

Analysing highly polar trace substances in water by ion chromatography high resolution mass spectrometry

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Background

- Highly polar and persistent trace substances from multiple sources are reaching the water cycle and accumulate.
 - Widely used reversed phase chromatography (C18) for analysing trace substances in water are not able to retard very polar compounds.
- Monitoring and analytical gaps are still existing.
→ Other chromatographic methods are needed. We developed and validated a method with

Anionic chromatography

because anionic compounds are highly mobile in water.

Conclusion

- LOQs are close to 0.1 µg/L precautionary drinking water values → Enrichment to reduce LOQs
- Application of developed IC-HRMS method for real samples sufficiently robust → Larger monitoring campaigns

Outlook:

→ Development of data processing workflow for

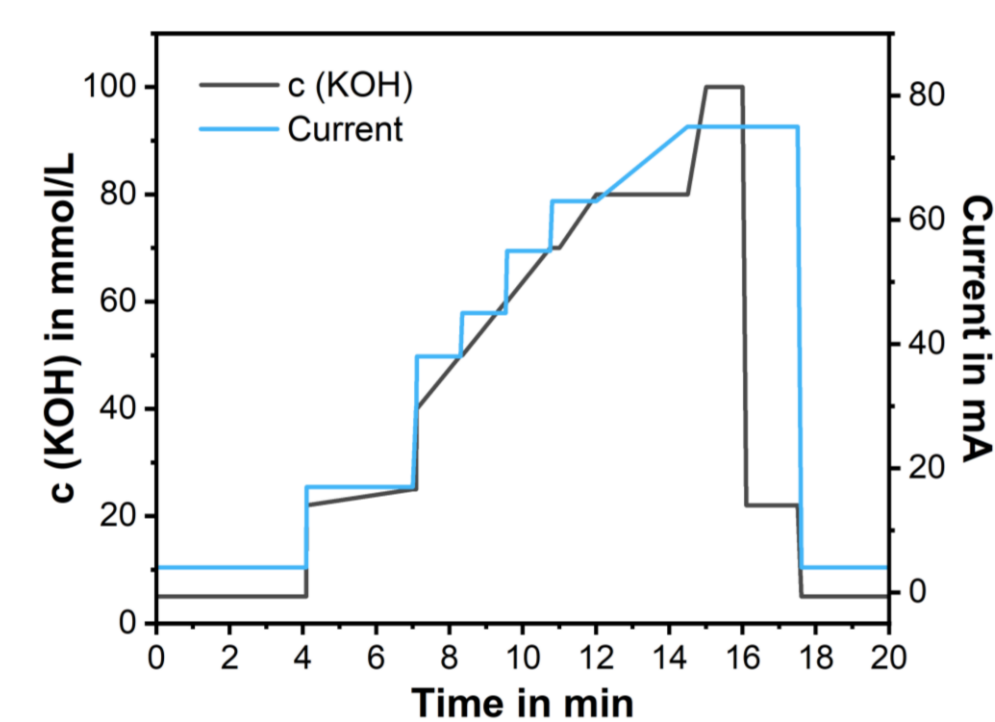
Non-target Screening

to track unknown anionic compounds in raw and drinking water

Gradient

- c(KOH): 5 mmol/L - 100 mmol/L
- Current of suppressor is aligned with c(KOH)
- Run-time: 20 min

Neutralisation of KOH due to ion exchange

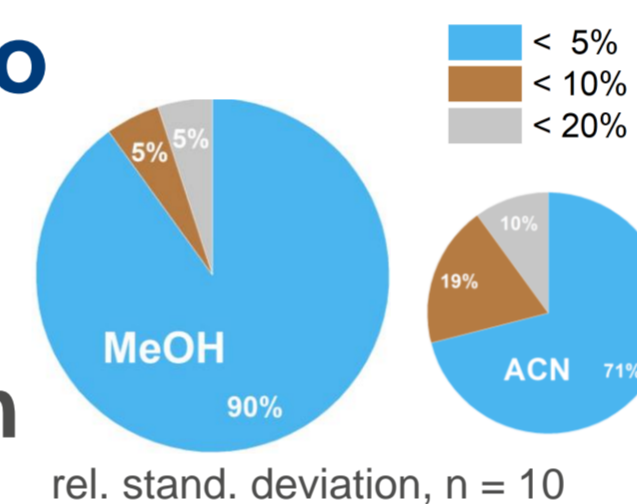


Make-up solvent

Solvent	Viscosity	Max. Flow rate
Isopropanol	2.2 mPa s	0.01 mL/min
Ethanol	1.2 mPa s	0.04 mL/min
Methanol	0.6 mPa s	0.10 mL/min
Acetonitrile	0.4 mPa s	0.10 mL/min

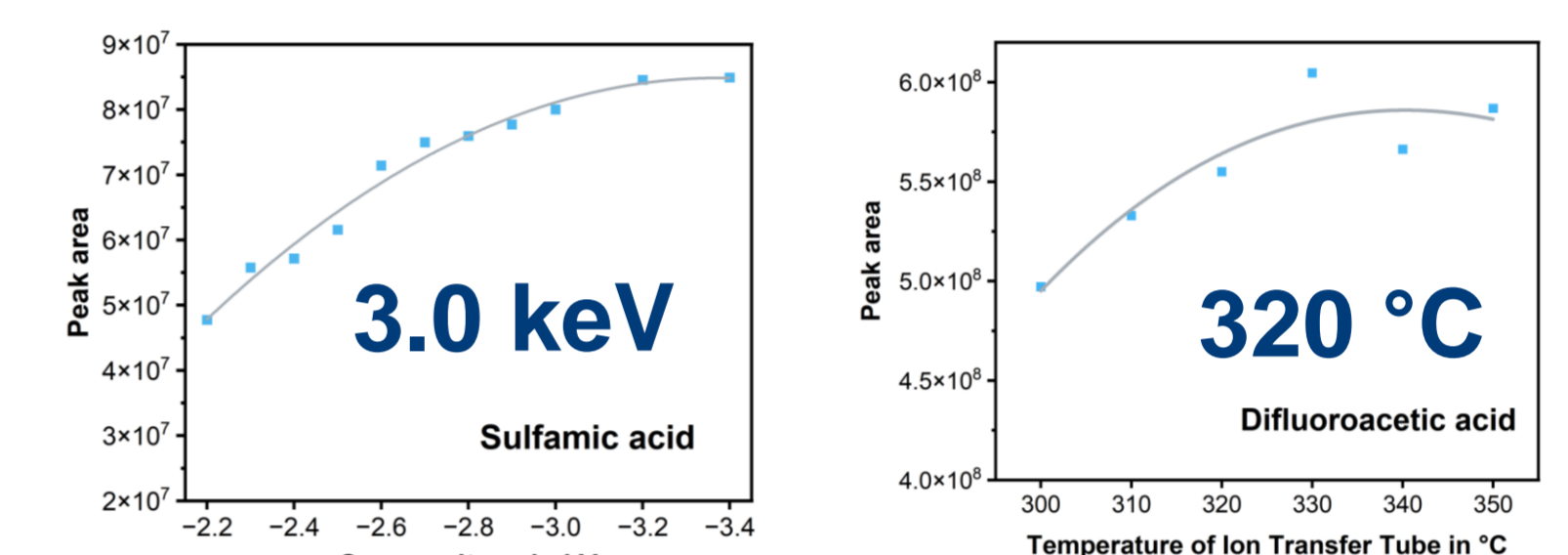
+ 0.08 mL/min MeOH to enhance ionisation

Precision



rel. stand. deviation, n = 10

ESI Source



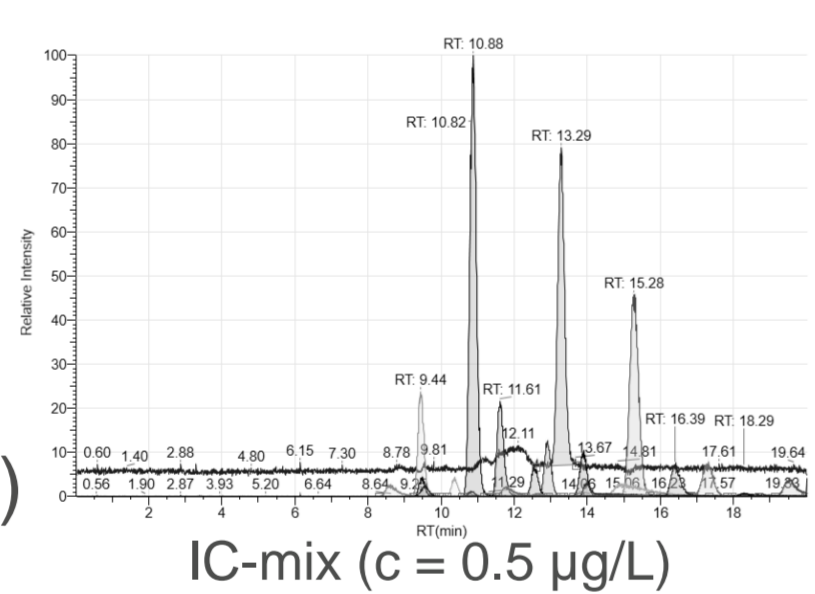
Compromise of the settings for spray-voltage and temperatures from each substance for the overall method

(Pre-) Column

- (AG 24 +) AS 24, 2 mm x 250 mm
- Flow rate 0.3 mL/min
- Temp.: 30 °C

RTs are very stable

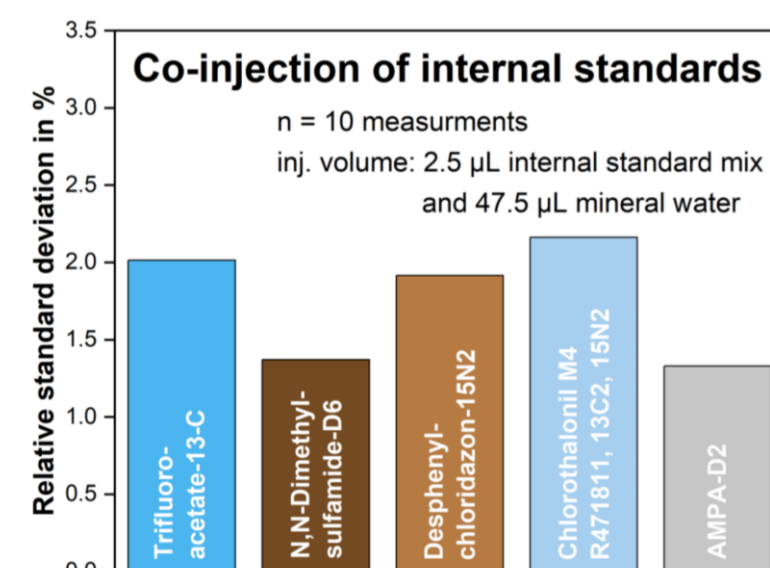
(RSD < 0.15%, n = 10)



19 and 21 were excluded, because of its peak width > 5 min

Autosampler

- Temperature: 15 °C
- Injection volume: 47.5 µL + 2.5 µL

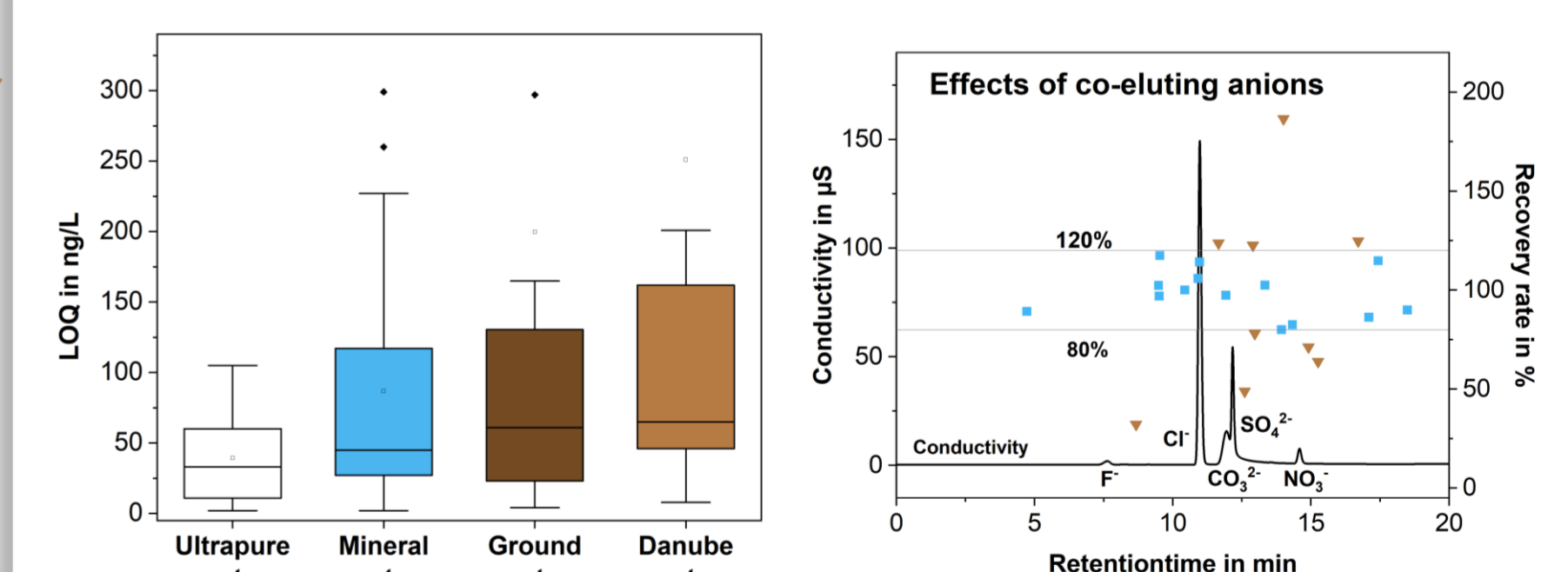


Co-injection of isotope labeled standards with high precision

Test substances

#	Substance	Min log D (pH 4 - 9)	Molecular mass in g/mol	#	Substance	Min log D (pH 4 - 9)	Molecular mass in g/mol
1	α-amino-3-hydroxy-5-methyl-4-isoxazole-propionic acid (AMPA)	-4.72	111.04	13	Glyphosate	-8.57	169.07
2	Carboxy-acyclovir	-1.58	239.19	14	Hexafluorophosphate	0.96	144.96
3	Chlorothalonil R471811	-1.71	347.56	15	Monobromoacetic acid	-3.03	138.95
4	Clopyralid	-1.30	192.00	16	Monochloroacetic acid	-3.21	94.50
5	Cyanuric acid	0.98	129.07	17	N,N-dimethylsulfamide	-1.54	124.16
6	Desphenyl chloridazone	-1.01	145.55	18	Oxamic acid	-4.60	89.05
7	Dibromoacetic acid	-2.89	217.84	19	Oxipurinol	-3.64	152.11
8	Dichloroacetic acid	-2.47	128.94	20	Perfluorobutanoic acid	-1.22	214.04
9	Difluoroacetic acid	-3.34	96.03	21	Perfluorobutanesulfonic acid	0.86	300.10
10	Dimethenamid M31	-2.58	347.45	22	Sulfamic acid	-3.79	97.09
11	Ethephon	-3.66	144.49	23	Trichloroacetic acid	-2.00	163.39
12	Glufosinate	-6.78	181.13	24	Trifluoroacetic acid	-2.62	114.02

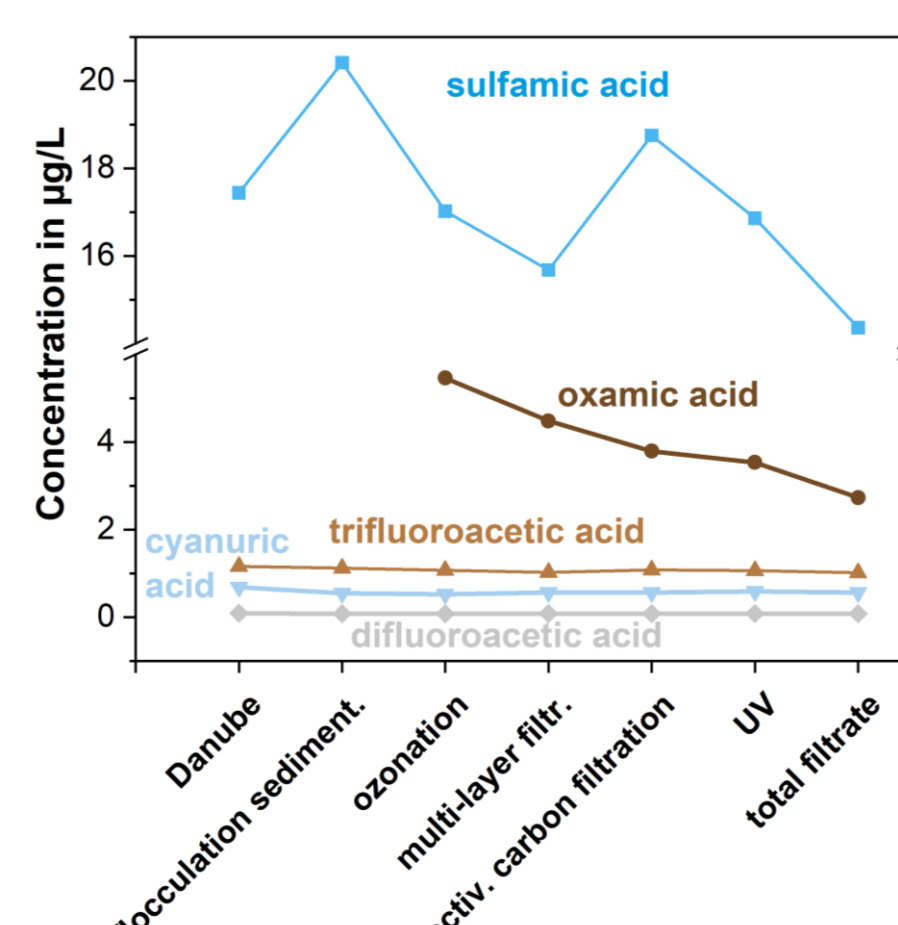
Validation



- LOQ ~ 100 ng/L (Eurachem validation guide)
- Correlation of recovery and co-eluting inorganic anions is not clear

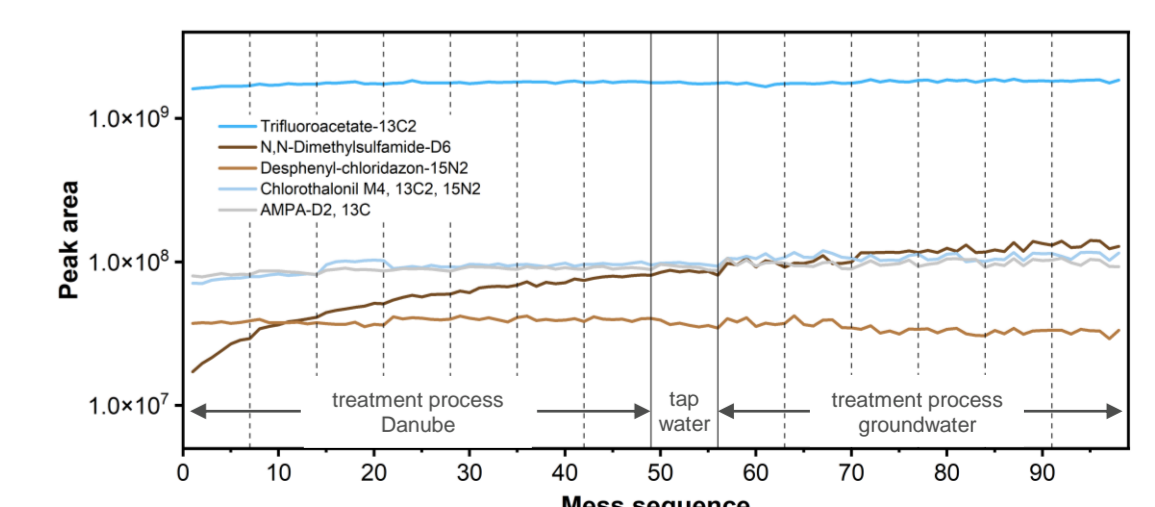
Application: Real samples

- Five target substances were detected in Danube water and its processing steps
- Oxamic acid is formed during ozonation
- No significant degradation is observed
- Concentrations are below the limits for drinking water



Quality control

- Co-injection of isotope-labeled standards to check stability of measurement and system
- Fluctuation of peak areas increases with complex matrix (salt content)
- Increase of N,N-Dimethylsulfamide-D6 currently inexplicable



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