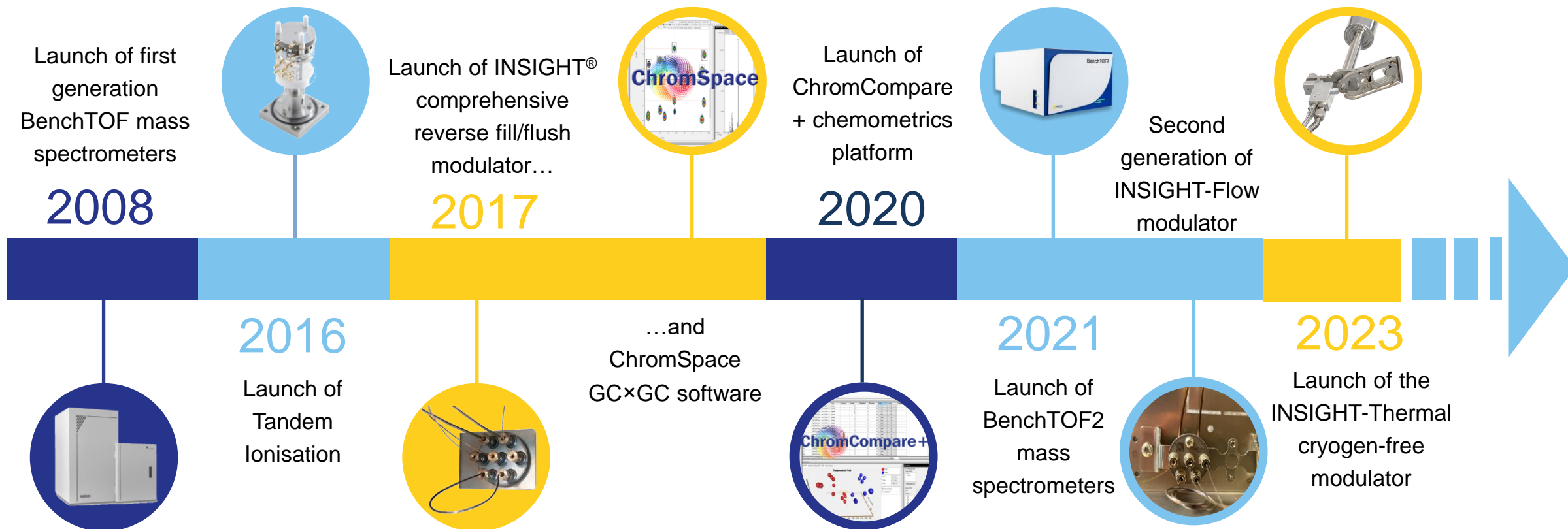


# A holistic view of river water quality using passive sampling and GC×GC–TOF MS

Presented by: Dr Jonathan Grandy

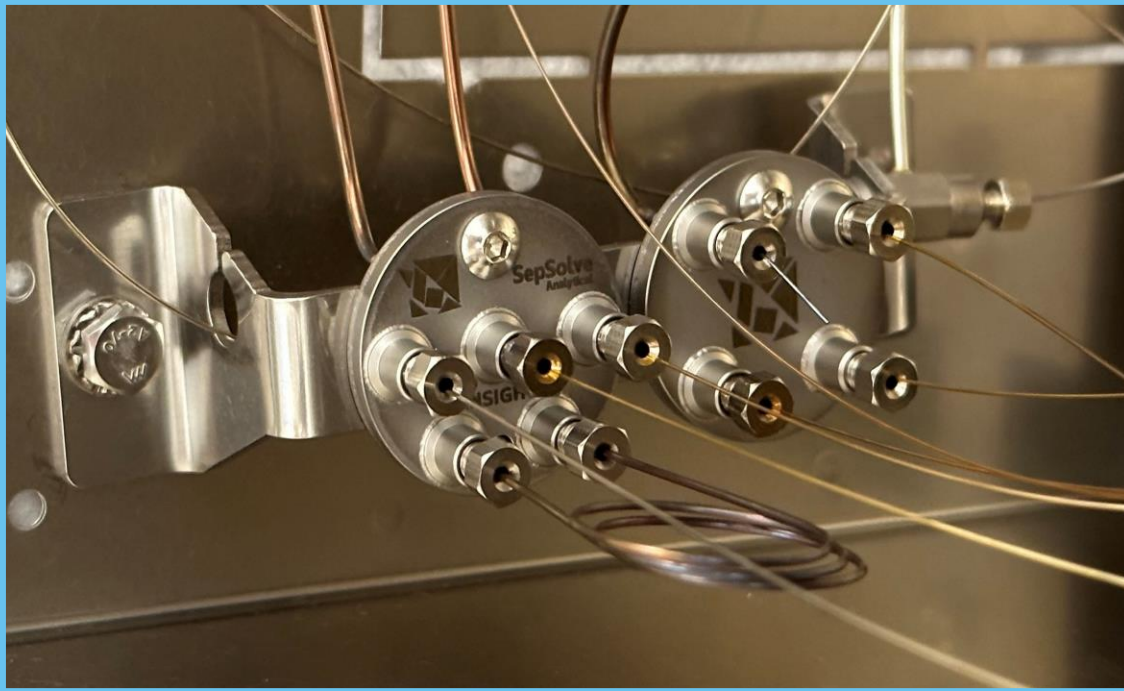
Sampling performed by Natural Resources Wales and Analysis  
in conjunction with Sepsolve Peterborough

# GC×GC at SepSolve Analytical



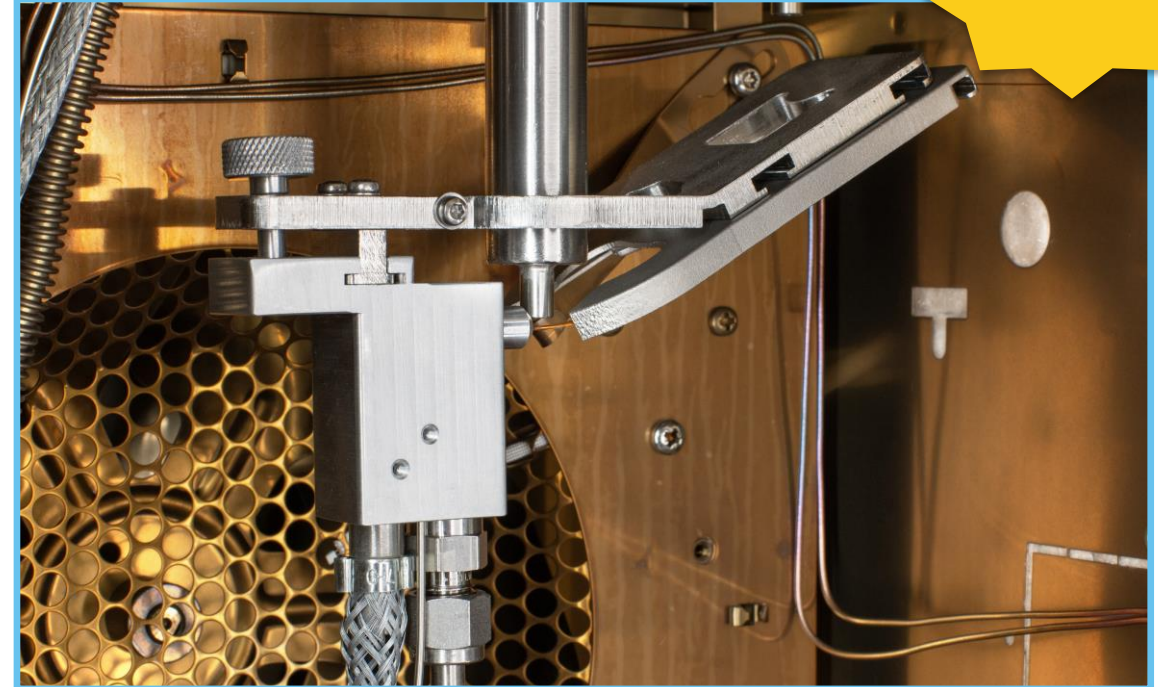
# The INSIGHT® modulator series

## INSIGHT-Flow



- Reverse fill/flush (RFF) flow modulator
- Bleed line control kit for greater flexibility in method development
- Optional 4-port purged splitter

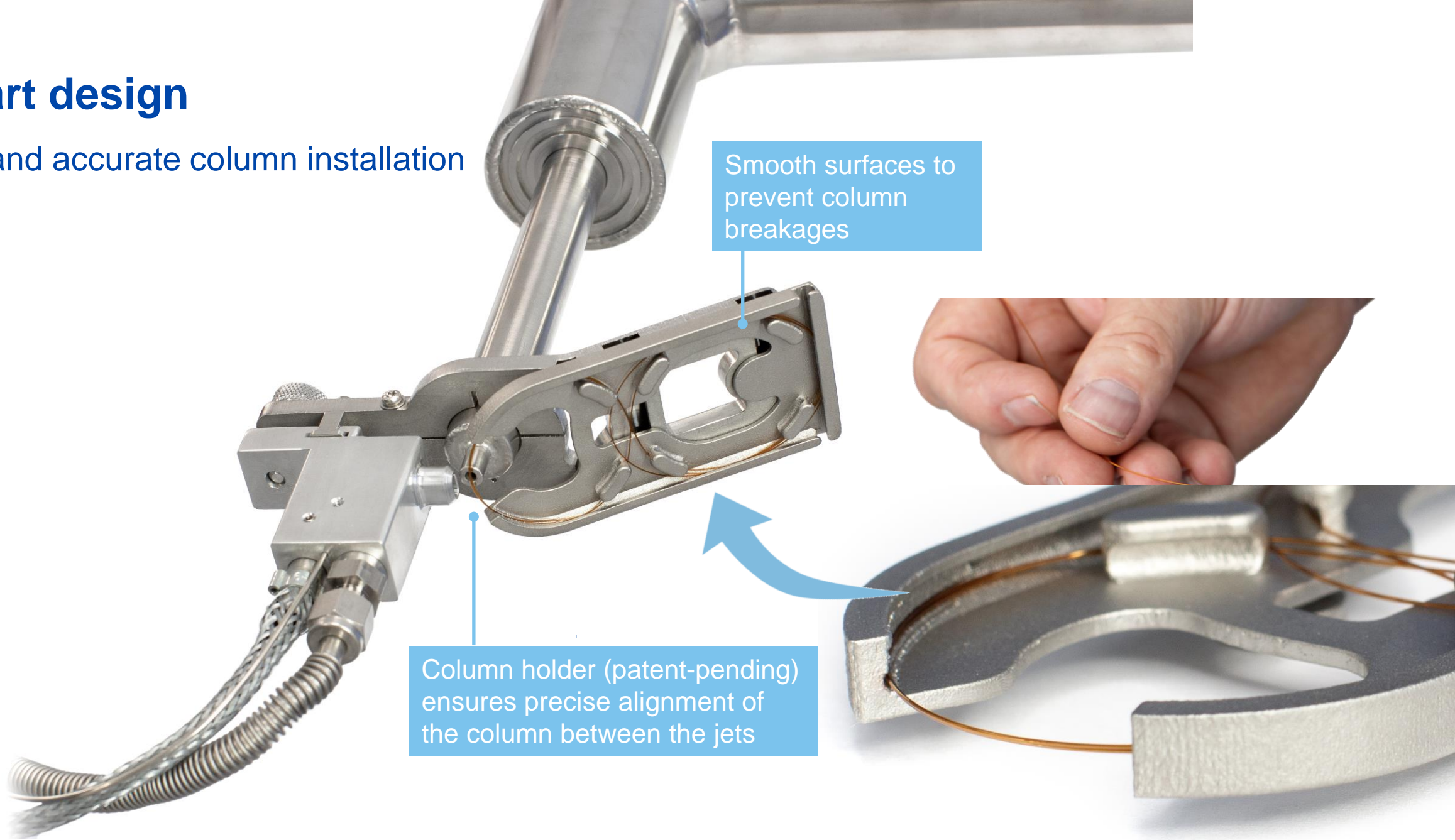
## INSIGHT-Thermal



- Cryogen-free thermal modulator using delay loop technology
- Advanced control of cold jet flow rate
- Smart column holder design for easy set-up

# Smart design

Fast and accurate column installation



Smooth surfaces to prevent column breakages

Column holder (patent-pending) ensures precise alignment of the column between the jets

# Fully unattended analysis to maximise sample throughput

The screenshot displays the ChromSpace sequence editor interface. The main window shows a sequence table with 8 rows of samples. The 'Global Method' column is highlighted in blue. The 'Instruments' panel on the right shows the status of two instruments: INSIGHT-Thermal Modulator and Agilent 8890 GC, both in 'Idle' state.

Project: Pyrolysis oils  
Path: C:\ProgramData\Marks International\Chromspace vthermalData

	Sample Type	File Name	Comment	Global Method	Mod period	ICFVariables	Vial	Rep
1	Sample	23_08_23 Pyrolysis oil A		Pyrolysis oils	6	Injection: Standard Injector: GC_Front Volume: 5 Metho	1	
2	Sample	23_08_23 Pyrolysis oil B		Pyrolysis oils	6	Injection: Standard Injector: GC_Front Volume: 5 Metho	2	
3	Sample	23_08_23 Pyrolysis oil C		Pyrolysis oils	6	Injection: Standard Injector: GC_Front Volume: 5 Metho	3	
4	Sample	23_08_23 Pyrolysis oil D		Pyrolysis oils	6	Injection: Standard Injector: GC_Front Volume: 5 Metho	4	
5	Sample	23_08_23 Crude oil A		Crude oils	8	Injection: Standard Injector: GC_Front Volume: 5 Metho	5	
6	Sample	23_08_23 Crude oil B		Crude oils	8	Injection: Standard Injector: GC_Front Volume: 5 Metho	6	
7	Sample	23_08_23 Crude oil C		Crude oils	8	Injection: Standard Injector: GC_Front Volume: 5 Metho	7	
8	Sample	23_08_23 Crude oil D		Crude oils	8	Injection: Standard Injector: GC_Front Volume: 5 Metho	8	

Instruments

INSIGHT-Thermal Modulator  
Idle

Agilent 8890 GC  
Idle

ChromSpace

- Full control of all jet parameters and easy sequencing of instrument methods

# Fully unattended analysis to maximise sample throughput

The screenshot shows the 'View Method' window for an 'INSIGHT-Thermal Modulator Agilent 8890'. It features a graph and several parameter tables.

**Graph Data:**

Time (mins)	Cold jet flow (L/min)	Hot jet T (°C)
0	15	100
10	12.5	125
20	10	150
30	7.5	175
40	5	200
50	2.5	225
60	2.5	250
70	2.5	275

**Modulation Settings:**

Initial	Start time (s)	Hot jet (ms)	Mod period (s)
Initial	0	100	6.0
Interval 1	600	200	6.0
Interval 2	1200	300	6.0

**Hot jet Settings:**

Initial	C/Min	Set C	Hold Time (m)
Initial		150	2.0
Ramp 1	4.0	400	10.0

**Cold jet Settings:**

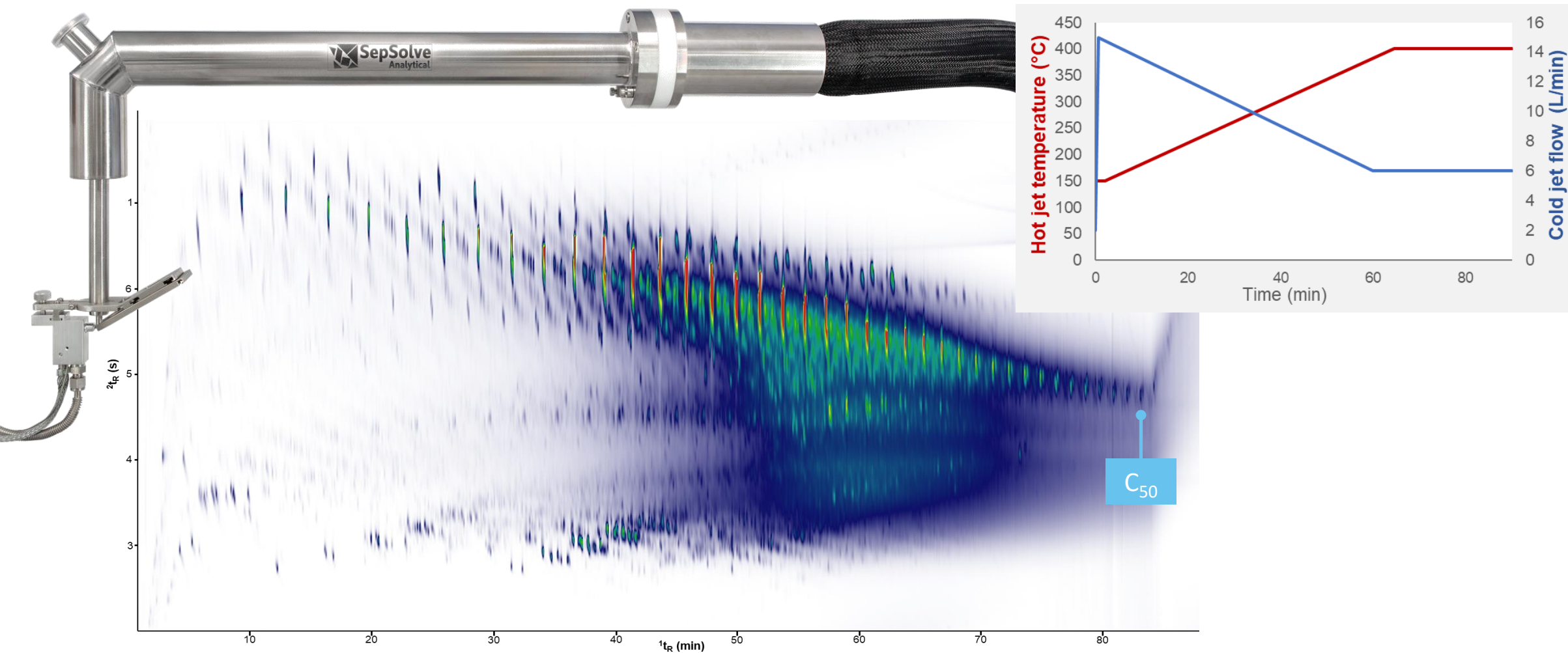
Initial	L/Min2	Set Flow (L/Min)	Hold Time (m)
Initial		2	0.0
Ramp 1	20.0	15	0.0
Ramp 2	0.2	6	14.0

**Annotations:**

- Apply linear ramp rates to cold jet flow (pointing to Ramp 1 in Hot jet settings)
- Unlockable parameters for fast method development (pointing to the lock icon in Cold jet settings)

# Extending the analyte range

Efficient modulation of C<sub>7</sub> to C<sub>50+</sub>



# Standby flows to prevent icicle formation

Have the confidence to leave your samples running unattended

The screenshot displays the ChromSpace sequence editor interface. The main window shows a sequence of 24 samples, each with a status of 'Active'. The samples are organized into three groups: Pyrolysis oils (rows 1-8), Crude oils (rows 9-16), and VGO (rows 17-24). The 'Instruments' panel on the right shows the 'INSIGHT-Thermal Modulator' and 'Agilent 8890 GC' both as active components. A callout box highlights the 'Comms settings' dialog, which is open to the 'Standby time (mins)' and 'Cold Jet Flow (L/min)' settings. The 'Cold Jet Flow (L/min)' is set to 0.5, which is highlighted with a blue box. The 'Standby time (mins)' is set to 40. The 'Hot jet (°C)' is checked and set to 50. The 'MFC Gas Type' is set to N2. The 'Serial port' is set to COM4. The 'Trigger' is set to 'Open' for 'Start' and 'Closed' for 'Stop'. The 'OK' and 'Cancel' buttons are visible at the bottom of the dialog.

Sample	Status	Sample Type	File Name	Comment	Global Method	Vial	Process
1	Active	Sample	23_08_23 Pyrolysis oil A		Pyrolysis oils (version 1)	1	
2		Sample	23_08_23 Pyrolysis oil B		Pyrolysis oils (version 1)	1	
3		Sample	23_08_23 Pyrolysis oil C		Pyrolysis oils (version 1)	2	
4		Sample	23_08_23 Pyrolysis oil D		Pyrolysis oils (version 1)	2	
5		Sample	23_08_23 Pyrolysis oil E		Pyrolysis oils (version 1)	3	
6		Sample	23_08_23 Pyrolysis oil F		Pyrolysis oils (version 1)	3	
7		Sample	23_08_23 Pyrolysis oil G		Pyrolysis oils (version 1)	4	
8		Sample	23_08_23 Pyrolysis oil H		Pyrolysis oils (version 1)	4	
9		Sample	23_08_23 Crude oil A		Crude oils (version 1)	5	
10		Sample	23_08_23 Crude oil B		Crude oils (version 1)	5	
11		Sample	23_08_23 Crude oil C		Crude oils (version 1)	6	
12		Sample	23_08_23 Crude oil D		Crude oils (version 1)	6	
13		Sample	23_08_23 Crude oil E		Crude oils (version 1)	7	
14		Sample	23_08_23 Crude oil F		Crude oils (version 1)	7	
15		Sample	23_08_23 Crude oil G		Crude oils (version 1)	8	
16		Sample	23_08_23 Crude oil H		Crude oils (version 1)	8	
17		Sample	23_08_23 Vac gas oil A		VGO (version 1)	9	
18		Sample	23_08_23 Vac gas oil B		VGO (version 1)	9	
19		Sample	23_08_23 Vac gas oil C		VGO (version 1)	10	
20		Sample	23_08_23 Vac gas oil D		VGO (version 1)	10	
21		Sample	23_08_23 Vac gas oil E		VGO (version 1)	11	
22		Sample	23_08_23 Vac gas oil F		VGO (version 1)	11	
23		Sample	23_08_23 Vac gas oil G		VGO (version 1)	12	
24		Sample	23_08_23 Vac gas oil H		VGO (version 1)	12	

- Cold jet flow defaults to 0.5 L/min between runs and sequences to prevent issues, such as icicle formation, previously experienced during unattended operation or over weekends



# Monitoring river water quality

What are the challenges?

- Constantly seeking lower detection limits
- New sampling techniques (e.g., passive sampling) deliver extracts with greater complexity
- Focus is typically on “priority”(organochlorines) substances, but what about those of emerging concern?



# What are the emerging contaminants?



Pharmaceuticals and hormones



Personal care products and fragrances



Industrial additives and by-products



Water treatment by-products



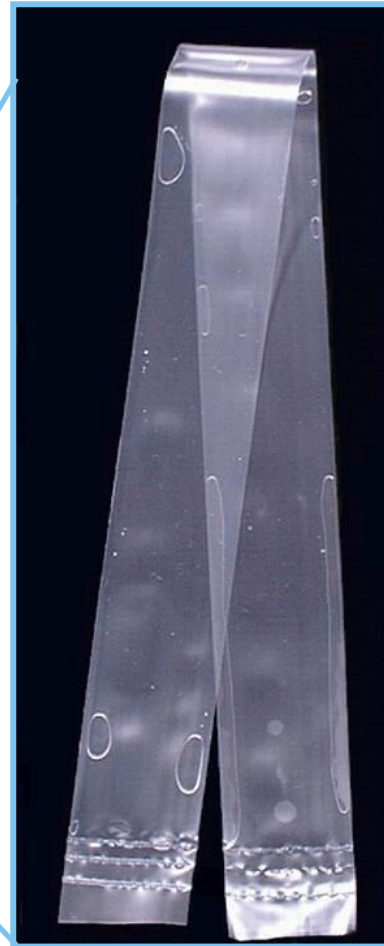
Caffeine and nicotine (and their metabolites)



Flame/fire retardants and surfactants

# Experimental

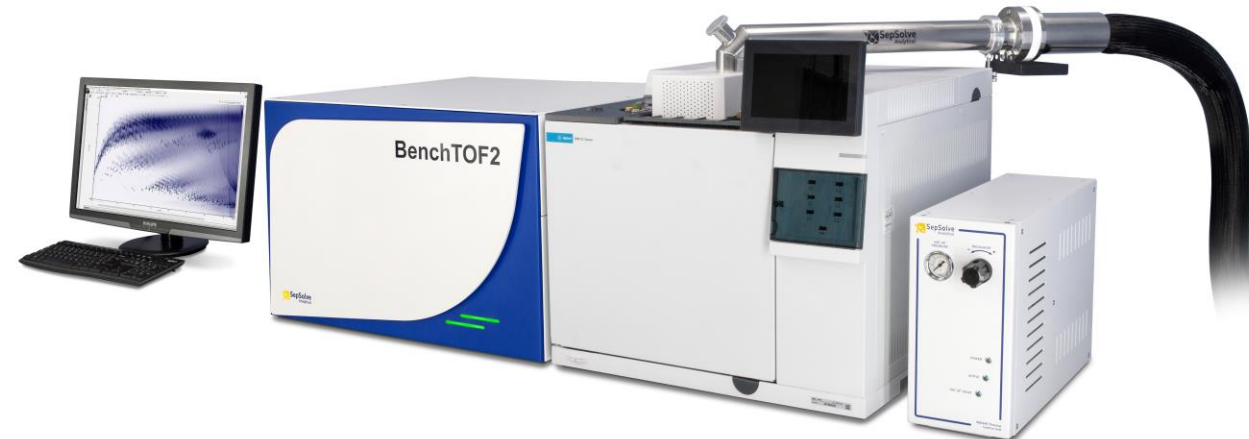
## Semi-permeable membrane device (SPMD)



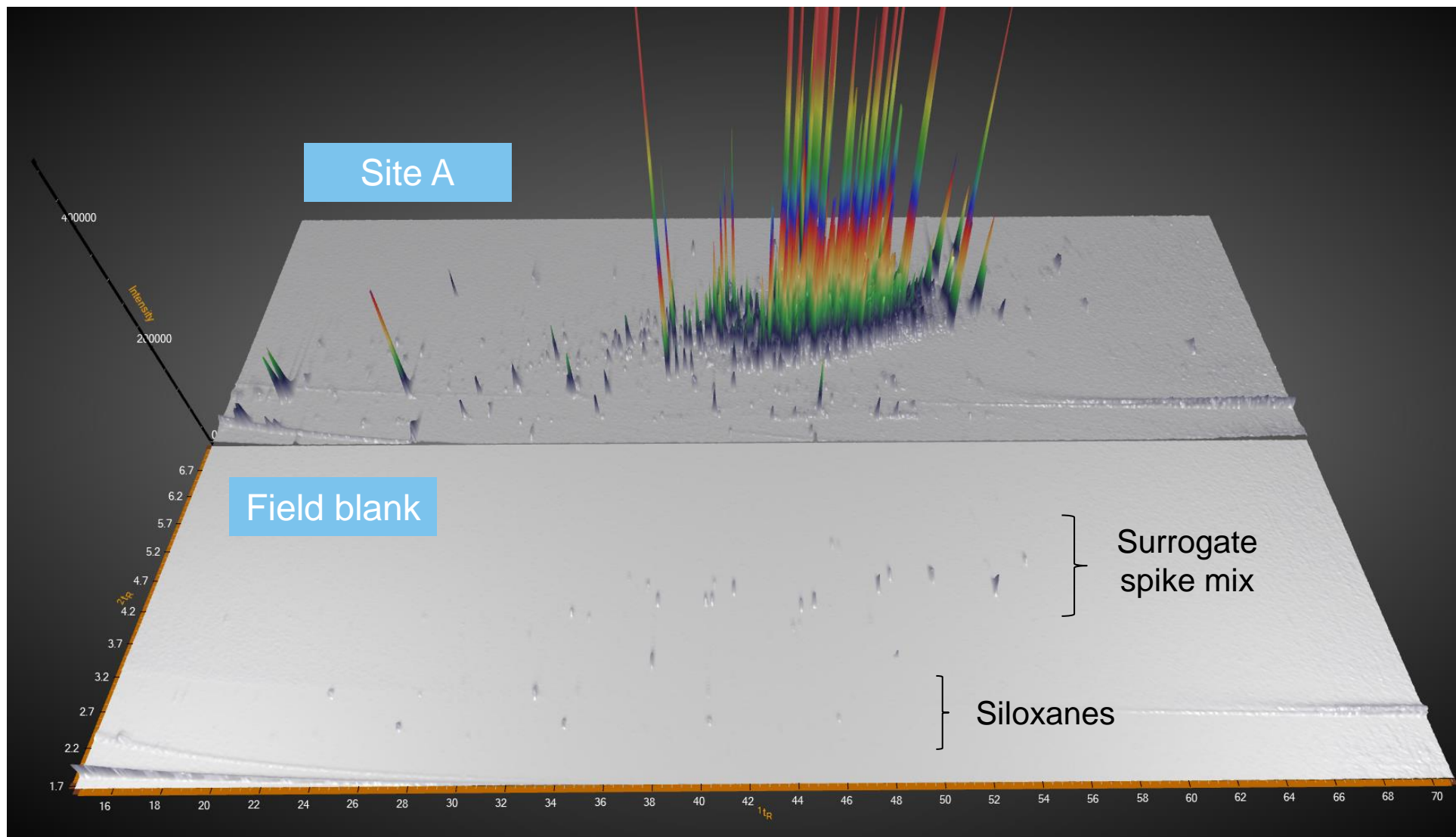
- May pick up temporal contaminant releases overcoming a limitation of grab sampling
- Designed to concentrate hydrophobic chemicals (with  $\log K_{ow} > 4$ ), more sensitive to heavier VOC's and SVOC's
- Extraction for 4 weeks, stored at -18 C under argon, desorbed with hexane cleaned by SEC and reconstituted to 1 mL

# Experimental

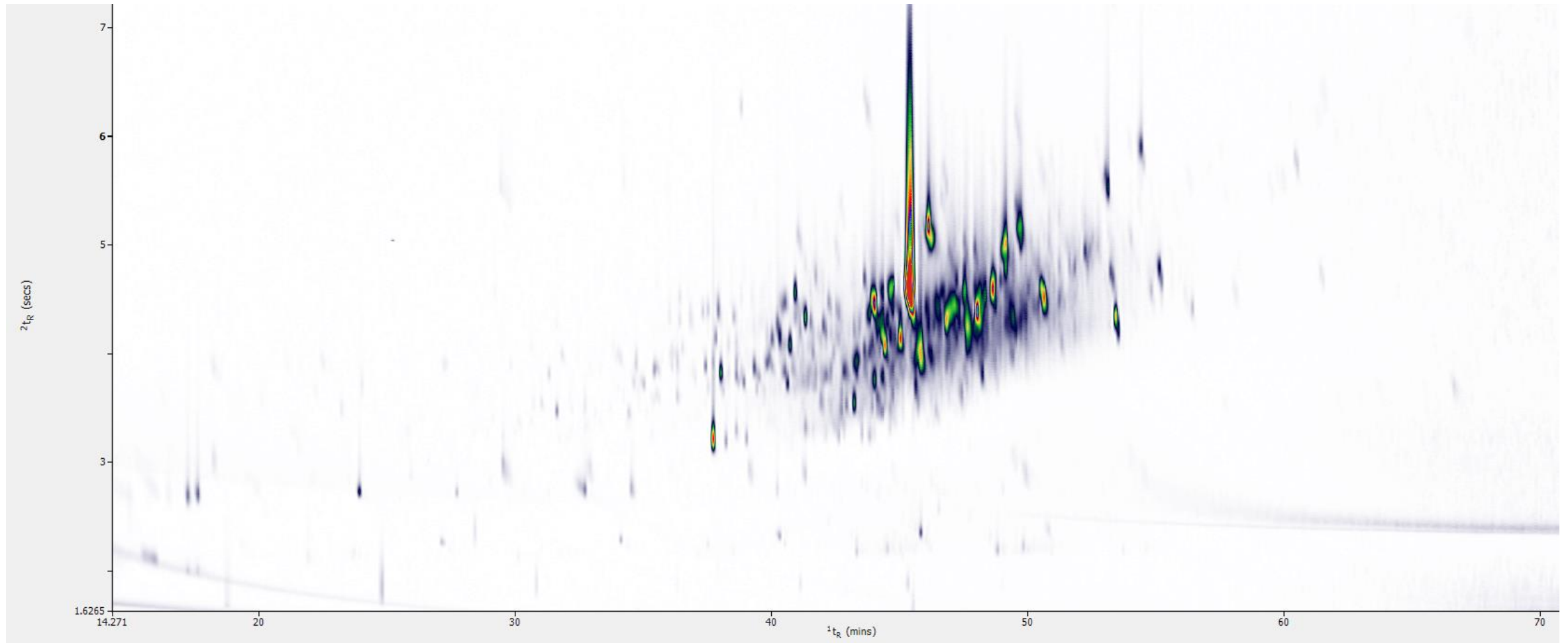
- **Samples:** Passive sampling extracts from 2 sampling locations in a UK river
- **GC×GC:** INSIGHT-Thermal modulator; Modulation period ( $P_M$ ): 6.0 s.
- **MS:** Instrument: BenchTOF2™; Mass range: m/z 30–600; Acquisition rate: 100 Hz in Tandem Ionisation® mode at 70 eV and 14 eV.
- **Software:** Full instrument control and data processing by ChromSpace®



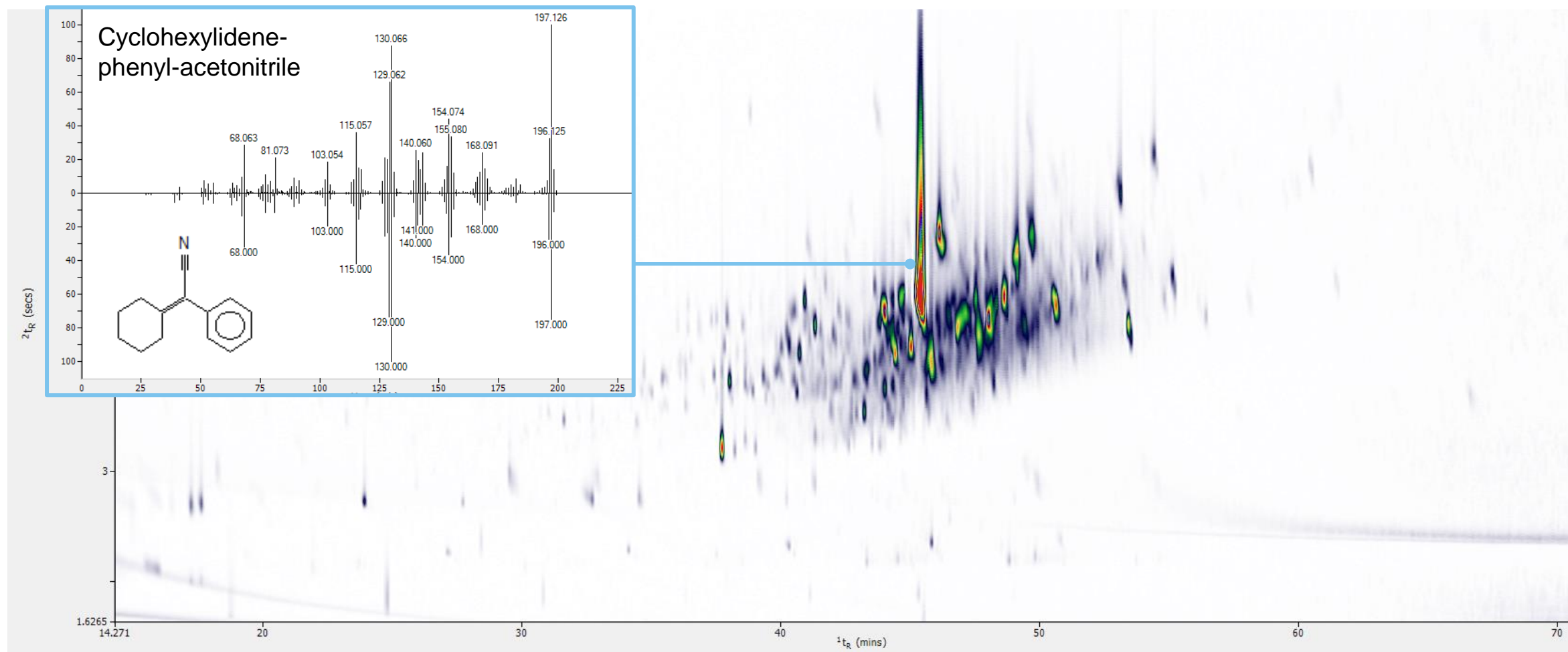
# Passive sampling of a UK river with GC×GC–TOF MS



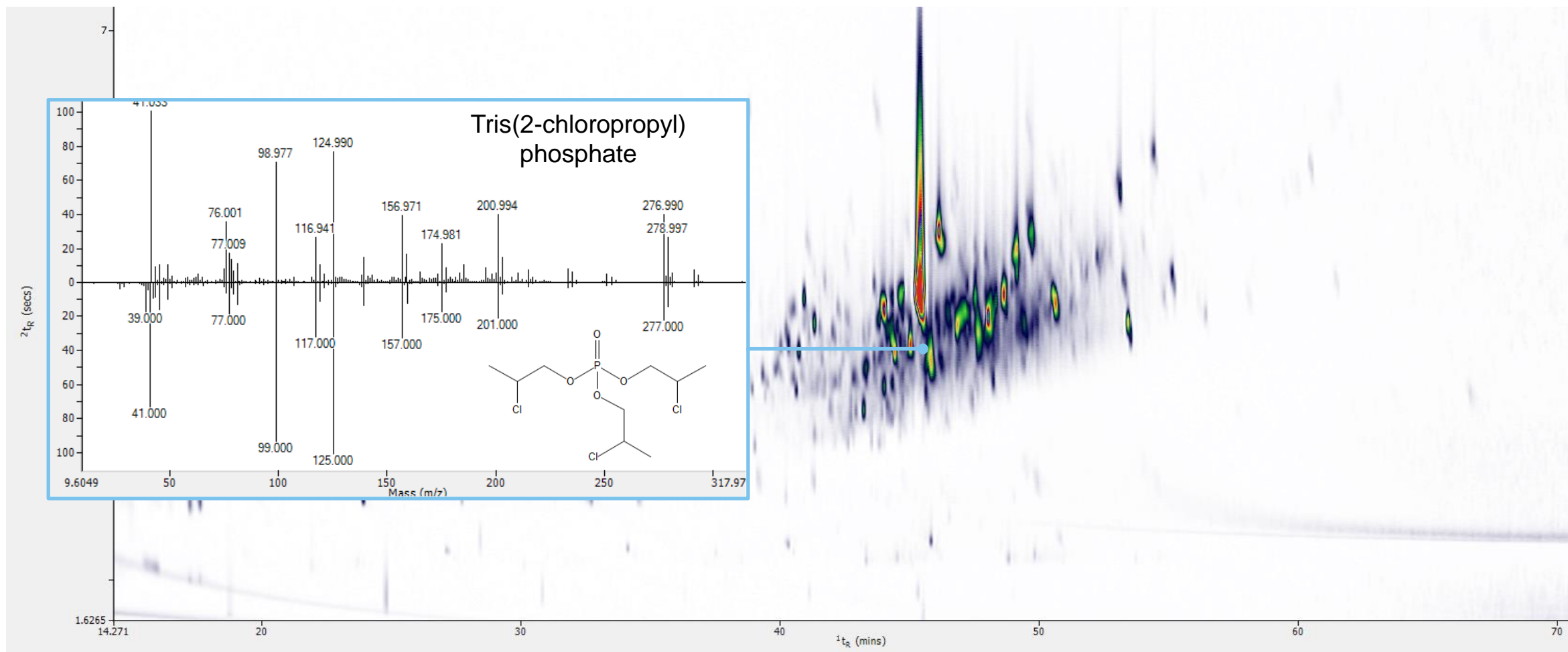
# Passive sampling of a UK river with GC×GC–TOF MS



# Screening for emerging contaminants

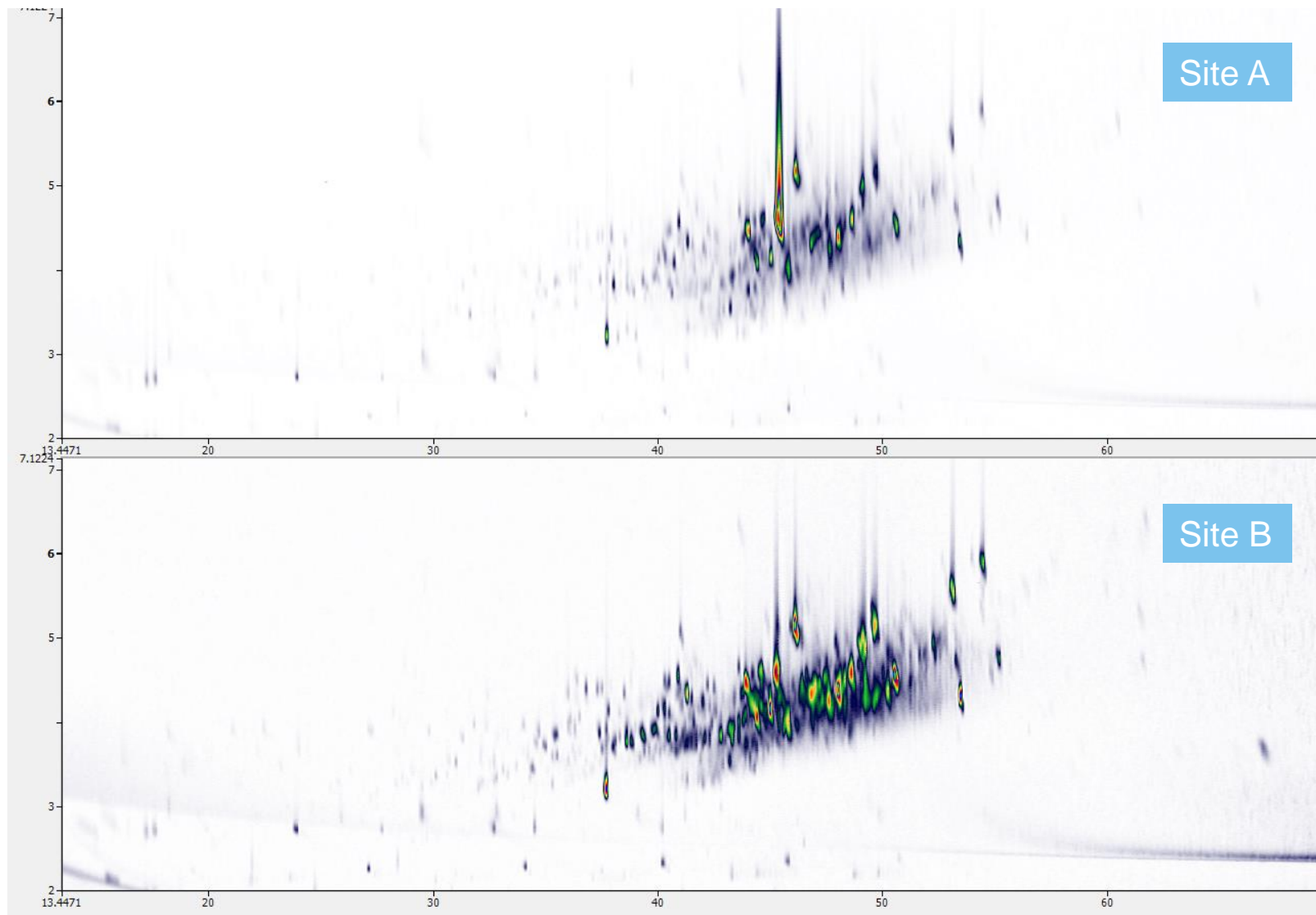


# Screening for emerging contaminants

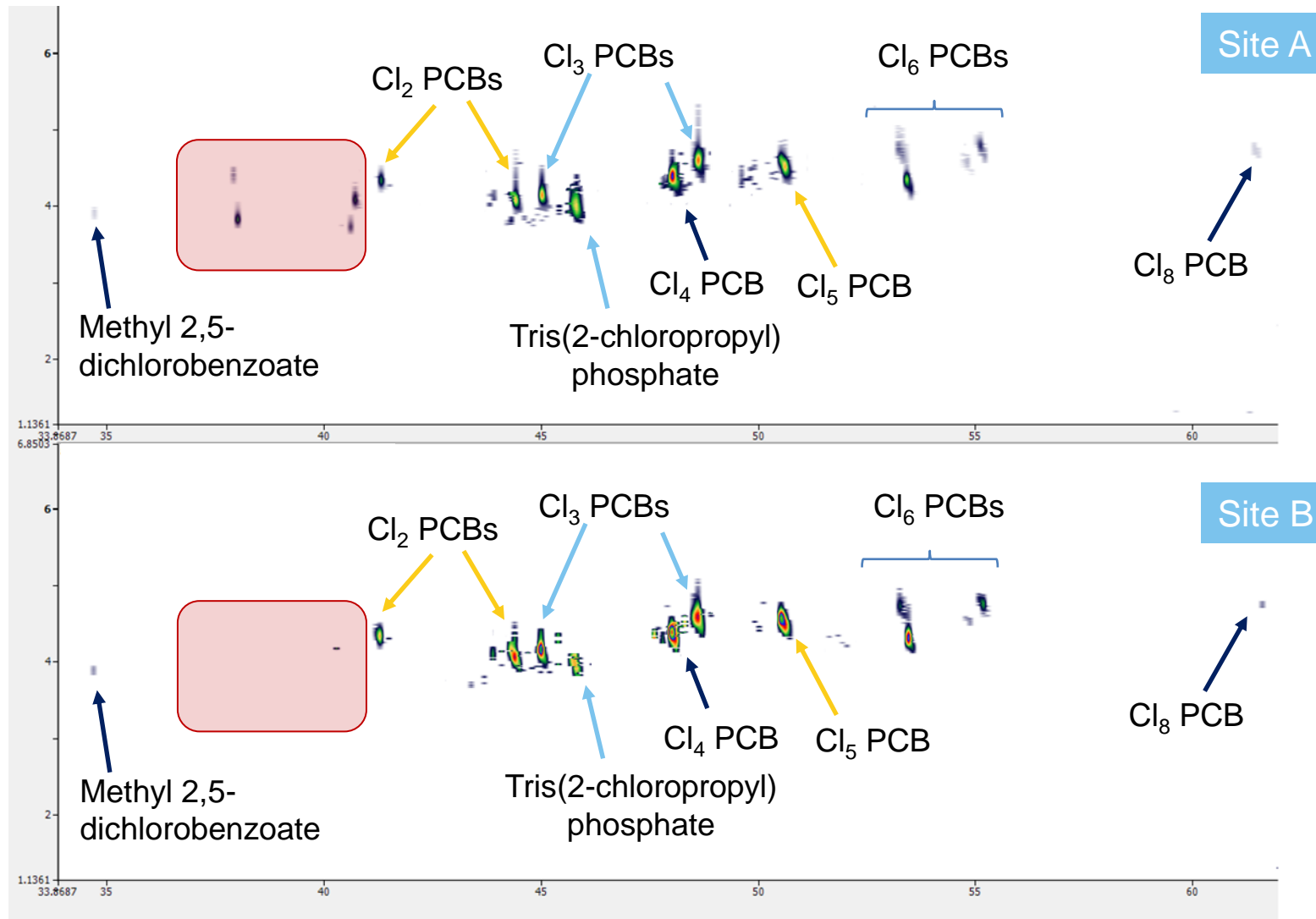




# Comparison of sampling sites



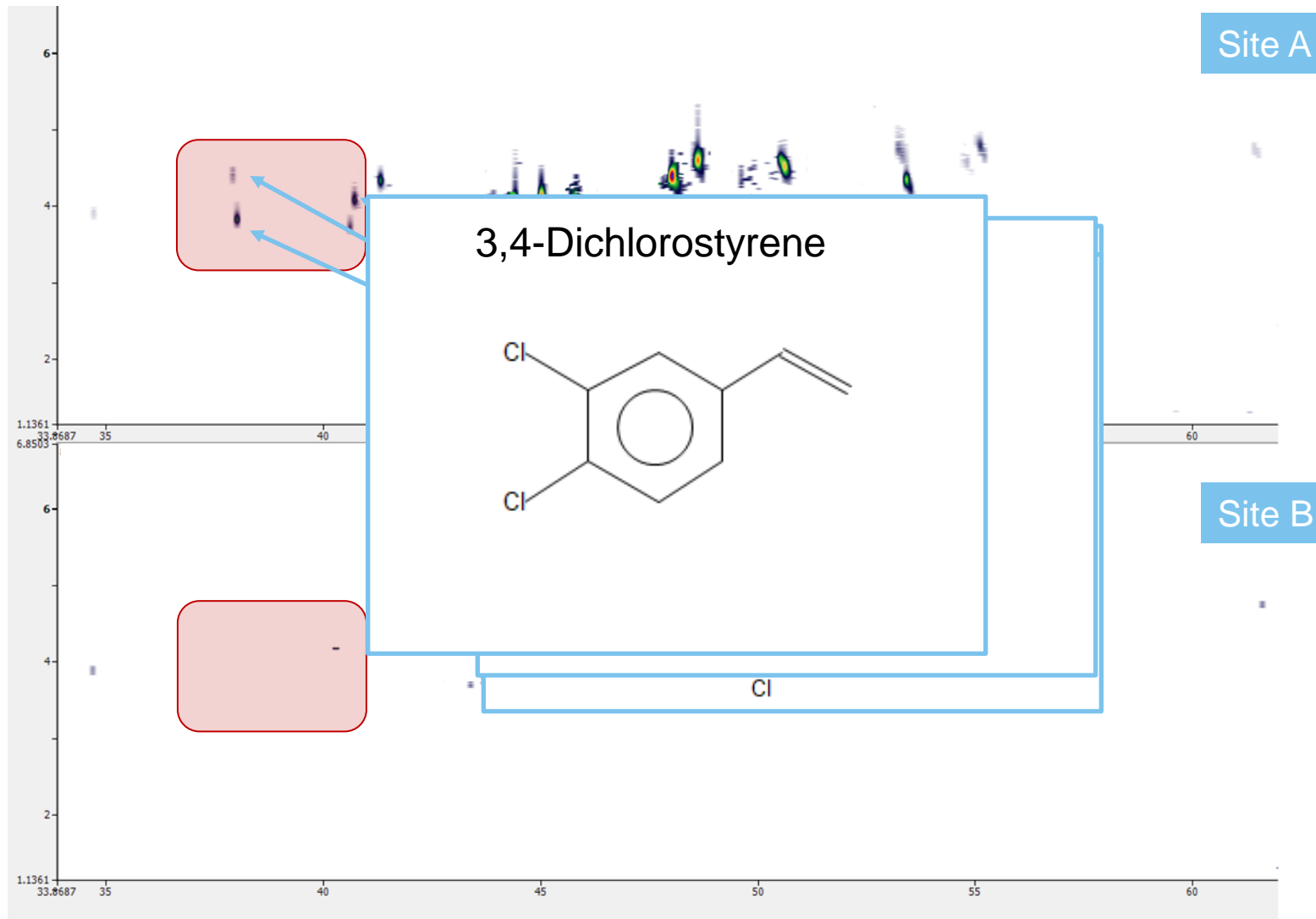
# Comparison of sampling sites



Filtered  
for  
organochlorines



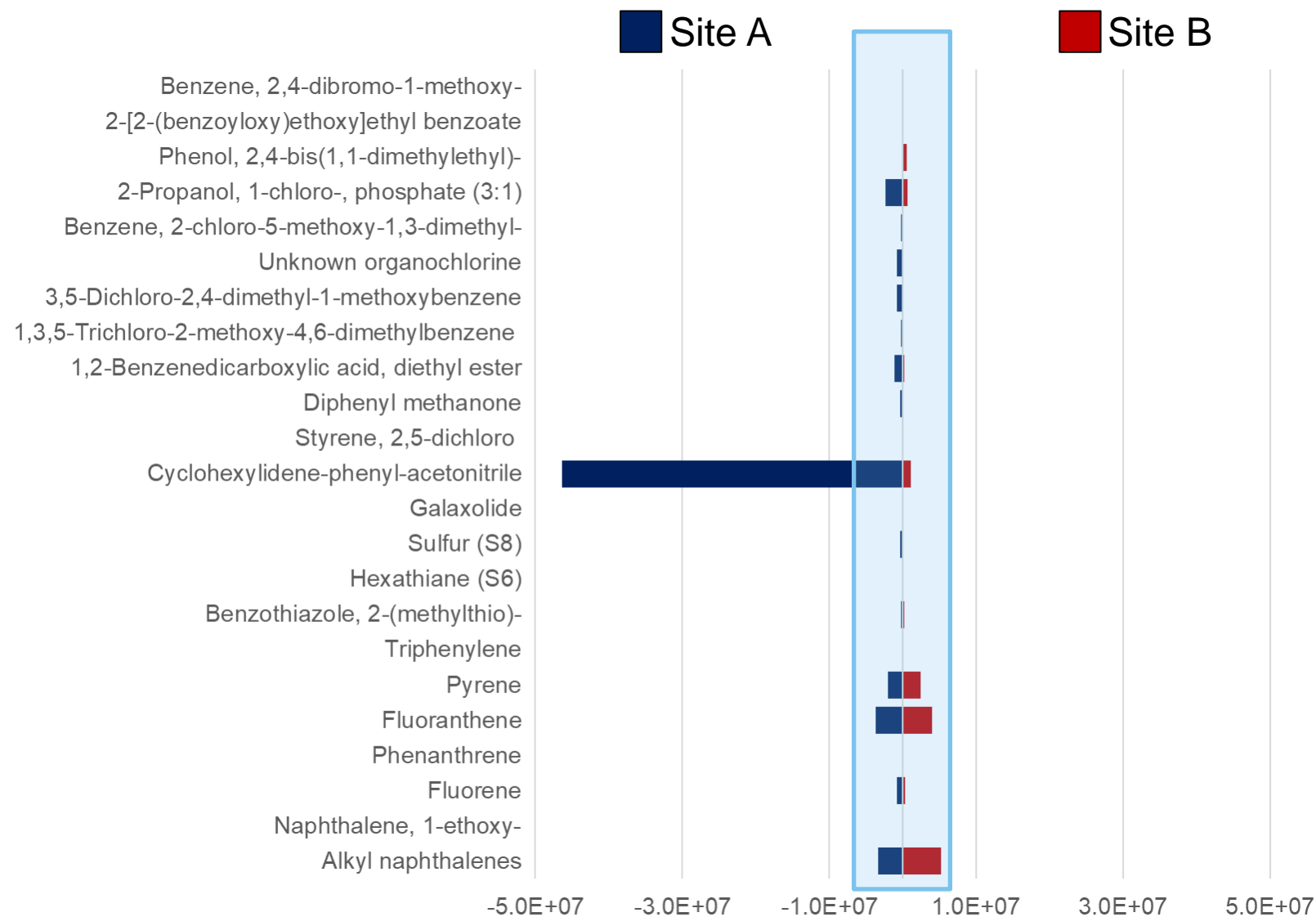
# Comparison of sampling sites



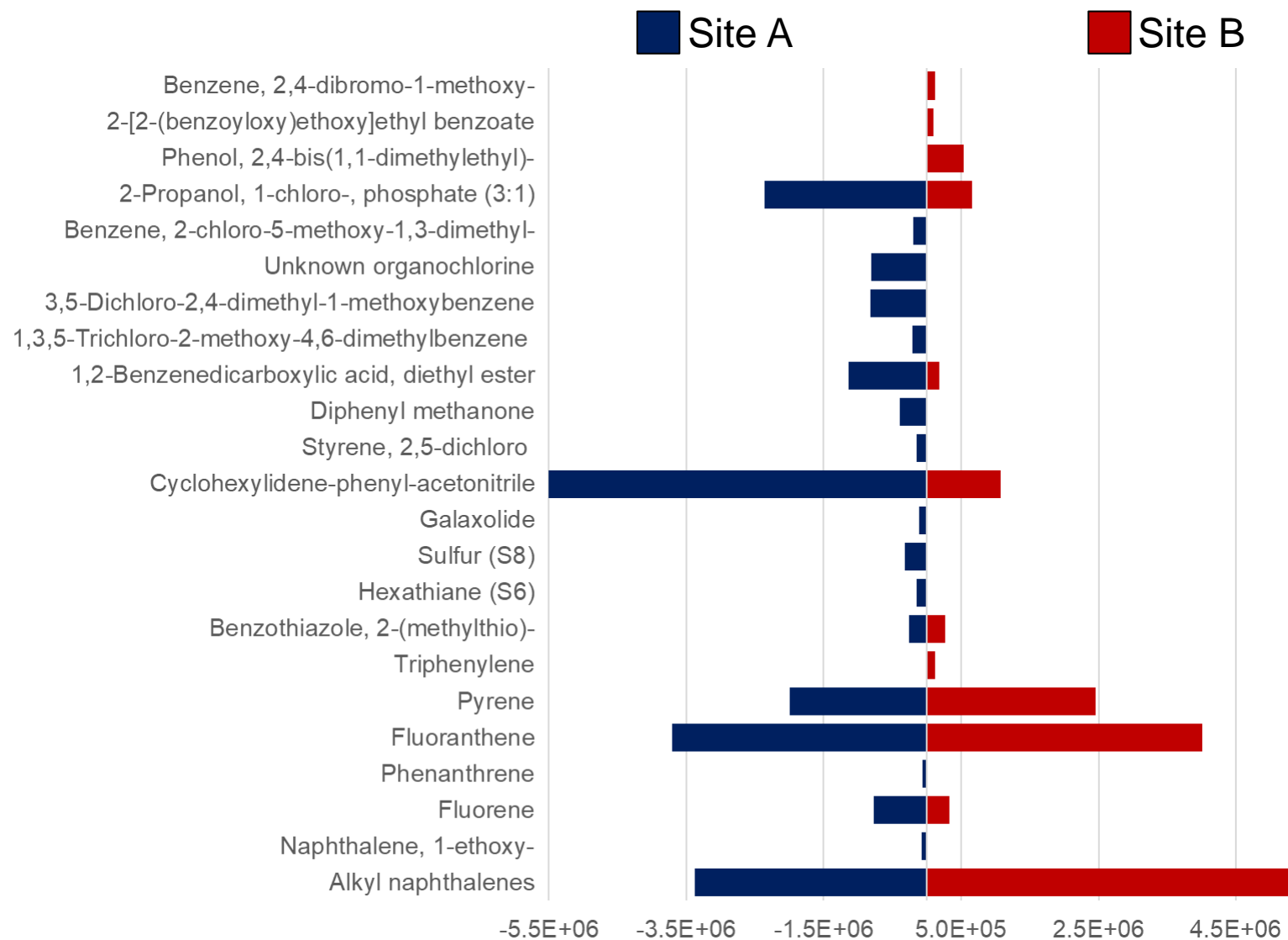
Filtered  
for  
organochlorines



# Comparison of sampling sites



# Comparison of sampling sites



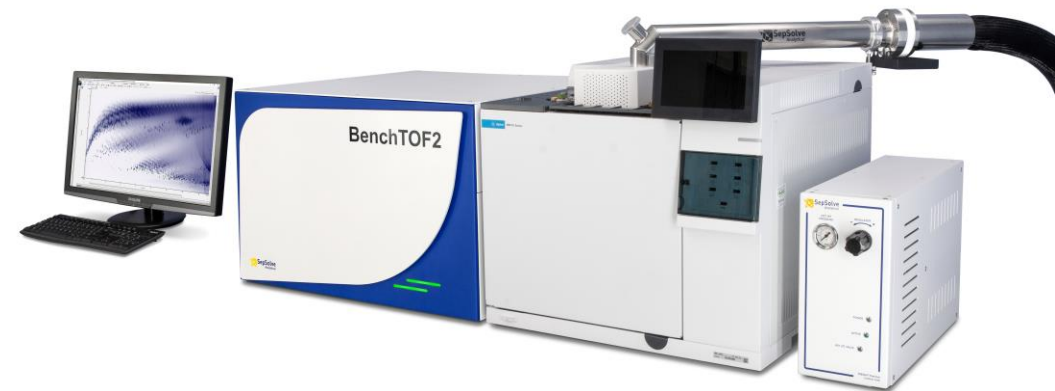
# Future work

- 11 sampling sites in total
- Field blanks performed at each site
- Apply new processing workflows to compare the sites



# Summary

- Passive sampling coupled with GC×GC–TOF MS
  - Minimises the risk of missing pollution events
  - Gives greater insight into river quality
- The new INSIGHT-Thermal modulator provides improvements in productivity and performance for thermally modulated GC×GC
  - Ramped cold jet flow rates for efficient modulation of high boilers.
  - Easy to configure column holder for simple set-up and repeatable results
  - Retrofittable to all popular GCs
- Further work on-going to compare multiple sampling sites along a UK river using GC×GC–TOF MS



# Thanks for listening! Any questions?

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LinkedIn: [www.linkedin.com/company/sepsolve-analytical](http://www.linkedin.com/company/sepsolve-analytical)