) in wastewater sludge and biosolids Usman M. Ismaila, Chedly Tizaouia & Rob Jenkinsb

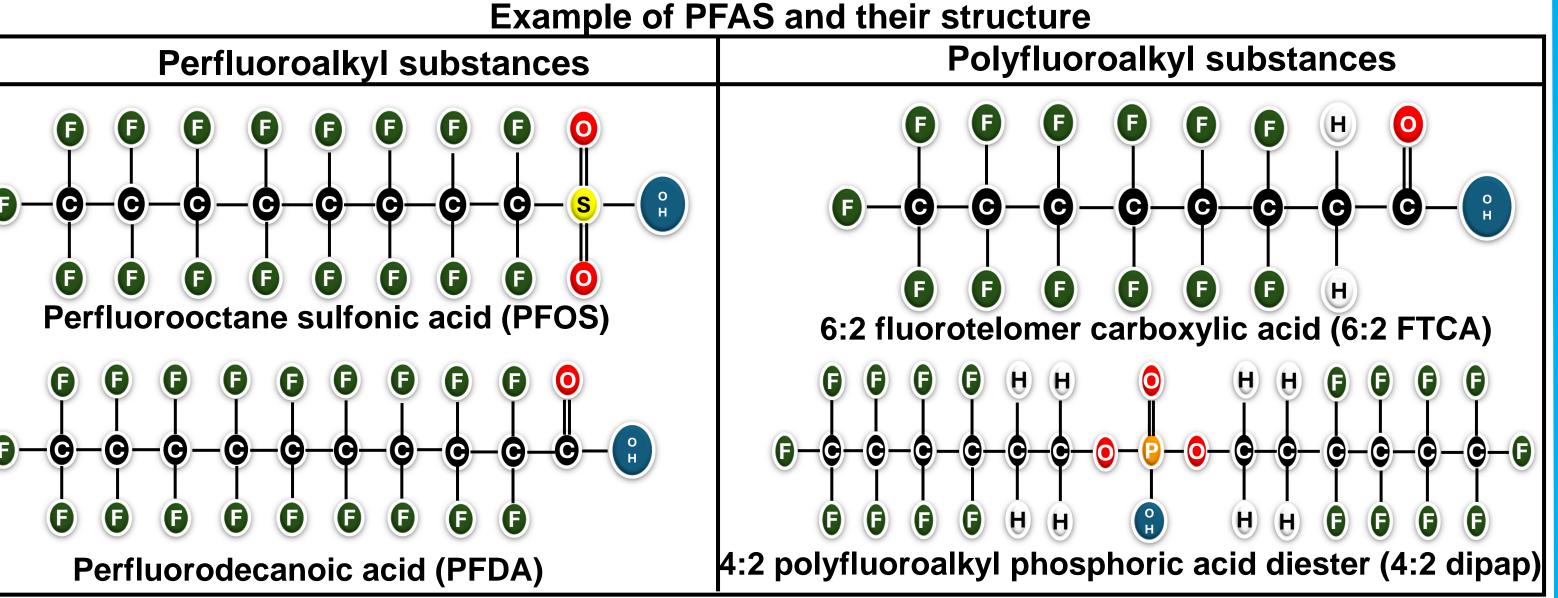
^aWater and Resources Recovery Research Lab, Department of Chemical Engineering, Faculty of Science and Engineering, Swansea University, Swansea, SA1 8EN, UK ^bDŵr Cymru (Welsh Water), Linea, Fortran Road, St Mellons, Cardiff CF3 0LT, UK

Correspondence to: 2438589@swansea.ac.uk; c.tizaoui@swansea.ac.uk



Introduction

- Per- and polyfluoroalkyl substances (PFAS); a group of over 4000 synthetic organofluorine chemicals
- Different compounds can be produced by altering the chain length or functional head of different PFAS



Key Properties

- Thermal Resistance **Chemical Resistance**
- Hydrophobic

environment

- Oleophobic
- Called Forever Chemicals Harmful to humans and



Regulations

- PFOS and PFOA production has been phased out
- Enforceable limits are set for six PFAS in drinking water in the US [1] 1st draft of sludge risk assessment for PFOA and PFOS has been published
- In the UK, sewage sludge is tested for PFAS through the CIP3

Biosolids production in the UK

- Biosolids: Sewage sludge that has been processed to meet certain regulations
- About 8500 WWTWs produce 53 million tonnes of untreated sewage sludge yearly in the UK
- Sewage sludge is then processed at around 200 large treatment facilities
- Processing technologies include anaerobic digestion (73%), lime stabilization (22%) and others including thermal drying and composting (1%) [2].
- Processed sludge is used for agriculture (87%), land reclamation (6%), Incineration (4%) and Industrial (3%)
- PFAS present in wastewater matrix adsorbed onto biosolids due to the hydrophobic properties of PFAS
- Land application of biosolids is a potential route for PFAS into the environment
- Around 3.76 million metric tonnes d.w. of processed sludge (biosolids) is land applied annually in the UK [2]
- **USEPA** reports that around 2.12 million dry metric tons of biosolids is land applied annually in USA [3]

PFAS in sludge and how it is cycled in the environment Stormwater run-off **Industries e.g PFAS** manufacturing, electroplating Industrial **Domestic** Combined sewer line sewer line Treated sewer line Effluent **Biosolids** Dewatering **Stabilization** Land application of biosolids **Biosolids** in landfill Leaching into groundwater Air transport by wind PFAS wash off to rivers Uptake by plants **Human Exposure**

Workflow for PFAS quantification in biosolids

- Sludge and biosolids are complex matrices, and EPA method 1633 [4], illustrated here can be used to analyze samples.
- Development of method 1633 is a significant progress, however, it was developed with 40 PFAS compounds in mind.
- Other methods such as untargeted analysis and total oxidizable precursors should be further explored

EPA 1633 method for PFAS analysis in sludge/biosolids Sampling from WWTWs Grab sampling techniques should be used. Use HDPE bottles with PP caps

Sample transport and preservation Store at = 0-6 or < -20 °C. Max hold time = 90 days

Sample preparation and extraction Dry and ground biosolids. Add extracted internal standard (EIS) and extract with 0.3%NH₄OH in MeOH

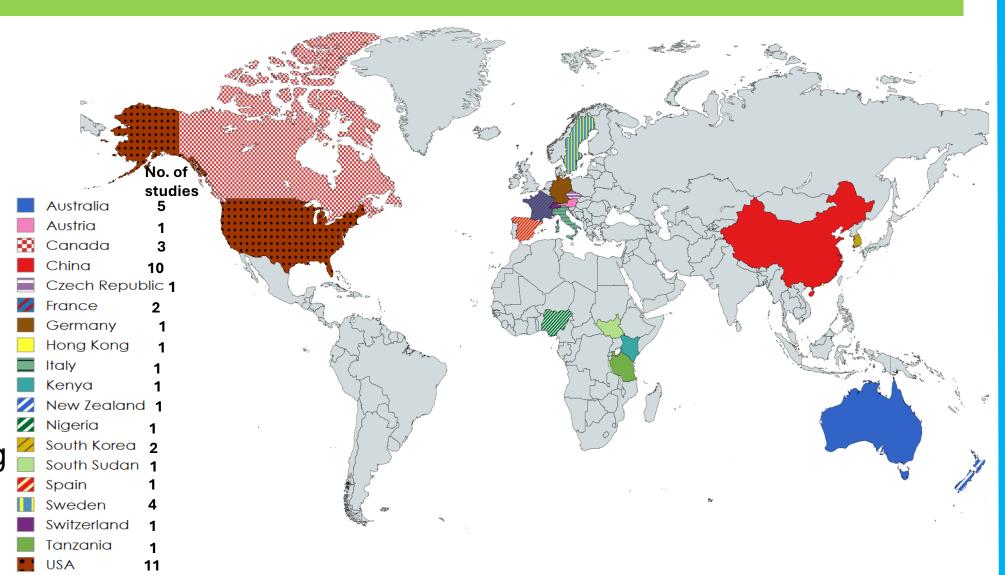
Extract clean-up and concentration Add loose carbon to clean sample, filter and evaporate extract in fume hood

Solid phase extraction Reconstitute extract and use WAX cartridge to separate PFAS. Add non-extracted internal standard (NIS) to the extract

Analysis, quantification and results reporting Analyze sample using LC-MS/MS operated in –ve electrospray ionization mode

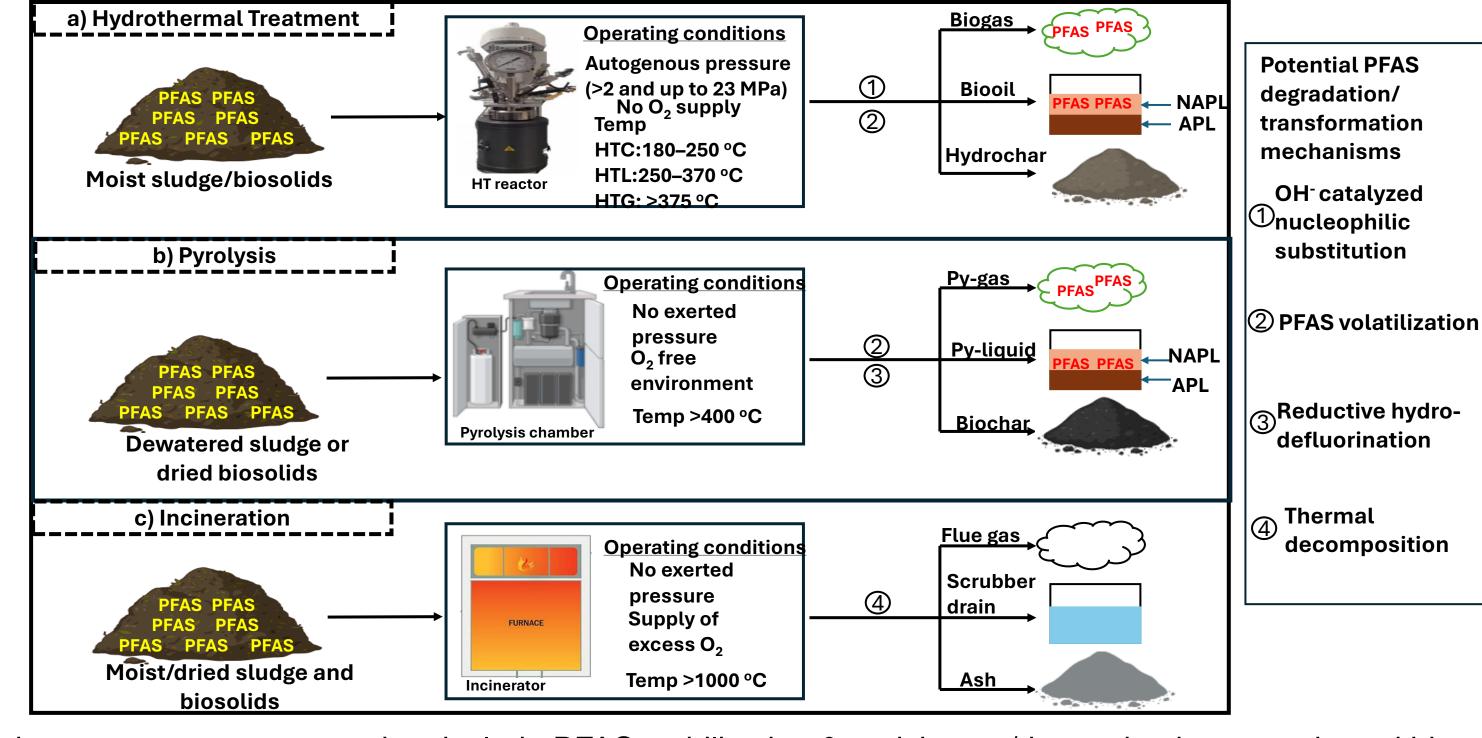
PFAS in biosolids across different countries

- PFAS have been detected in biosolids across all inhabited continents where studies have been conducted
- PFOS is the most widely detected compound. PFDA is a common carboxylated PFAS. Dipaps were found to be prevalent in specific studies conducted in Australia and Canada
- The maximum reported PFAS concentration in sludge was 22000 ng/g dw for 6:2 FTCA. This was obtained from a WWTP processing industrial sludge [5]



Treatment of PFAS in sludge/biosolids

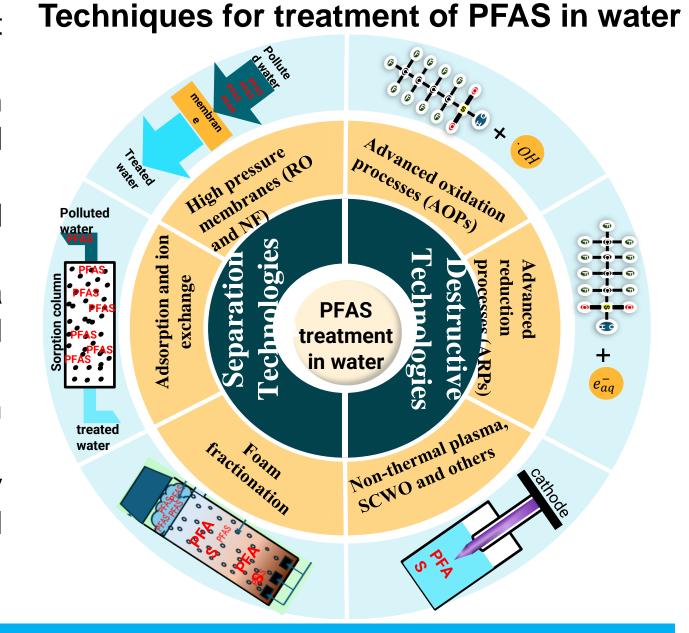
- Common treatment methods and suitable operating conditions for each are illustrated in this section
- Pyrolysis and HT are preferred because the solid residue generated i.e., biochar and hydrochar have an economic value. Furthermore, research has indicated that the solid residues are PFAS-free
- Several mechanisms are involved during the treatment processes
- Common ones include; Decomposition of PFAS due to high temperature, substitution of fluorine atom on
- PFAS by hydroxide (OH-) leading to structure collapse, PFAS defluorination through reductive mechanisms and PFAS volatilization



Other management approaches include PFAS stabilization & enrichment/desorption in contaminated biosolids

Treatment of PFAS in biosolids associated water

- has seen significant in water treatment advancements
- PFAS desorbed from biosolids, and concentrated into an aqueous medium can be further treated using advanced water treatment options
- Separation and destructive technologies are two broad classifications of treatment
- Ion-exchange and adsorption have been investigated in a large-scale setting for PFAS removal in water. Good removal efficiencies were noted
- PFAS surface-active nature of make foam fractionation an interesting option
- Non-thermal plasma treatment utilizes both highly oxidative and reductive species, hence, can be an ideal method for PFAS destruction in water



Conclusions and recommendations

- Land application of PFAS-contaminated biosolids can result in a continuous loop of PFAS cycling in the environment
- Innovative analytical and detection methods for PFAS in environmental media are currently investigated
- Pyrolysis, HT treatment and stabilization approaches have shown potential for PFAS treatment and management in biosolids
- Foam fractionation and non-thermal plasma are novel and innovative approaches that can be used for PFAS separation and destruction in water

Advancing public awareness, policy making and regulation enforcement

Development of

and detection

methods

simpler analytical

treatment options Recommendations

Life cycle and

cost analysis of

technologies

catalyst Upscaling of and treatment train treatment

Equipment for PFAS research in WR3 Lab









Enhancing the

destruction of

PFAS

short-chain and

on PFAS destruction

other recalcitrant

TOC and elemental analyzer

HT equipment



Non-thermal plasma equipment



Acknowledgments

Usman M. Ismail would like to thank Dŵr Cymru (Welsh Water) and Swansea University for jointly supporting his PhD program.

Swansea University

Prifysgol Abertawe



References

[1]. USEPA, 2024. https://www.epa.gov/sdwa/and-polyfluoroalkyl-substances-pfas

[2]. Biosolids Assurance Scheme, 2024. https://assuredbiosolids.co.uk/.

[3]. USEPA, 2022. https://www.epa.gov/biosolids/basic-information-about-biosolids. [4]. USEPA, 2024. https://www.epa.gov/system/files/documents/2024-01/method- 1633-final-for-web-posting.pdf

[5.]. Zhang et al., 2024. https://doi.org/10.1016/j.jhazmat.2023.133270. Other readings:

Buck et al., 2011. https://doi.org/https://doi.org/10.1002/ieam.258. Ismail et al., 2023. https://doi.org/10.3390/toxics11040335