The impact of on-site wastewater effluent on rural karstified aquifers

Luka Vucinic, David O'Connell, Donata Dubber, Patrice Behan, Quentin Crowley, Catherine Coxon, and Laurence Gill

Ireland's European Structural and Investment Funds Programmes 2014-2020
Co-funded by the Irish Government and the European Union

European Union
European Regional Development Fund

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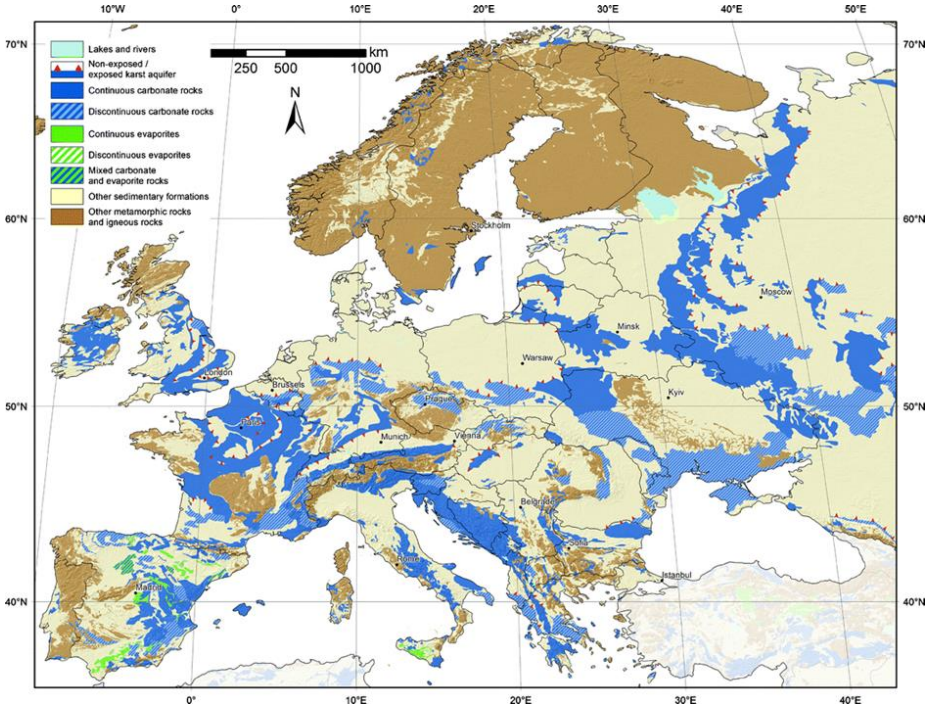
Karst aquifers

- **Karst aquifers** represent one of the most important drinking water resources especially considering that roughly a quarter of the world's population relies on fresh water supply from these aquifer types (Ford and Williams, 2007).

- In Europe approximately 22% of the rocks on land surface of the continent are (more or less) karstified (Chen *et al*., 2017).

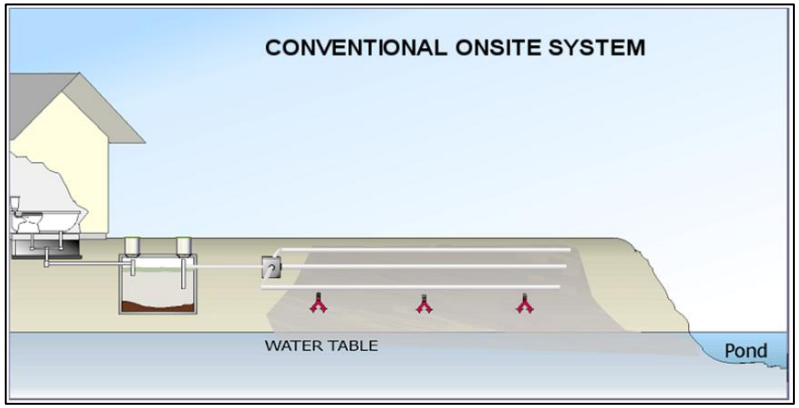


Karst aquifer map of Europe (Chen et al., 2017)

Karst in Ireland & DWTSs

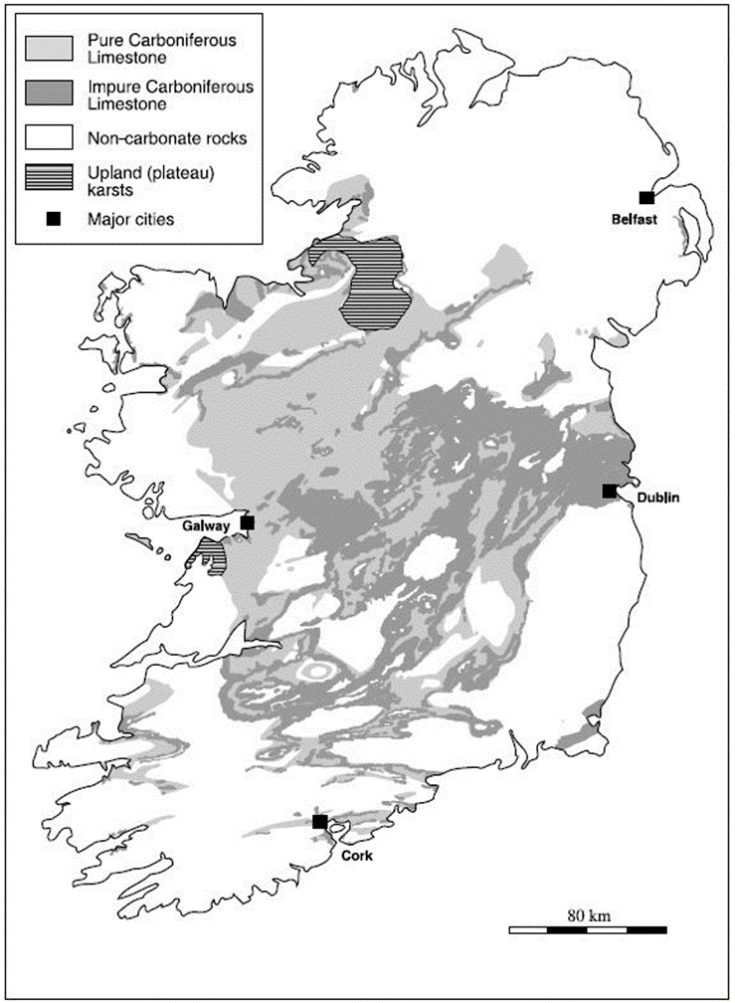
- **Roughly 50% of the Republic of Ireland is underlain by Carboniferous limestone**.

- **The Irish karst terrain is mainly lowland.** In particular, over 90% of the limestones in Ireland are below 150 m above sea level with the majority of these limestones situated below 100 m above sea level (Drew, 2008).



Conventional on-site wastewater treatment system (Joubert et al., 2003)

- **The domestic wastewater of around one third of the population in Ireland (around 500 000 homes) is treated by on-site domestic wastewater treatment systems (DWTSs) of which approx. 87% are septic tanks.**

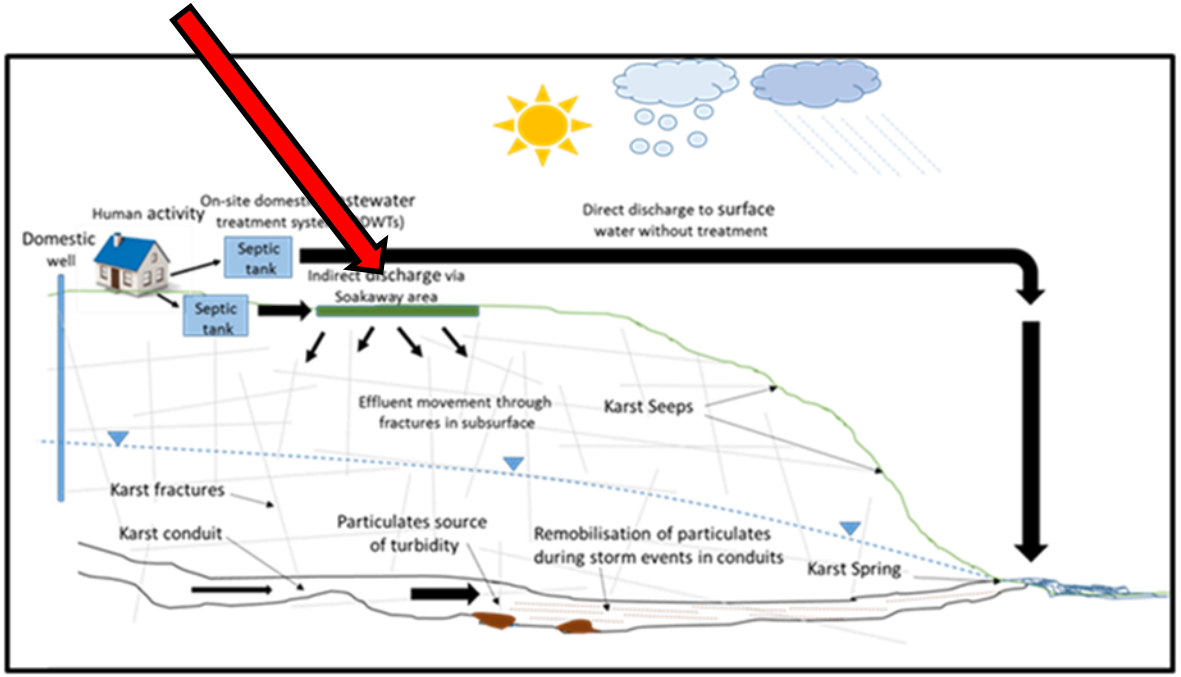


The distribution of Carboniferous limestone formations in Ireland (Drew, 2008)

Contamination of karst aquifers with DWTS effluent

- **<u>Groundwater pollution</u>** is a complex problem that can be associated with a variety of sources, but **human wastewater effluent** and **diffuse agricultural sources** are generally considered among the most significant threats to groundwater quality worldwide.

- This is particularly true in rural and suburban areas where the primary wastewater treatment options for communities without access to centralized wastewater treatment facilities are **on-site domestic wastewater treatment systems (DWTSs).**

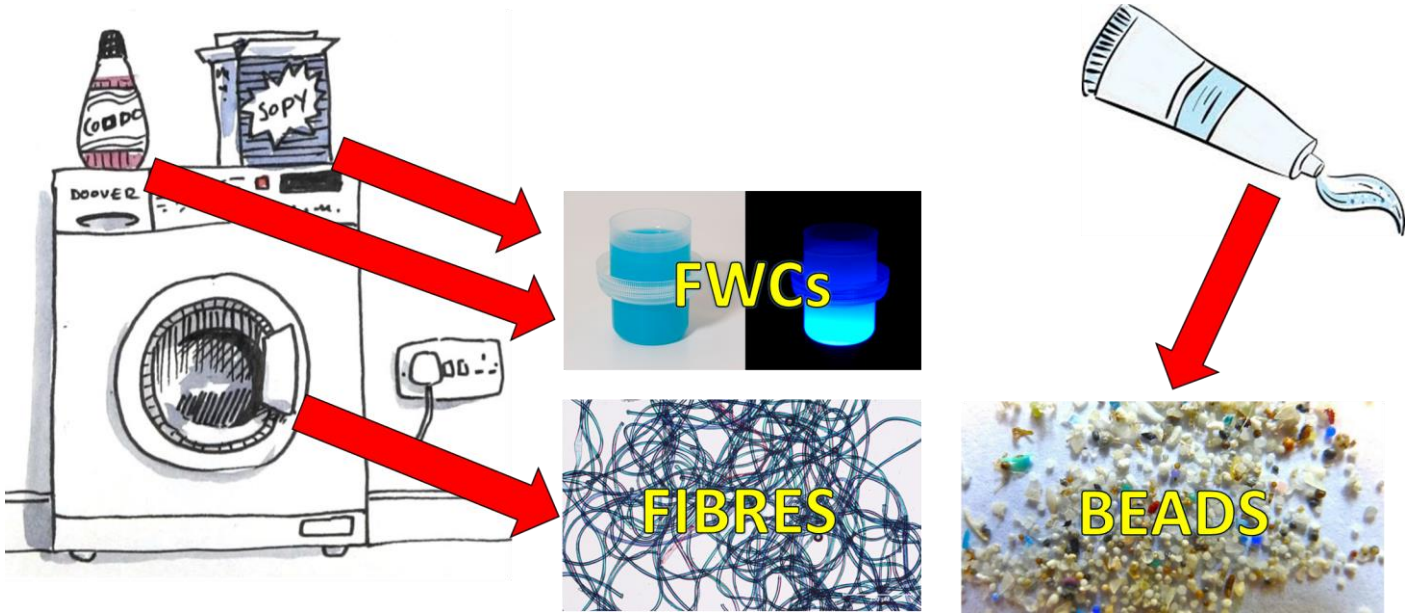


DWTS related particulate movement through karst system

Contamination of karst aquifers with DWTS effluent

- **The domestic wastewater is primarily discharged from toilets, washing machines, showers and dishwashers**, thus, a wide range of contaminants (including source-specific chemical tracers such as **fluorescent whitening compounds – FWCs**) eventually reach the environment even after on-site wastewater treatment processes.

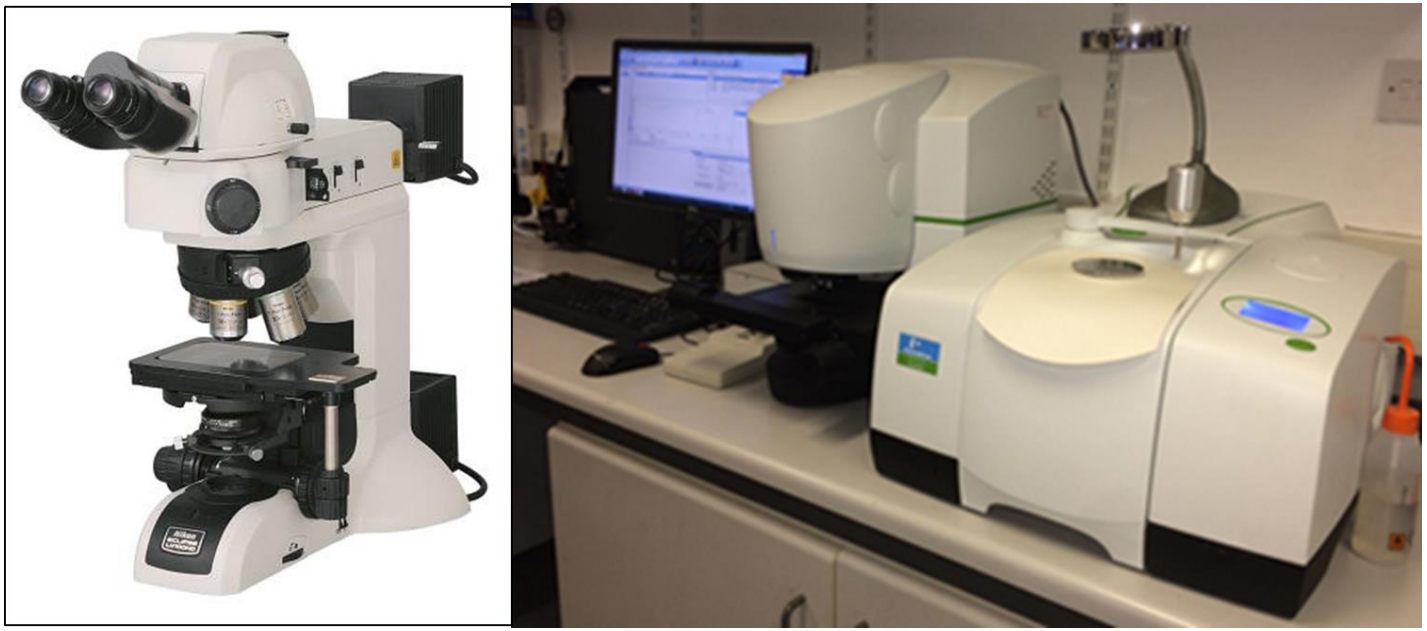
- **Microplastic particles**, as contaminants of emerging concern, are found with other solid materials in the wastewater effluent principally due to household washing and cleaning processes.



The main sources of household-derived microplastics (predominantly microfibres and microbeads) and FWCs

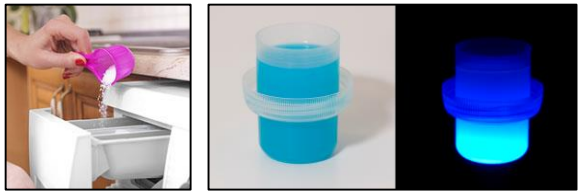
Microplastics

- Sampling of karst groundwater at springs: 5 liters + 5 liters (sample + replica).
- Samples and replicas have been filtered; collected microplastic particles were counted and analysed individually.

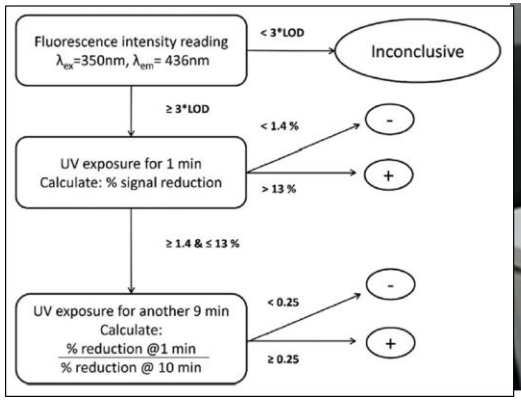


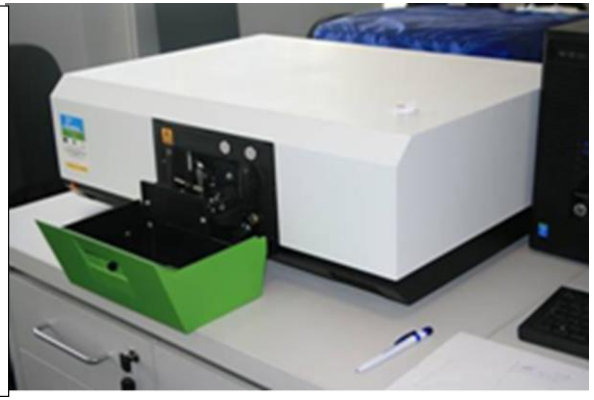
Analysis of microplastic particles (from filters) using LV100ND microscope (left) and Perkin Elmer 200i Spotlight Microscope FTIR Spectrometer (right)

Fluorescent whitening compounds (FWCs)



- **Fluorescent whitening compounds (FWCs)**, also known as optical brighteners (OB), are added to common laundry detergents due their favourable ability to make fabrics appear brighter in colour and prevent yellow staining and fading over time.
- *Two commonly used optical brighteners are **DSBP** (4,40-bis(2-sulfostyry) biphenyl) and **DAS1** (4,40- diamino-2,20-stilbene-disulfonic acid).*
- Their specific anthropogenic origin, specificity, hydrophilic nature and low potential for biodegradability has led to studies into their use as a tracer for domestic wastewater.





Analysis of FWCs using Perkin Elmer LS 55 Fluorescence Spectrometer (right) and in accordance to the suggested modified photodecay method (left) for detection (see Dubber and Gill, 2017)

Chloride and Bromide

Analysis of Cl and Br using
IC Dionix ICS-1500 with AS40 automated sampler

Cl concentrations
double-checked using Thermo F.
Scientific Konelab analyzer

Faecal sterols and stanols

- All faecal material contains **sterols**, and their breakdown products, **stanols**.
- The types and distribution of sterols and stanols in faeces vary between humans and different animals, which gives rise to distinct faecal sterol profiles or fingerprints.
- Distinguishable faecal sterol characteristics for humans, herbivores and birds have been found to be sufficiently distinctive to be of diagnostic value in identifying sources of faecal contamination in water.

Extraction of faecal sterols and stanols (left) and quantification using GC-MS (right)

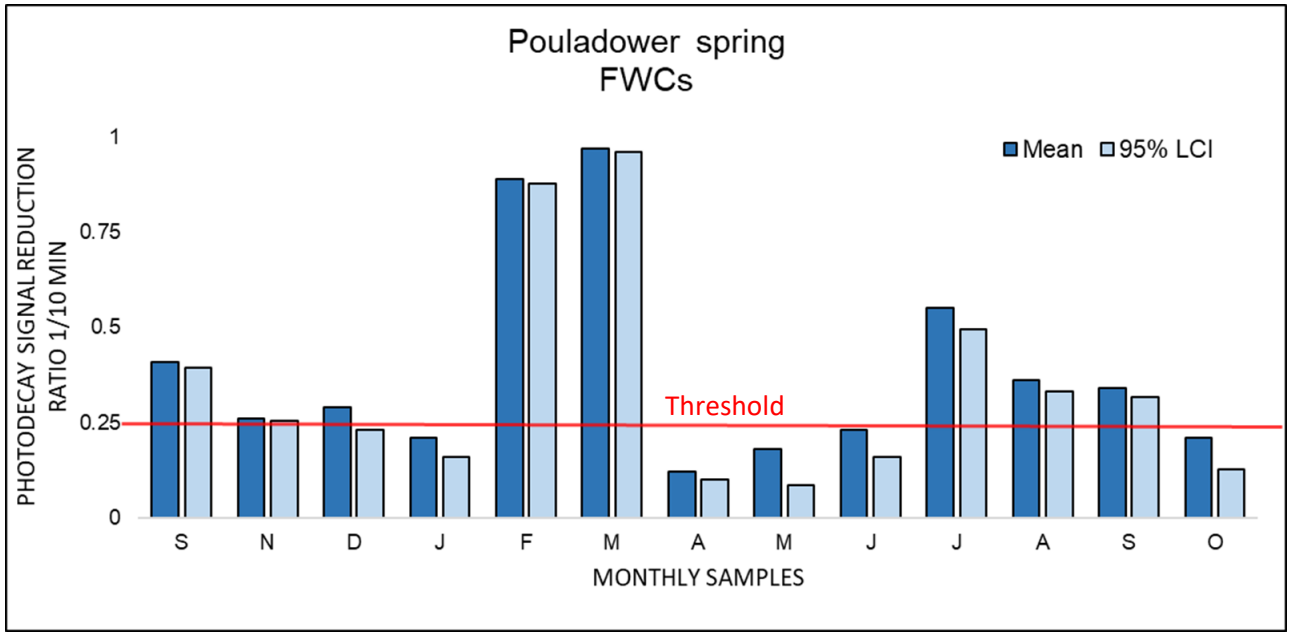
Faecal sterols and stanols

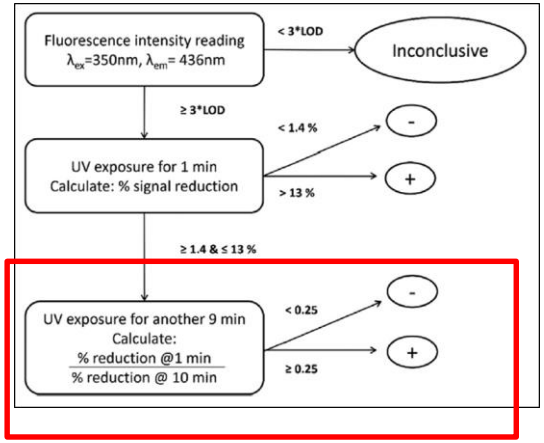
Common name	Full name	Formula
Internal standard		
Cholestane	5α-Cholestane	$C_{27}H_{48}$
Animal sterols		
Cholesterol	Cholest-5-en-3β-ol	$C_{27}H_{46}O$
Coprostanol	5β-cholestan-3β-ol	$C_{27}H_{48}O$
Epicoprostanol	5β-cholestan-3α-ol	$C_{27}H_{48}O$
Cholestanol	5α-cholestan-3β-ol	$C_{27}H_{48}O$
Phytosterols		
Campesterol	24-methylcholest-5-en-3β-ol	$C_{28}H_{48}O$
Campestanol	24-methyl-5α-cholestan-3β-ol	$C_{28}H_{50}O$
Stigmasterol	24-ethylcholesta-5,22-dien-3β-ol	$C_{29}H_{48}O$
β-Sitosterol	24-ethylcholest-5-en-3β-ol	$C_{29}H_{50}O$
24-ethyl-coprostanol	24-ethyl-5β-cholestan-3β-ol	$C_{29}H_{52}O$
24-ethyl-epicoprostanol	24-ethyl-5β-cholestan-3α-ol	$C_{29}H_{52}O$
Sitostanol/Stigmastanol	24-ethyl-5α-cholestan-3β-ol	$C_{29}H_{52}O$

Results & Discussion

- FWCs method has been modified to increase the sensitivity of previously developed photodecay methods by up to 59%.

- Since no quantitative measurements for FWCs are possible using this method, a simple presence/absence approach (according to the suggested photodecay signal reduction ratio 1/10 min threshold) must be applied to quantify the detectability of FWCs in groundwater samples.

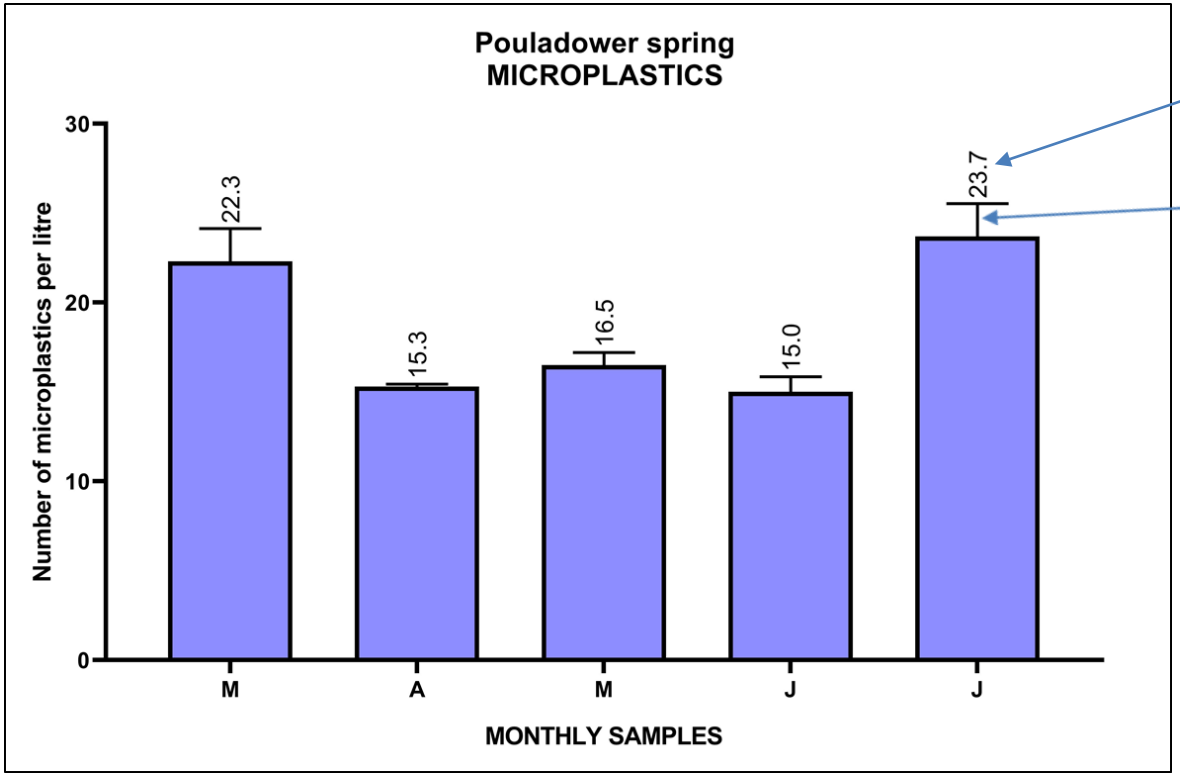




***Note: For practical reasons, only Pouladower spring (Co. Clare) results are presented at the EGU 2020**

Results & Discussion

- More than 97% of all isolated microplastic particles have been classified as fibres. Most of non-fibres were (micro)beads, although, a few fragments have been found as well.
- **Polyethylene (PE) fibres were identified as a dominant microplastic pollutant at all monitored karst springs.**



Mean value

SD

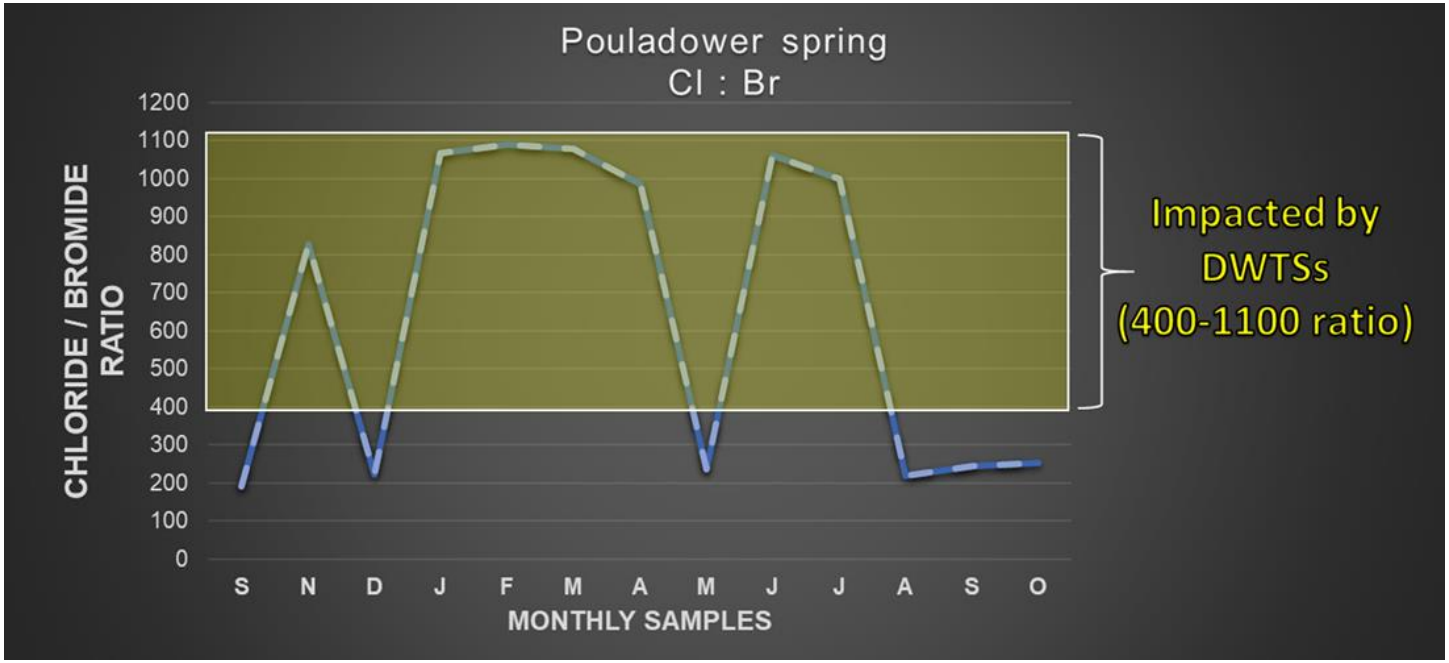
Microplastic concentrations (Mean and SD) at Pouladower spring between March and July 2018

***Note: For practical reasons, only Pouladower spring (Co. Clare) results are presented at the EGU 2020**

Results & Discussion

- **While behaviour of Cl and Br in the environment can be described as similar** (e.g. both are highly soluble, act conservatively when ionized in water, are minimally affected by adsorption to sediment once dissolved in water, are not altered by oxidation-reduction reactions and neither occur in high concentrations in common rock forming minerals – with the exception of evaporites) **their natural abundances are different** (since bromide is naturally found in very small concentrations). **Thus, a relatively small change in the total mass of Br will result in a large change in the overall Cl:Br ratio, if Cl remains relatively unchanged (Davies *et al.*, 1998).**

- **Cl : Br ratios between 400 and 1100 are indicating potential DWTS impacts on groundwater quality.**



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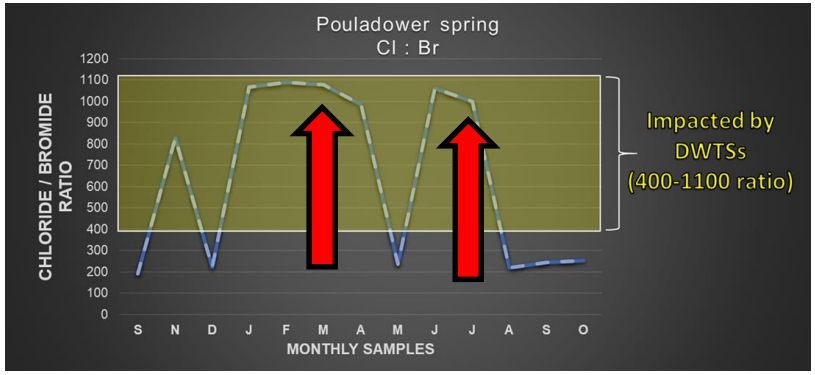
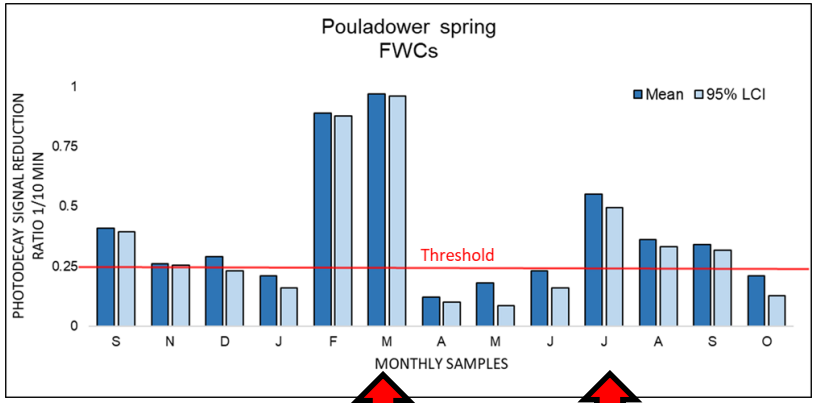
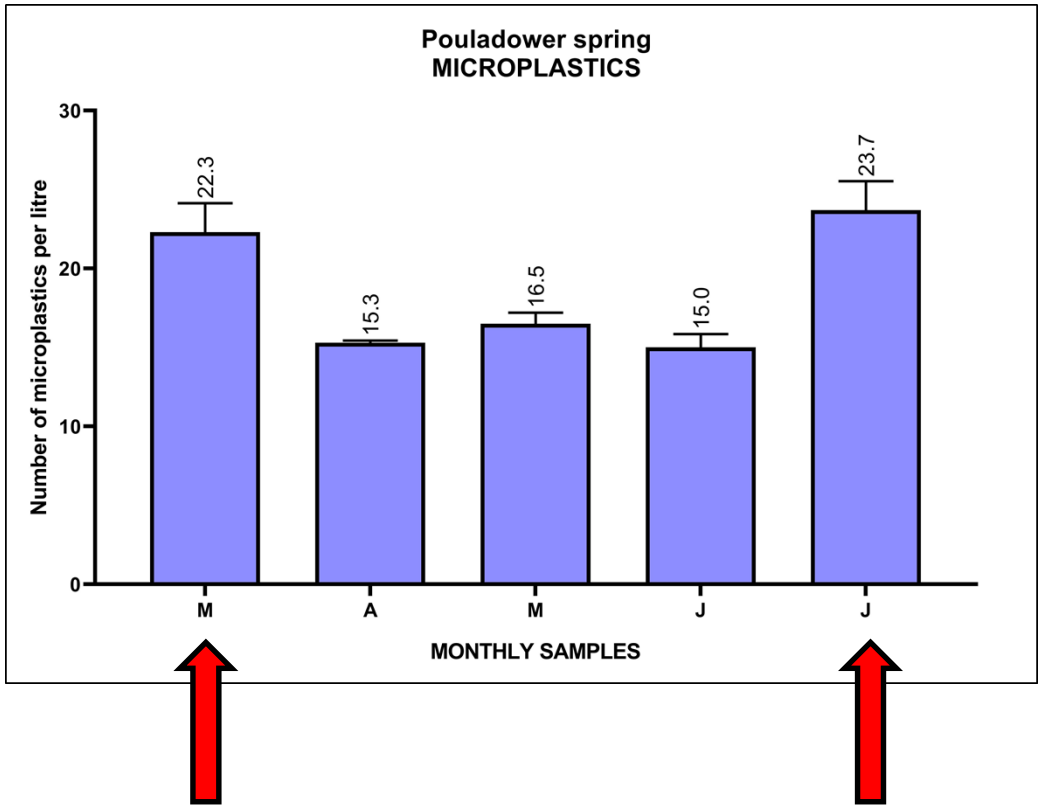
Results & Discussion

- **Elevated microplastic concentrations were observed in March and July 2018 at Pouladower spring when strong positive FWCs signals were detected. Additionally, Cl:Br ratio interpretation has confirmed DWTS effluent impact on groundwater quality in those samples.**

- **Analysis of faecal sterols and stanols confirmed (additionally) presence of contaminants of DWTS origin**, although, for practical reasons these graphs/data were excluded from presentation.







Conclusions

- FWCs can be successfully used as a tracer of DWTS effluent pollution of karst aquifers. Method used in this study is inexpensive and reliable;
- Detection of strong FWCs signals generally correlates well with elevated microplastic concentrations in groundwater;
- The majority of microplastics in rural karst aquifer systems can be linked to DWTS origin on the basis of their properties and detection of FWCs;
- Cl : Br ratio can be useful as a cheap indicator of DWTS pollution but only to additionally confirm DWTS impacts, not as a single tracer.
- Analysis of faecal sterols and stanols is as a powerful technique, but too expensive, complicated, and time-consuming. Expensive equipment and highly trained personnel are also needed.


Thank you
& stay safe!
vucinicl@tcd.ie
@TheKarstMan

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