

# The First Global Reconnaissance of Organic Pollutants in Tap Water

John Wilkinson<sup>1</sup>, Brett Sallach<sup>1</sup>, Neville Llewellyn<sup>2</sup>, Ramón González-Méndez<sup>3</sup>, Olaf Scheibner<sup>4</sup>, Martin Jech<sup>5</sup>, Christina Jacob<sup>6</sup>, Jeff Stubbs<sup>2</sup>; <sup>1</sup> University of York, Environment and Geography Department, York, UK; <sup>2</sup>Thermo Fisher Scientific, London, UK; <sup>3</sup>Coventry University, UK; <sup>4</sup>Thermo Fisher Scientific, Dreieich, Germany; <sup>5</sup>Thermo Fisher Scientific, Prague, Czech Republic; <sup>6</sup> Thermo Fisher Scientific, San Jose, CA, USA.

## ABSTRACT

**Purpose:** To demonstrate the feasibility of using a Thermo Scientific™ EQuan MAX Plus™ LC-MS system coupled to a Thermo Scientific™ Q Exactive™ Focus Hybrid Quadrupole-Orbitrap™ Mass Spectrometer to conduct non-targeted surveillance of a selection of global drinking water supplies and selected river systems.

**Methods:** EQuan on-line SPE High Resolution Accurate Mass using Full Scan and data dependent MS2, with Thermo Scientific™ TraceFinder™ software and Thermo Scientific™ Compound Discoverer™ software.

**Results:** The use of HRAM technology combined with on-line SPE and Compound Discoverer software has been demonstrated to be a powerful tool for the investigation of the occurrence of non-target unknown compounds in Global drinking water and selected rivers. The overview of Global Detection rates appears to show that contaminant, including illicit drugs, occurrence in drinking water is more prevalent in affluent First World locations. DEET occurrence was widespread with a strong presence in sub-Saharan Africa.

## INTRODUCTION

Considerable knowledge gaps exist regarding the occurrence of micro-organic pollutants in aquatic environments and drinking water resources; this is particularly the case in low to middle-income countries and those outside of North America and Western Europe.

It is of concern that, of the 196 countries recognised by the United Nations, data for the occurrence of micro-organics, including pharmaceuticals, is only available for 71.

Building on a previous targeted monitoring campaign, here we present an insight into the non-targeted (unknown-unknown) surveillance monitoring of world-wide sampling locations across 69 sites across 51 countries, which represent the full spectrum of socio-economic indicators. Analysis was achieved using an EQuan large-volume on-line SPE sampler coupled to a Q Exactive Focus Orbitrap, with data analysis performed using Compound Discoverer utilising the Thermo Scientific™ mzCloud™ mass spectral library.

The aim of this work is to assess the feasibility and performance of using a 1 mL sample on-line solid phase extraction and a Q Exactive Focus Orbitrap MS, for the identification of micro-organic contaminants and environmental levels.

**Sample Collection:** During the course of 2019, tap water samples were collected from 69 cities in 51 countries located across 6 continents (Figure 1). All samples were collected in duplicate, filtered in the field with a 0.45 µm pore size glass microfibre syringe filter and frozen at -20°C until analysis. Procedural blanks were collected using LCMS-grade water in approximately 20% of sampling locations.

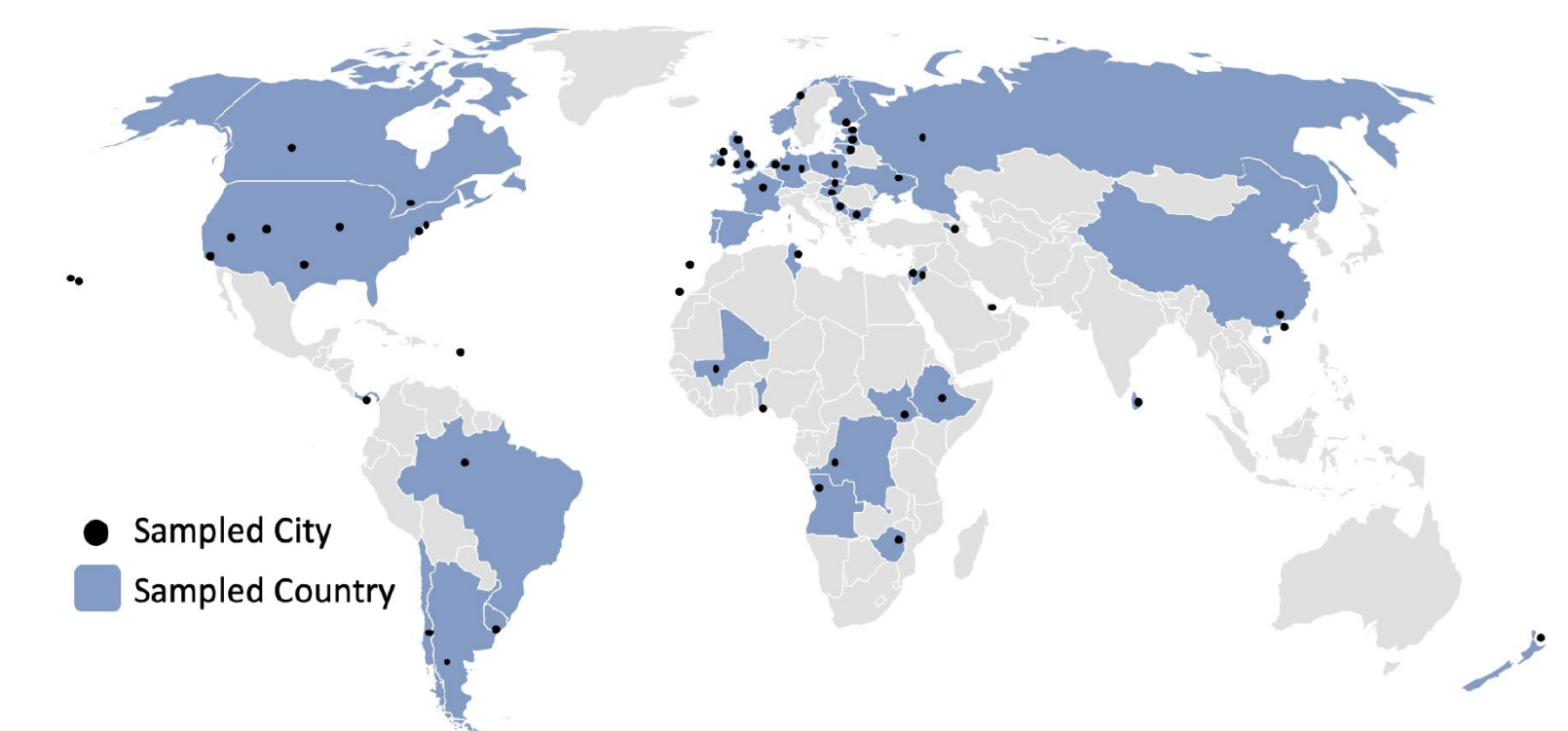


Figure 1. Sampling locations where tap water was collected for analysis

## MATERIALS AND METHODS

**Liquid Chromatography:** Separations were carried out on EQuan MAX Plus Thermo Scientific™ Vanquish™ UHPLC system using a Thermo Scientific™ TriPlus™ RSH autosampler. A 1 mL sample was loaded onto a Thermo Scientific™ Accucore™ aQ C18 12 µm 5x2.1 mm trap column. Backflush and separation used a binary gradient of A - 5mM Ammonium Formate & 0.1% Formic Acid, and B - MeOH 5mM Ammonium Formate & 0.1% Formic Acid through an Accucore™ aQ C18 100x2.1, 2.6 µm at 25°C with a flow rate of 300 µL/min; with a linear gradient from 100% A to 100% B over 20 minutes.

**Mass Spectrometry:** The MS analysis was performed on a Thermo Scientific Q Exactive Focus bench-top high resolution mass spectrometer using heated electrospray ionization (HESI). Acquisition was performed using Full Scan Data Dependent MS2 (ddMS2) where data were collected at a resolving power of 70,000 and 17,500 (FWHM) respectively; separately in Positive and Negative polarities. The acquisition was run in Discovery mode using an Exclusion list generated from a system blank. Previous work with this instrument method has shown it to deliver validated quantitation data for a broad range of pharmaceuticals, pesticides and industrial chemicals, to low ng/L concentrations.

## Data Acquisition and semi-quantitation

The Global set of Drinking and River Water samples were acquired using TraceFinder Software and the raw data files fed into Compound Discoverer 3.1 for subsequent Unknown Identification; which as well as delivering identification also gives peak areas equivalent to those generated by TraceFinder 5.1

## Unknown Identification using Compound Discoverer 3.1

The raw data were processed using Compound Discoverer 3.1 (CD) using an Unknown Identification workflow template, Figure 2.0 Workflow Nodes: 'Predict Compositions', mzCloud™, mzVault™ (containing Norman Network MassBank library), ChemSpider and Mass Lists databases were used to identify unknown peaks. Initial unfiltered results were approximately 52000 hits, which were reduced to less than 500 via a simple CD filtering protocol, then further reduced by manual review.

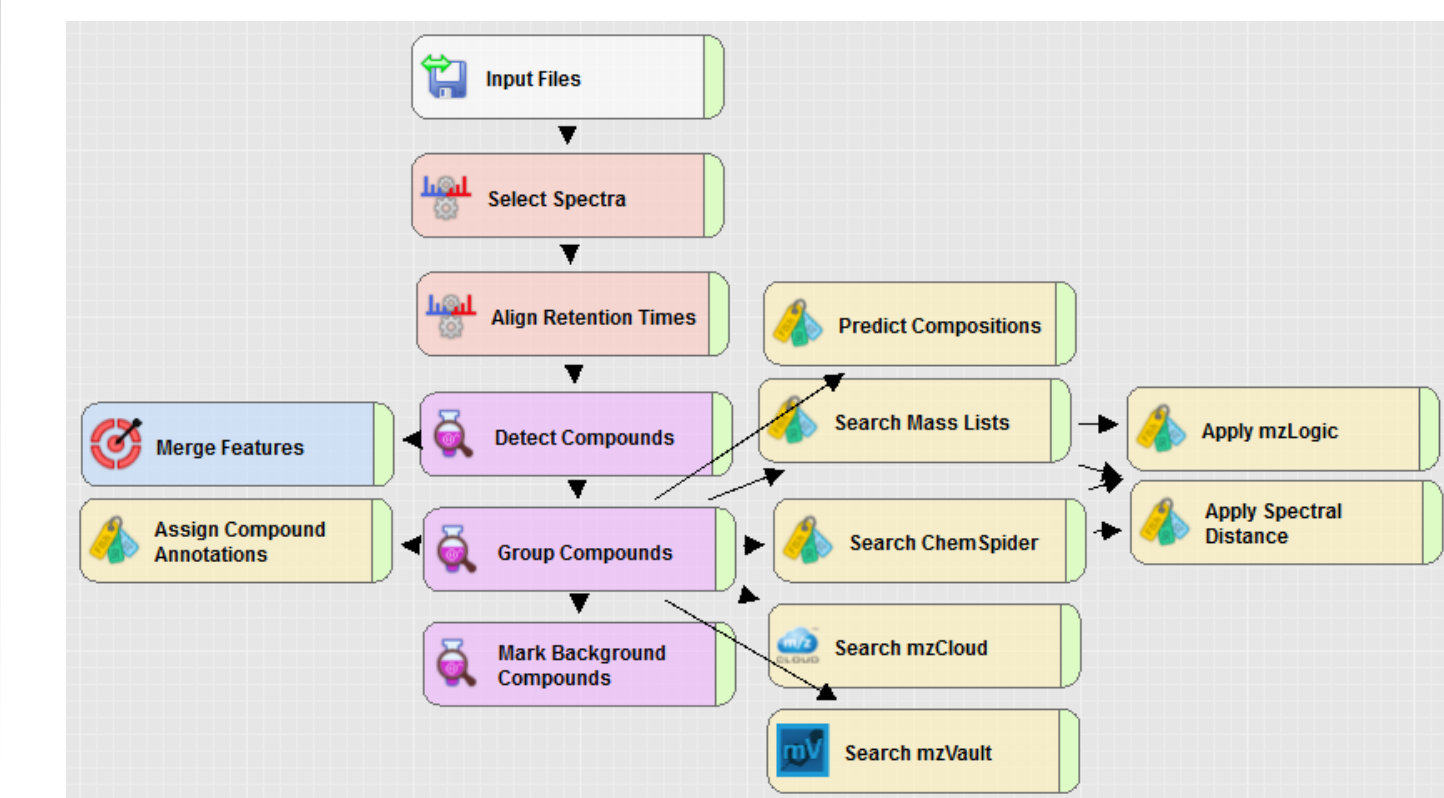


Figure 2. Compound Discoverer 3.1 using an Unknown Identification workflow

## RESULTS

Before any interpretation of the results should be considered, it is worth recalling that these data were obtained via grab sampling methodology and therefore represent a snapshot in time at every location.

At least one contaminant was identified in tap water from 58 of 69 sampled cities. A maximum of 15 were identified (New Zealand) while the median number of contaminants identified was 2 (75<sup>th</sup> percentile of 4 detects), Figure 3. From the peak areas (Table 1), for many of the pesticide and medicinal compounds, the concentration can be estimated and is highly likely to be below action levels for drinking water treatment supply.

Table 1. Top 20 Compounds Detected (by peak area)

Checked	Name	Formula	Annotation Sc	Molecular Weight	RT [min]	Area (Max)
✓	DEET Drug	C12 H17 N O	■■■■	191.13129	11.539	1215155166
✓	Tributyl phosphate Industrial applications as an ext	C12 H27 O4 P	■■■■	266.16515	15.451	5015077615
✓	Bis(4-ethylbenzylidene)sorbitol Industrial	C24 H30 O6	■■■■	414.20427	14.104	2075471473
✓	Benzoylecgonine DOA Cocaine metabolite	C18 H19 N O4	■■■■	289.13164	6.503	1722054937
✓	Caffeine Drug Stimulant	C8 H10 N4 O2	■■■■	194.08060	6.206	7924731668
✓	Bis(2-ethylhexyl) phthalate Industrial	C24 H38 O4	■■■■	390.27690	19.102	5114520381
✓	Paracetamol Drug	C8 H9 N O2	■■■■	151.06352	3.849	4740856804
✓	4-Acetamidopyridine Drug metabolite	C13 H15 N3 O2	■■■■	245.11671	5.304	4726202557
✓	Theobromine Food additive found in chocolate, as	C7 H8 N4 O2	■■■■	180.06495	4.242	2994418801
✓	Ephedrine Drug for low blood pressure	C10 H15 N O	■■■■	165.11554	4.298	1490025895
✓	Acebutolol Blood pressure drug	C18 H28 N2 O4	■■■■	336.20487	7.398	1415287632
✓	Paraxanthine Drug like caffeine	C7 H8 N4 O2	■■■■	180.06491	4.971	1357719296
✓	Bis(2-ethylhexyl) phthalate Industrial	C24 H38 O4	■■■■	390.27701	19.024	1257035955
✓	Bis(4-ethylbenzylidene)sorbitol Industrial	C24 H30 O6	■■■■	414.20435	14.945	1208701622
✓	Gabapentin Drug anticonvulsant	C9 H17 N O2	■■■■	171.12603	7.155	1180129697
✓	Bis(4-ethylbenzylidene)sorbitol Industrial	C24 H30 O6	■■■■	414.20438	15.136	1179651734
✓	Testosterone Steroid Hormone	C19 H28 O2	■■■■	288.20936	14.814	1036045510
✓	Methylenedione Drug anabolic-androgenic steroid	C10 H28 O2	■■■■	286.19363	13.933	995377147
✓	Sulfamethoxazole Antibiotic	C10 H11 N3 O3 S	■■■■	253.05229	6.330	968561089
✓	Trimethoprim Antibiotic used mainly in the treatme	C14 H18 N4 O3	■■■■	290.13799	5.674	965345035

Pharmaceuticals accounted for 78% of what was identified in tap water (Table 1) with 142 out of 180 total detections. Perfluoroalkyl substances were the least frequently detected class with only Frankfurt (Germany), Auckland (New Zealand) and Santiago (Chile) the only locations where PFASs were identified. Interestingly, all three of these samples were detected at the cities' airport tap water.

Table 2. Summary of pollutants detected in the tap water of each monitored city

	Pesticide	Drug	DOA	Anabolic Steroids	PFAS	Total
<b>North America</b>						
Canada_Calgary		1				1
Canada_Toronto	2					3
USA_CO, Denver	2		1			3
USA_CO, Colorado Springs	1					1
USA_Hawaii, Kauai	1					1
USA_Los Angeles, CA						1
USA_MO, St Louis	3	2				2
USA_NY, New York	2	2				2
USA_Reno, NV	1	1				1
USA_Philadelphia	1	3				4
Antigua_St Johns						
<b>South America</b>						
Chile_Santiago		1		1		2
Argentina_Bariolche	1	1				1
Brazil_Manaus	1	2				3
Ecuador_Guayaquil	3	1				4
Uruguay_Montevideo	2	2				2
Antigua_St Johns	4	3				7
<b>Australasia</b>						
New Zealand	2	9	2	1	1	15
Cook Islands_Rarotonga						
<b>Africa</b>						
Angola_Luanda		2				2
Angola_Bottled Water		7		1		8
Benin_Cotonou						
Congo_DRC_Kinshasa		3				3
Ethiopia_Addis Ababa	1	4		1		6
Kenya_Nairobi	1	5	1			6
Mali_Bamako	2	1				3
South Sudan_Juba	2	1				4
Tunisia_Tunis	3	1				4
<b>Asia</b>						
Armenia_Yerevan		4		1		5
India_Hyderabad	1	2				1
Sri Lanka_Private Well		1				1
Sri Lanka_Public Well		2				2
<b>Middle East</b>						
Jordan_Amman		1		1		2
Palestine		2				2
Qatar_Doha		1				1
<b>Far East</b>						
China_Kaiping		4				3
China_Panyu		5	1			6
Hong Kong_Kai Tak		11	2			13
<b>Europe</b>						
Belgium_Antwerp		1	4			5
Belgium_Brussels		2	8	1		11
Bulgaria_Sofia		1				1
England_London		1				1
England_York						
England_Coventry		1	3			4
Wales_River Dee		4	2	1		3
Scotland_Glenceo		1				1
Spain_Lanzarote		1				1
Northern Ireland_Belfast						
Estonia_Tallinn						
Finland_Helsinki				1		1
France_Paris				2		2
France, St Martin Island						
Germany_Berlin		1	1			2
Germany-Frankfurt				1		1
Hungary_Budapest		2				1
Ireland_Dublin		1				1
Israel_Tel Aviv						
Latvia_Riga				6		6
Lithuania_Vilnius	1			2		2
Luxembourg_Lux City				1		1
Netherlands_Utrecht				3		3
Norway_Sandnessjoen				2		2
Poland_Warsaw						
Romaia_Bucharest				3		3
Russia_Moscow				2		2
Serbia_Belgrade	1			1		1
Slovakia_Bratislava				3		3
Ukraine_Karkiv	3			1		4
<b>Total</b>	<b>37</b>	<b>141</b>	<b>9</b>	<b>7</b>	<b>3</b>	<b>180</b>

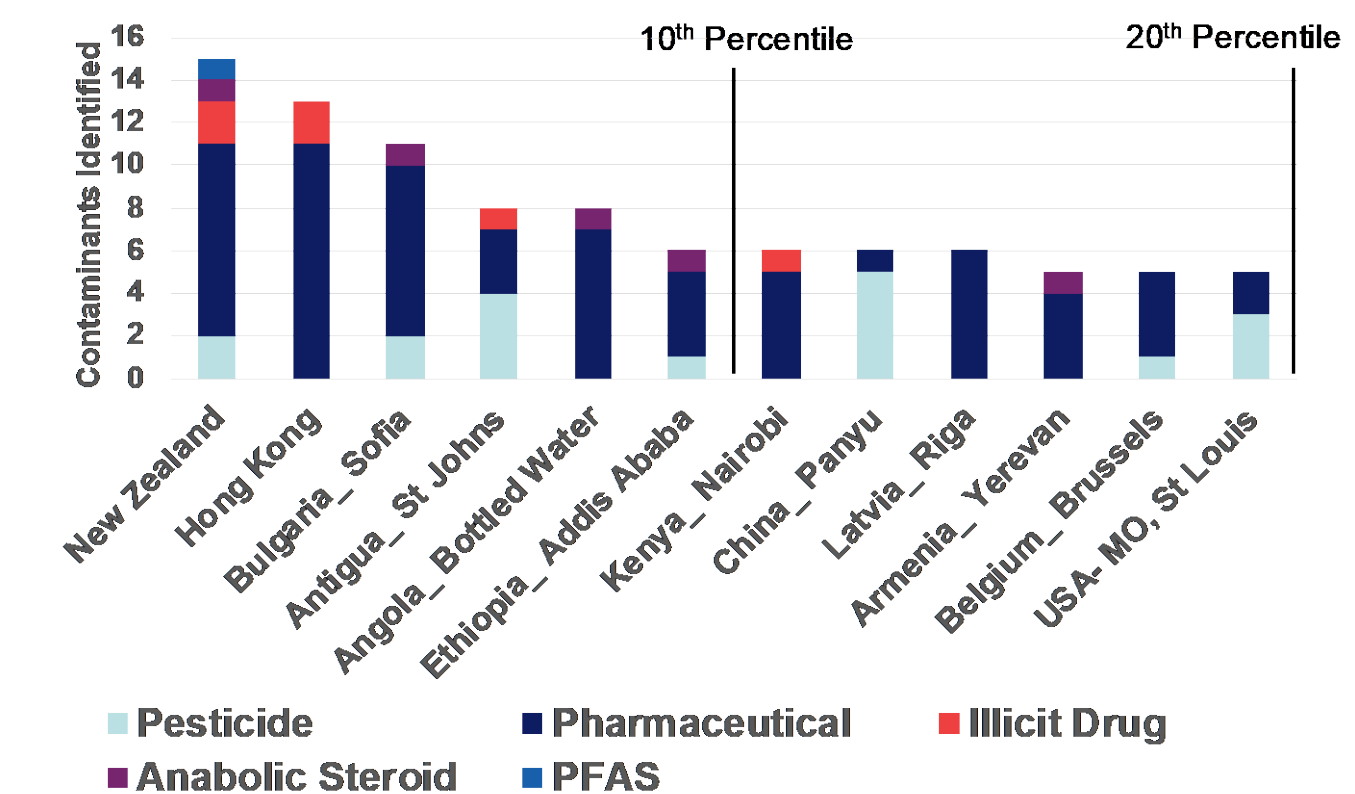
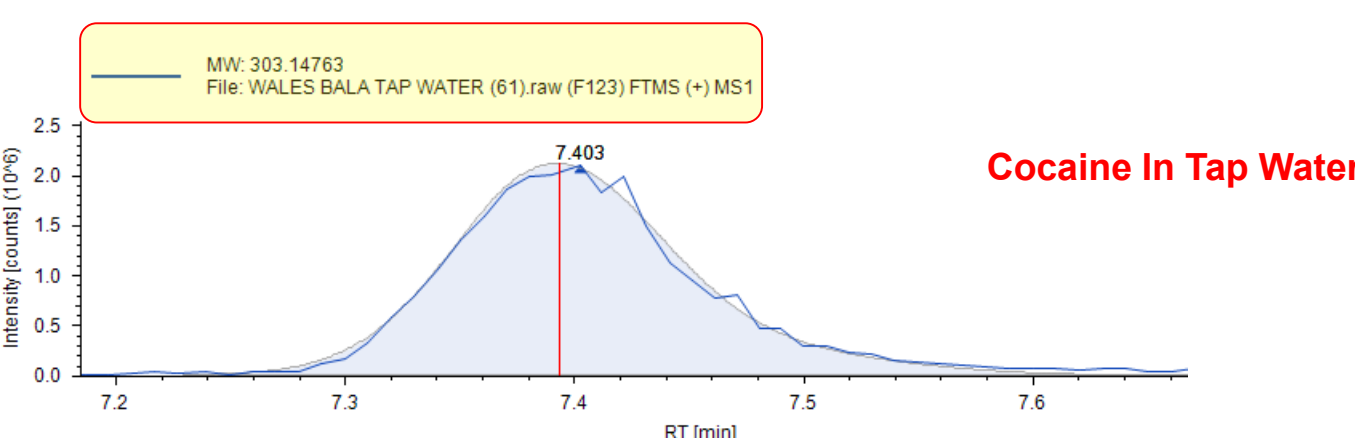
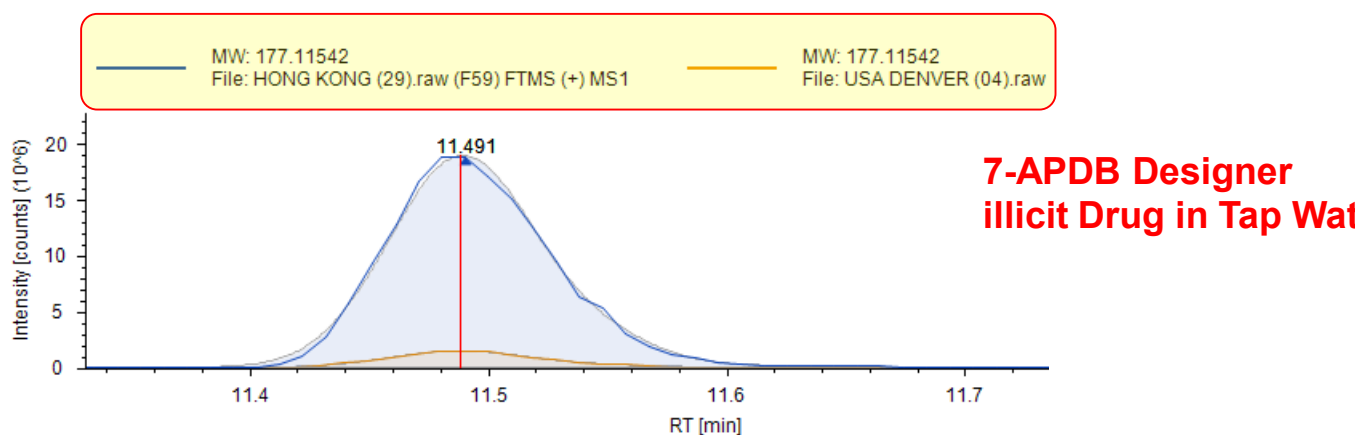


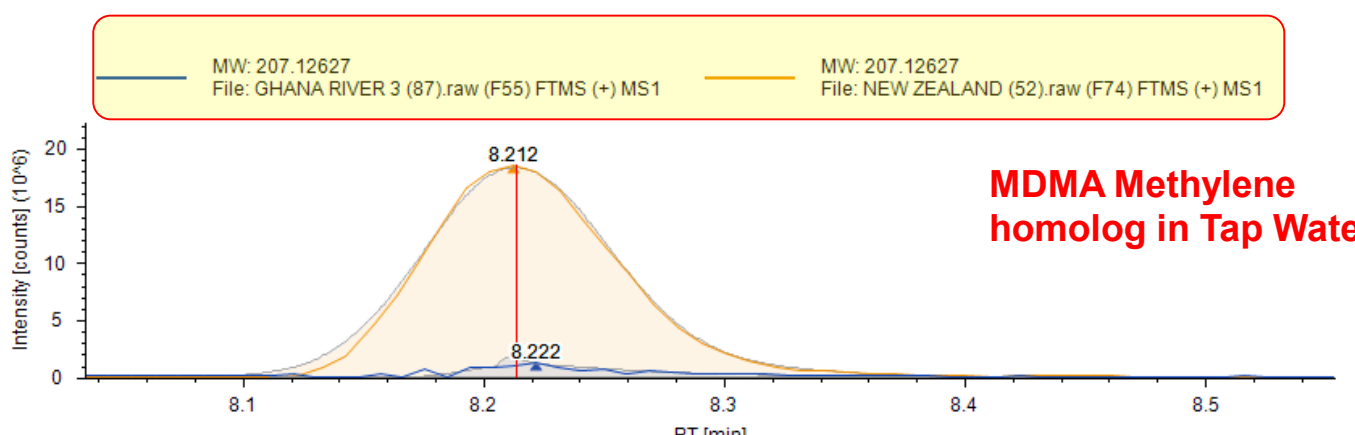
Figure 3. Top 20<sup>th</sup> percentile of sampled cities for the occurrence of various classes of organic contaminants



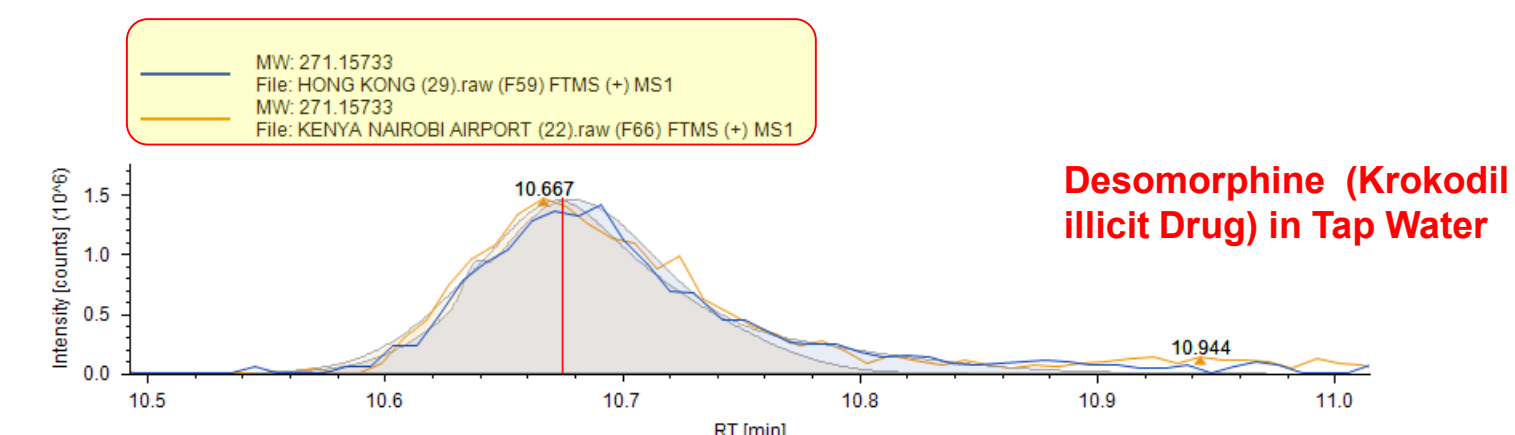
(a) Cocaine was detected in the tap water collected in the city of Bala, Wales, UK (21 June 2019)



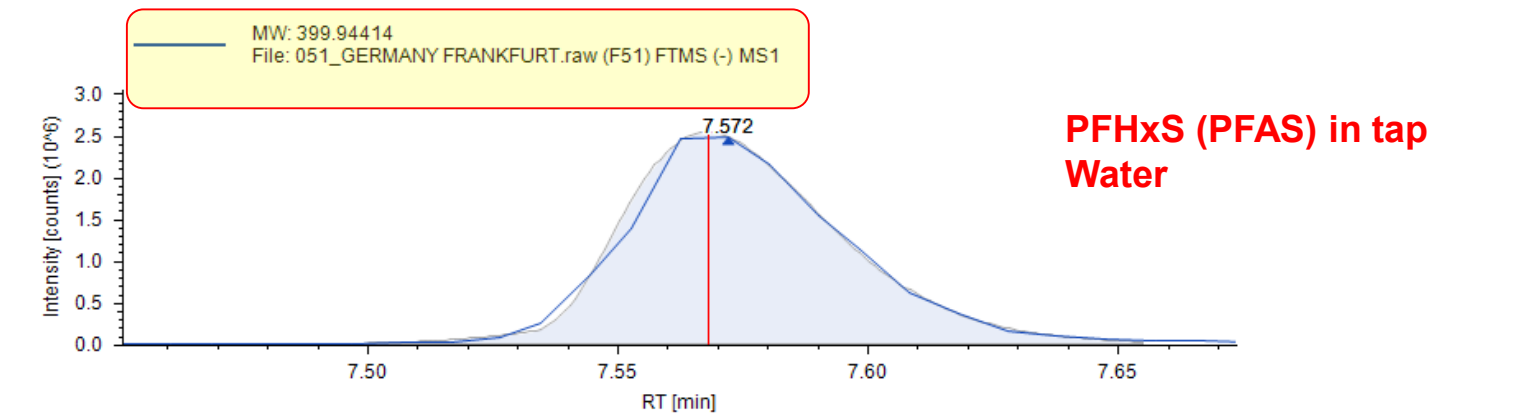
(b) 7-APDB is a stimulant of the amphetamine class which is an analogue of 3,4-Methylenedioxyamphetamine (MDA). The illicit substance was detected in the tap water of Hong Kong (Kowloon, 11 Nov. 2019) and central Denver (August 2019)



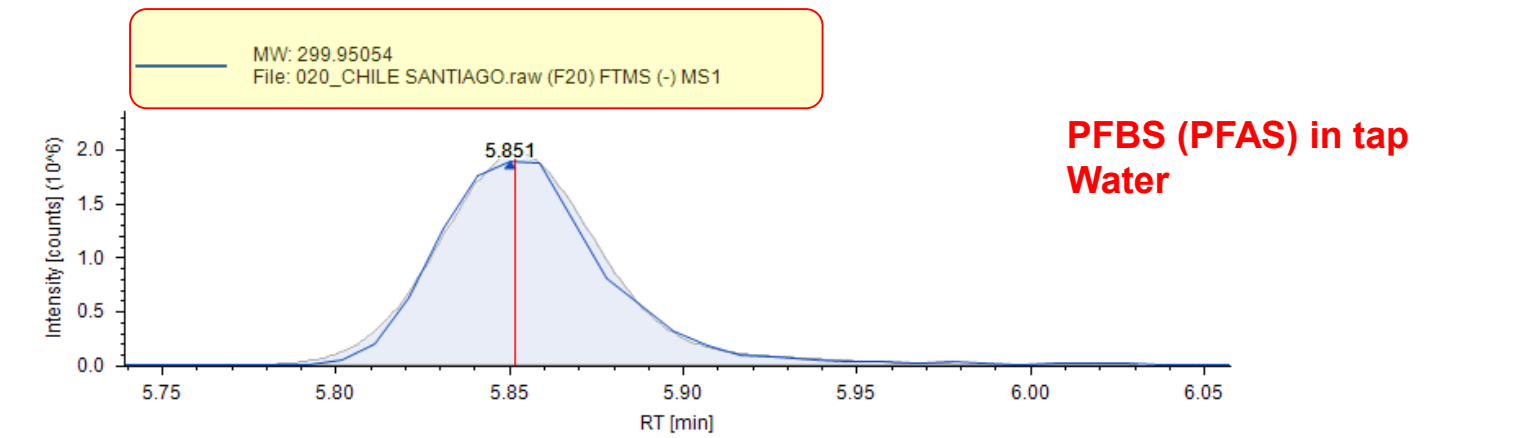
(c) A methylene homologue of 3,4-Methylenedioxymethamphetamine (a.k.a., MDMA, ecstasy or molly) was detected in the tap water of Auckland Airport (16 Nov. 2018)



(d) Originally a semi-synthetic opioid medication, desomorphine (aka., krokodil) is now considered a Schedule 1 substance by the United States Drug Enforcement Agency. The substance was detected in tap water from Hong Kong (Kowloon, 11 Nov. 2019) and at the Nairobi International airport (12 Sept. 2019)



(e) Perfluorohexane sulfonate (PFHxS) was detected in tap water collected at Frankfurt International Airport (22 July 2018)



(f) Perfluoro-1-butanefulfonic acid (PFBS) was detected in tap water collected at Santiago International Airport (30 December 2019)

Figure 4 (a-f). Examples of contaminants detected at specific locations

The relatively high detection rate of pharmaceuticals, pesticides and illicit drugs in developed high-income counties (Bulgaria, Hong Kong and New Zealand) is noteworthy and may represent the flux of chemicals present within their relatively affluent societies and to a lesser extent, drinking water treatment technology.

## DISCUSSION/CONCLUSIONS

The use of HRAM technology combined with on-line SPE and Compound Discoverer software has been demonstrated to be a powerful tool for the investigation of the occurrence of non-target unknown compounds in Global drinking water and selected rivers. For many of the pesticide and medicinal compounds, the concentration can be estimated and is highly likely to be below action levels for drinking water treatment supply.

Full details of the study together with in depth analysis will be published in due course in the scientific press.

## ACKNOWLEDGEMENTS

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## TRADEMARKS/LICENSING

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