SUPPORTING INFORMATION

Non-target screening reveals time trends of polar micropollutants in a riverbank filtration system

Vittorio Albergamo [a*], Jennifer E. Schollée [b], Emma L. Schymanski [b,c], Rick Helmus [a], Harrie Timmer [d], Juliane Hollender [b,e] and Pim de Voogt [a,f]

[a] Institute for Biodiversity and Ecosystem Dynamics, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands
[b] Eawag, Swiss Federal Institute of Aquatic Science and Technology, Überlandstrasse 133, 8600 Dübendorf, Switzerland
[c] Luxembourg Centre for Systems Biomedicine, University of Luxembourg, House of Biomedicine II 6, avenue du Swing, L-4367 Belvaux, Luxembourg
[d] Oasen, Nieuwe Gouwe O.Z 3, 2801 SB Gouda, The Netherlands
[e] Institute of Biogeochemistry and Pollutant Dynamics, ETH Zürich, Universitätstrasse 16, 8092 Zürich, Switzerland
[f] KWR Watercycle Research Institute, Groningenhaven 7, 3430 BB, Nieuwegein, The Netherlands
[*] Corresponding author: v.albergamo@uva.nl

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S-1: Standards and chemicals

Methanol (≥ 99.9%) was purchased from Fisher Scientific (Wohlen, Switzerland). Ultrapure water was obtained from a Barnstead Nanopure stationary laboratory water system (Barnstead Nanopure Thermo Scientific, San Jose, U.S.). Formic acid (≥ 98 %) used as mobile phase modifier was purchased from Merck (Darmstadt, Germany). Isotope-labelled internal standards (listed in table S-1.1) used for mass recalibration, t_R alignment and intensity normalisation and reference standards (listed in table S-1.2) used for confirmation of chemical identities were purchased from CDN Isotopes (Canada), Dr. Ehrenstorfer (Germany), HPC Standards (Germany), LGC Standards (Switzerland), Molcan (Canada), MolPort (Latvia), Monsanto (Belgium), Novartis (Switzerland), Riedel-de-Häen (Germany), Sigma-Aldrich (Switzerland and The Netherlands), or Toronto Research Chemicals (Canada) at purities ≥ 95% (analytical grade).

Table S-1.1. List of isotope-labelled internal standards, their molecular formula and CAS number.

Name	Formula	CAS
2,2-Difluoro-2-deoxyuridin-13C,15N2	C8H10F2O5[13]C1[15]N2	1233921-75-9
2,4-D-D3	C8H3D3Cl2O3	202480-67-9
2,6-Dichlorbenzamide-3,4,5-D3	C7H2D3Cl2N1O1	1219804-28-0
5-Metyhl-1H-benzotriazole-D6	C7H1D6N3	1246820-65-4
Alachlor-D13	C14H7D13Cl1N1O2	1015856-63-9
Aldicarb (N-methyl-13C-D3-carbamoyl-13C)	[13]C2C5H11D3N2O2S1	1261170-77-7
Amisulpride-D5	C17H22D5N3O4S1	1216626-17-3
Atenolol acid-D5	C14H16N1O4D5	1215404-47-9
Atenolol-D7	C14H15D7N2O3	1202864-50-3
Atomoxetine-D3	C17H18D3N1O1	1217776-38-9
Atorvastatin-D5	C33H30D5F1N2O5	222412-82-0
Atrazine-D5	C8H9D5Cl1N5	163165-75-1
Atrazine-2-Hydroxy-D5	C8H10D5N5O1	1276197-25-1
Atrazine-desisopropyl-D5	C5H3D5Cl1N5	1189961-78-1
Azithromycin-D3	C38H69D3N2O12	163921-65-1
Bentazon-D6	C10H6D6N2O3S1	25057-89-0 (unlabelled)
Benzotriazole-D4	C6H1D4N3	1185072-03-0
Bezafibrat-D4	C19H16D4Cl1N1O4	1189452-53-6
Bicalutamid-D4	C18H10D4F4N2O4S1	1185035-71-5
Caffeine-D9	C8H1N4O2D9	72238-85-8
Candesartan-D5	C24H15D5N6O3	1189650-58-5
Carbamazepine-10,11-epoxide-13C, D2	C14H10D2N2O2[13]C1	36507-30-9 (unlabelled)
Carbamazepin-D8	C15H4D8N2O1	298-46-4 (unlabelled)
Carbendazim-D4	C9H5D4N3O2	291765-95-2
Cetirizin-D8	C21H17D8Cl1N2O3	774596-22-4
Chloridazon-D5	C10H3D5Cl1N3O1	1346818-99-4
Chloridazon-desphenyl-15N2	C4H4Cl1N1[15]N2O1	1189649-21-5
Chloridazon-methyl-desphenyl-D3	C5H3D3Cl1N3O1	17254-80-7 (unlabelled)
Chlorotoluron-D6	C10H7D6Cl1N2O1	1219803-48-1
Chlorpyrifos-D10	C9H1D10Cl3N1O3P1S1	285138-81-0
Chlorpyrifos-methyl D6	C7H1D6Cl3N1O3P1S1	2083629-84-7

Name	Formula	CAS
Chlothianidin-D3	C6H5D3Cl1N5O2S1	1262776-24-8
Citalopram-D6	C20H15D6F1N2O1	1190003-26-9
Clarithromycin-D3	C38H66D3N1O13	959119-17-6
Climbazol-D4	C15H13D4Cl1N2O2	1185117-79-6
Clofibric acid-D4	C10H7D4Cl1O3	1184991-14-7
Clopidogrel-(+/-)-d4	C15H10D4Cl1N1O2S1	1219274-96-0
Clotrimazol-D5	C22H12D5Cl1N2	1185076-41-8
Clozapine-D8	C18H11D8Cl1N4	1185053-50-2
Codeine-13C,D3	C17H18D3N1O3[13]C1	76-57-3 (unlabelled)
Cyclophosphamid-D4	C7H11Cl2N2O2P1D4	173547-45-0
Cyprodinil-D5	C14H10D5N3	1773496-67-5
Desethylatrazine 15N3	C6H10Cl1N2[15]N3	6190-65-4 (unlabelled)
Diazepam-D5	C16H8Cl1N2O1D5	65854-76-4
Diazinon-D10	C12H11D10N2O3P1S1	100155-47-3
Dicamba-D3	C8H3D3Cl2O3	349553-95-3
Dichlorprop-D6	C9H2D6Cl2O3	120-36-5 (unlabelled)
Diclofenac-D4	C14H7D4Cl2N1O2	153466-65-0)
Diflufenican-D3	C19H8D3F5N2O2	1185009-29-3
Dimethenamid-D3	C12H15D3Cl1N1O2S1	1246816-31-8
Dimethoate-D6	C5H6D6N1O3P1S2	1219794-81-6
Diuron-D6	C9H4D6Cl2N2O1	1007536-67-5
Eprosartan-D3	C23H21D3N2O4S1	1185243-70-2
Erythromycin-13C2	C35H67N1O13[13]C2	114-07-8 (unlabelled)
Fenofibrate-D6	C20H15D6Cl1O4	1092484-56-4
Fluconazol-D4	C13H8F2N6O1D4	1124197-58-5
Fluoxetine-D5	C17H13F3N1O1D5	1173020-43-3
Furosemid-D5	C12H6Cl1N2O5S1D5	1189482-35-6
Gabapentin-D4	C9H13N1O2D4	1185039-20-6
Gemcitabine-13C,15N2	C8H11F2N1O4[13]C1[15]N2	1262897-74-4
Hydrochlorothiazide-C13, D2	C6H6Cl1N3O4S2D2[13]C1	1190006-03-1
Hydromorphone-D3	C17H16D3N1O3	136765-37-2
Ibuprofen-D3	C13H15D3O2	121662-14-4
Imidacloprid D4	C9H6D4Cl1N5O2	1015855-75-0
Indomethacin-D4	C19H12Cl1N1O4D4	87377-08-0
Irbesartan-D3	C25H25D3N6O1	1185120-76-6
Irgarol-D9	C11H10D9N5S1	1189926-01-9
Isoproturon-D6	C12H12D6N2O1	217487-17-7
Lamotrigine-13C3,D3	C6[13]C3H4D3Cl2N5	1246815-13-3)
Levetiracetam-D3	C8H11D3N2O2	1217851-16-5
Lidocaine-D10	C14H12N2O1D10	851528-09-1
MCPA-D3	C9H6D3Cl1O3	352431-14-2
Mecl0zine-D8	C25H19D8Cl1N2	1246816-06-7
Mecoprop D6	C10H5D6Cl1O3	1705649-54-2
Mefenamic acid-D3	C15H12D3N1O2	1189707-81-0
Mesotrion D3	C14H10D3N1O7S1	104206-82-8 (unlabelled)

Name	Formula	CAS
Metformin-D6	C4H5N5D6	1185166-01-1
Methiocarb-D3	C11H12D3N1O2S1	1581694-94-1
Methylprednisolon-D3	C22H27O5D3	18462-27-6 (unlabelled)
Metolachlor-D6	C15H16D6Cl1N1O2	1219803-97-0
Metolachlor-ESA D11	C15H12D11N1O5S1	947601-85-6 (unlabelled)
Metoprolol-D7	C15H18D7N1O3	1292906-91-2
Metronidazol-D4	C6H5D4N3O3	1261392-47-5
Metsulfuron-methyl-D3	C14H12D3N5O6S1	74223-64-6
Morphine-D3	C17H16D3N1O3	67293-88-3
N,N-diethyl-3-methylbenzamide-D10	C12H7D10N1O1	1215576-01-4
N4-Acetyl-Sulfamethoxazol-D5	C12H9D4N3O4S1	1215530-54-3
N4-Acetyl-Sulfathiazol-D4	C11H7D4N3O3S2	127-76-4 (unlabelled).
Naproxen-D3	C14H11O3D3	1094102-82-5
Nelfinavir-D3	C32H42D3N3O4S1	1217629-70-3
Octilinone-D17	C11H2D17N1O1S1	1185109-79-8
O-Desmethylvenlafaxin-D6	C16H19D6N1O2	1062605-69-9
Oxazepam-D5	C15H6Cl1D5N2O2	65854-78-6
Oxcarbazepine-D4	C15H8D4N2O2	1020719-71-4
Paracetamol-D4	C8H5D4N1O2	64315-36-2
Phenazon-D3	C11H9D3N2O1	342821-66-3
Pirimicarb-D6	C11H12D6N4O2	1015854-66-6
Pravastatin-D3	C23H33D3O7	1329836-90-9
Primidon-D5	C12H9D5N2O2	73738-06-4
Prochloraz-D7	C15H9D7Cl3N3O2	67747-09-5 (unlabelled)
Propazin-D6	C9H10D6Cl1N5	1655498-05-7
Propiconazol D5	C15H12D5Cl2N3O2	1246818-14-3
Propranolol-D7	C16H14D7N1O2	98897-23-5
Ranitidin-D6	C13H16N4O3S1D6	1185238-09-8
Ritalinic acid-D10	C13H7N1O2D10	19395-41-6 (unlabelled)
Ritonavir-D6	C37H42N6O5S2D6	1217720-20-1 CAS
Simazin D5	C7H7D5Cl1N5	220621-41-0
Sotalol-D6	C12H14D6N2O3S1	1246820-85-8
Sulcotrion-D3	C14H10D3Cl1O5S1	99105-77-8
Sulfadiazine-D4	C10H6D4N4O2S1	1020719-78-1
Sulfadimethoxin-D4	C12H10D4N4O4S1	1020719-80-5
Sulfamethazine-13C6	C6[13]C6H14N4O2S1	77643-91-5
Sulfamethoxazol-D4	C10H7D4N3O3S1	1020719-86-1
Sulfapyridin-D4	C11H7D4N3O2S1	1189863-86-2
Sulfathiazol-D4	C9H5D4N3O2S2	1020719-89-4
Tebuconazole D6	C16H16D6Cl1N3O1	107534-96-3 (unlabelled)
Tebutam-D4	C15H19D4N1O1	35256-85-0
Terbutryn-D5	C10H14D5N5S1	1219804-47-3
Terbutylazin-D5	C9H11D5Cl1N5	222986-60-9
Thiamethoxam-D3	C8H7D3Cl1N5O3S1	1294048-82-0
Tramadol-D6	C16H19N1O2D6	1109217-86-8

Name	Formula	CAS
Triclosan-D3	C12H4D3Cl3O2	1020719-98-5
Trimethoprim-D9	C14H9D9N4O3	1189460-62-5
Valsartan-13C5,15N	[13]C5C19H29[15]N1N4O3	137862-53-4
Valsartan-acid-D4	C14H6D4N4O2	164265-78-5
Venlafaxin-D6	C17H21N1O2D6	1062606-12-5
Venlafaxine-N,O-didesmethyl-D3	C15H20D3N1O2	1189468-67-4
Verapamil-D6	C27H32N2O4D6	1329611-24-6

Table S-1.2. List of unlabelled reference standards, their molecular formula and CAS number.

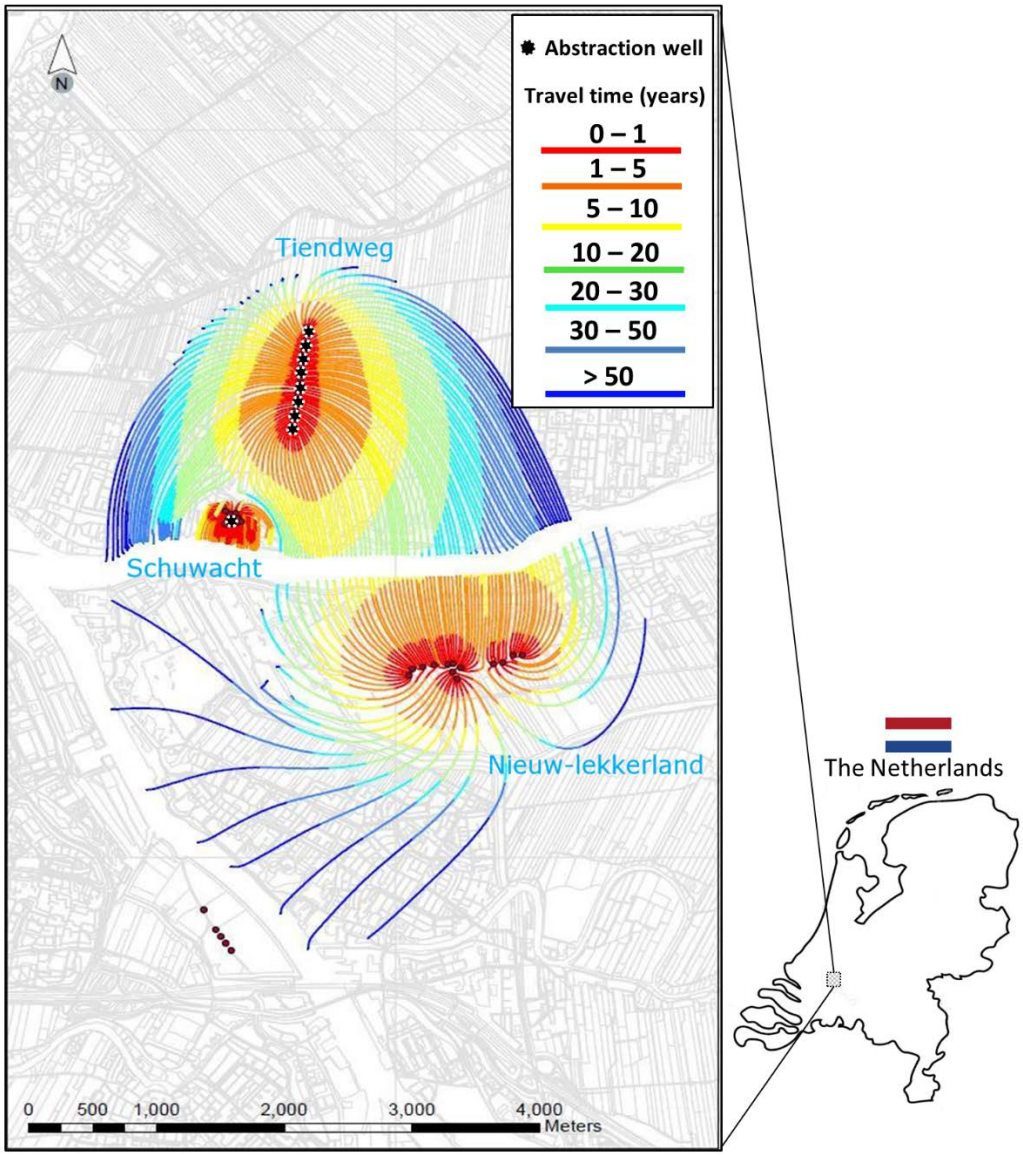
Compound	Formula	CAS
2-Amino-6-methylbenzothiazole	C8H8N2S	2536-91-6
1,3-Benzothiazole	C7H5NS	95-16-9
1,5-Naphthalenedisulfonic acid	C10H8O6S2	81-04-9
1-Naphthol-4-sulfonic acid	C10H8O4S	84-87-7
2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid	C6HF11O3	13252-13-6
2,6-dichlorobenzamide	C7H5Cl2NO	2008-58-4
2,6-Di-tert-butylpyridine	C13H21N	585-48-8
2-chloroaniline-5-sulfonic acid	C6H6ClNO3S	98-36-2
4-Amino-2,5-dichlorobenzenesulfonic acid	C6H5Cl2NO3S	88-50-6
4-Aminoacetanilide	C8H10N2O	122-80-5
4-Dimethylaminopyridine	C7H10N2	1122-58-3
4-Dodecylbenzenesulfonic acid	C18H30O3S	121-65-3
4-Hydroxymetanilamide	C6H8N2O3S	98-32-8
4-Toluenesulfonamide	C7H9NO2S	70-55-3
5-Amino-2-chlorotoluene-4-sulfonic acid	C7H8ClNO3S	88-53-9
Acesulfame	C4H5NO4S	55589-62-3
Acetanilide	C8H9NO	103-84-4
Amrinone	C10H9N3O	60719-84-8
Atrazine-desethyl-2-hydroxy	C6H11N5O	19988-24-0
Benzoguanamine	C9H9N5	91-76-9
Caffeine	C8H10N4O2	58-08-2
Camphorsulfonic acid	C10H16O4S	3144-16-9
Carbendazim	C9H9N3O2	10605-21-7
Chloridazon	C10H8ClN3O	58858-18-7
Chlortoluron	C10H13ClN2O	15545-48-9
Dibutyl phosphate	C8H19O4P	107-66-4
Diphenylphosphinic acid	C12H11O2P	1707-03-5
Diuron-desmethyl	C8H8Cl2N2O	3567-62-2
Gestageno	C21H30O3	68-96-2
Lamotrigine	C9H7Cl2N5	84057-84-1
Metamitron-desamino	C10H9N3O	36993-94-9
Methylisothiazolinone	C4H5NOS	2682-20-4
Mexiletine	C11H17NO	31828-71-4
Monobenzone	C13H12O2	103-16-2
Naphthionic acid	C10H9NO3S	130-13-2
O,O-Diethyl thiophosphate	C4H11O3PS	5871-17-0
Pargyline	C11H13N	306-07-0
p-Toluidine-m-sulfonic acid	C7H9NO3S	88-44-8
Simazine-2-hydroxy	C7H13N50	2599-113
Tetramethylsulfamide	C4H12N2O2S	3768-63-6
Tributyl phosphate	C12H27O4P	126-73-8
Zearalenol	C18H24O5	36455-72-8

S-2: Description of the riverbank filtration site

The studied well fields of the drinking water company Oasen (Gouda, The Netherlands) are situated next to the river Lek, a tributary of the river Rhine in the Netherlands. The wells abstract groundwater from sandy deposits of Pleistocene age at a depth of 10-30 meters below surface level. The aquifer is protected by an overlying aquitard of about 10 meters of peat and clay from the Holocene. The well fields have been operated since 1969. Groundwater abstraction rate from 1969 to 1974 was 1 - 1.5 million m^3/year. From 1975 onward the abstraction rate varied between 1.7 - 2.3 million m^3/year. Various research (1) reveals that, based on the hydro-chemical tracers in this water, the abstracted groundwater originates from the river Lek. Isotope research from 2006 (2) reveals that 93-100% of the abstracted water of well fields Lekkerkerk-Schuwacht and Lekkerkerk-Tiendweg is in fact infiltrated river water from the Rhine. The natural purification processes during the aquifer passage of this river bank improves the water quality considerably. However, the most persistent and mobile pollutants are not fully removed (3,4) which leads to the necessity of advanced purification treatment steps in the drinking water utility like activated carbon or reverse osmosis. The age of the abstracted riverbank filtration groundwater varies with the distance to the river and the hydrogeological conditions and was derived with calibrated hydrogeological groundwater flow models (Figure S-2.1). The Lekkerkerk-Schuwacht wells were built at a distance between 70 and 180 m from the riverbank, allowing abstraction of water with an age between 3 months and 10 years (Mean value: 2 years). As a result, the abstracted river bank groundwater of Lekkerkerk-Schuwacht reflects the relatively recent river water quality. From this well field, the well from where the youngest bank filtrate is abstracted (mean travel time = 1-year) was sampled and considered for this screening study. The Lekkerkerk-Tiendweg wells were built on a transect perpendicular to the riverbank, place between 950 and 1,800 m from the Lek. The age of the water from well field Lekkerkerk-Tiendweg varies between 6 years and > 100 years (Mean value: 20 years), allowing abstraction of groundwater reflecting river water quality from the past decades, when the Lek was much more polluted than nowadays, *e.g.* from the 1950s to 1980s.

Fortunately, thanks to strict regulations and international co-operation, the quality of the river water has improved significantly since 1970 (5). This can be observed from the individual wells of which the samples are taken in well field Lekkerkerk-Tiendweg, that are perpendicularly oriented towards the river. These wells abstract the complete range of historical river water quality from the pre-industrial period (> 100 years old) for the wells that are situated at the greatest distance to the river, to relatively recent river water (at least 6 years old) for the wells closest to the river. The wells in between include the period of maximum river water pollution (30-60 years old).

Figure S-2.1. Map of well fields site showing estimated flow lines and modeled travel time.



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2. Timmer H., Aandeel oevergrondwater berekend via zuurstof-18 isotopen onderzoek. Internal document Oasen, 2006;
3. Stuyfzand, P.J., 1989. Hydrology and water-quality aspects of Rhine bank groundwater in the Netherlands. J. Hydrol. 106, 341–363;
4. Hamann et al, 2016 The fate of organic micropollutants during long-term/long-distance river bank filtration;
5. http://news.bbc.co.uk/2/hi/europe/1371142.stm (accessed on May 15th 2019)

S-3: Additional details on the HRMS systems

S-3.1. Quadrupole-Orbitrap data-dependent acquisition settings

Full-scan HRMS1 spectra were acquired at a scan rate of 1Hz for masses ranging from *m/z* 100 to 1,000 and with a resolving power of 140,000 at *m/z* 200. HRMS2 spectra were acquired for the five most intense ions detected in each cycle of full-scan HRMS1 for masses ranging from *m/z* 200 to 2000 and with a resolving power of 17,500. A dynamic exclusion window of 8 seconds was set, *i.e.* a mass would be temporarily placed on an exclusion list for 8 seconds to ensure that one ion would not dominate all HRMS2 scans. The automatic gain control (AGC) target was set at 200,000 and maximum injection time was 100 milliseconds. For fragmentation, stepped normalised collision energies (NCE) ranging from 15% to 90% were derived from the *m/z* value of the non-target ions.

S-3.2 UHPLC-ESI-q-TOF/HRMS settings

The analyses to confirm the identities of the prioritised non-target features were conducted with a UHPLC system (Nexera, Shimadzu, Den Bosch, The Netherlands) coupled to a Bruker Daltonics maXis 4G high resolution q-ToF/MS upgraded with HD collision cell and equipped with an ESI source (Wormer, The Netherlands). The chromatographic conditions were identical to those described in the manuscript ("LC-HRMS analysis" in METHODOLOGIES section). The MS detector was internally calibrated before starting an analysis batch and additionally prior to any injection. This was achieved by infusing a 50 µM sodium formate solution in H2O:MeOH (1:1, v/v) with a loop injection of 20 µL and a loop rinse of 20 µL. Positive and negative ESI were achieved in separate runs by acquiring HRMS1 spectra for masses ranging from m/z 50 to 1,000 with a resolving power of 30,000–60,000 at full width at half maximum (FWHM) and with a spray voltage of +3.5 kV and −3.5 kV for positive and negative mode, respectively. The capillary temperature was 300 °C. HRMS2 spectra were recorded in data-dependent acquisition mode (*AutoMSMS*) with a resolving power of at least 20,000 FWHM.

S-4: enviMass settings (version 3.4)

- **Peak Picking***
  Extraction of ion chromatograms
  - Maximum retention time gap in an EIC (sec): 180
  - Maximum m/z deviation of centroid data point from its EIC mean (ppm): 5

  Peak picking
  - Minimum number of centroid data points per peak … : 5
  - … within a given RT window (sec): 20
  - Maximum RT gap to length to be interpolated (sec): 10
  - Maximum RT width of a single peak (sec): 120
  - Minimum log10(intensity) threshold: 5
  - Minimum Signal/Noise: 5
  - Minimum Signal/Base: 2
  - Maximum possible number of peaks within a single EIC: 3
  - Peak intensity: use peak area or peak intensoid? - Intensoid (max int.)
  - Peak mass definition: Mean

  Advanced settings
  - Upper log10(intensity) safety threshold: 7
  - How often can a peak detection fail to end the recursion? – peak picking: 2
  - Weight for assigning centroid data points to a peak - peak picking: 1
  - Percentage of low-intense data points to discard: 0

- **Instrument / Resolution**
  - 180 Q-Exactive, ExactivePlus/R140000@200

- **Mass recalibration**
  Positive / Negative ionisation
  - Include mass recalibration for positive/negative ion. mode files? - Yes
  - Reference compounds - Internal standards
  - Maximum allowable m/z correction (ppm): 10
  - Maximum m/z deviation of centroid data point from its EIC mean (ppm): 5
  - RT tolerance (sec): 30

- **Replicates**
  - m/z tolerance (ppm): 5
  - RT tolerance window of peaks caused by the same analyte across replicate samples (sec): 30
  - Absolute log intensity tolerance X: 5

- **Screening (Internal Standards)**
  - RT tolerance of peaks relative to their expected RT (sec): 30
  - RT tolerance of peaks in an isotopic pattern: (sec): 10
  - m/z tolerance (ppm): 5
  - Intensity tolerance (%): 30
  - Lower intensity threshold: 50000
  - Restrict screening to latest files? - FALSE
  - Cut-off score: 0.8
  - Exclude matches below cut-off – FALSE

- **Normalization**
  - Include normalization for positive/negative ion. mode files? - Yes
  - Minimum of screened files covered by each IS profile? (%): 60
  - Screening threshold: 0.8
  - Minimum number of IS profile peaks: 50
  - Use subsampling? – Yes
  - Number of blank/blind profiles subsample: 100
  - Number of sample profiles in subsample:100

- **Profiling**
  - Maximum number of newest samples to be processed per ion mode: 100
  - Peak mass deviation within profiles: 5 ppm
  - Peak deviation within profiles: RT tolerance (sec): 30
  - Minimum number of IS profile peaks: 50

* Detailed description of the peak picking parameters can be found at the following URL: https://www.envibee.ch/eng/enviMass/topics/peakpicking.htm (Accessed on May 13th 2019)

S-5: Overview on detection of the isotope-labelled standards

The masses of the 128 isotope-labelled standards (IS) were screened in all samples in both positive and negative ESI mode the enviMass settings indicated in section S-4. As 3 replicates of water samples from 9 abstraction wells were screened in this study, an IS was found in 27 samples implied detection in all enriched samples. In positive ionisation mode, 75 standards were detected in all samples, whereas in negative mode these were 43. Out of 128 IS, 25 could be ionised in both modes and were found in all samples, whereas 21 were not detected in either positive or negative ionisation mode, likely due to insufficient enrichment. In figures S-5.1 and S-5.2 the mass deviation and intensity distribution of the IS compounds is shown, along with information on the completeness of isotopic peaks detection (cut-off score = 0.8). In tables S-5.1 and S-5.2 the results of the IS screening in positive and negative ESI mode, respectively, are presented. In the positive ionisation mode data (Figure S-5.1) it can be seen that overall higher mass accuracy and intensities were obtained, compared to negative data (Figure S-5.2).

Figure S-5.1. Log-intensity and *m/z* deviation (ppm) distribution of the isotope-labelled standards in positive ESI mode

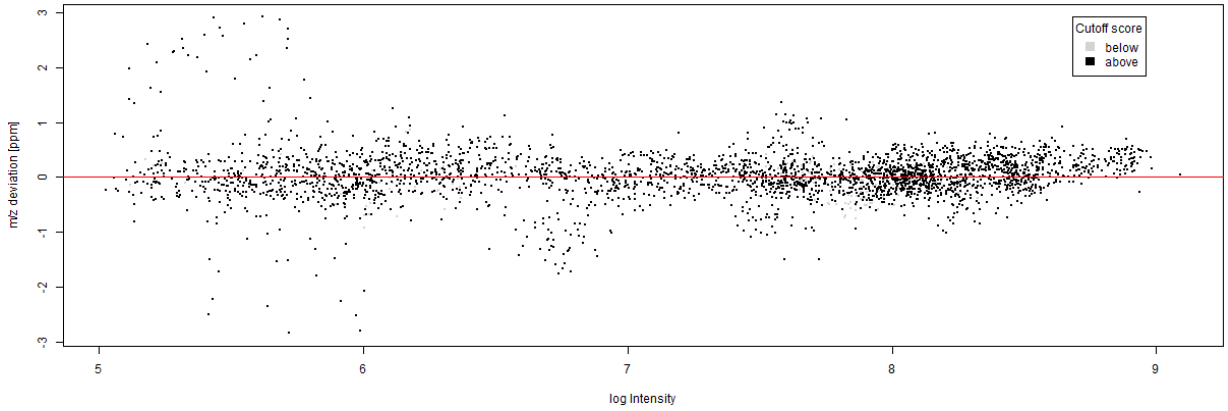

Figure S-5.2. Log-intensity and *m/z* deviation (ppm) distribution of the isotope-labelled standards in negative ESI mode

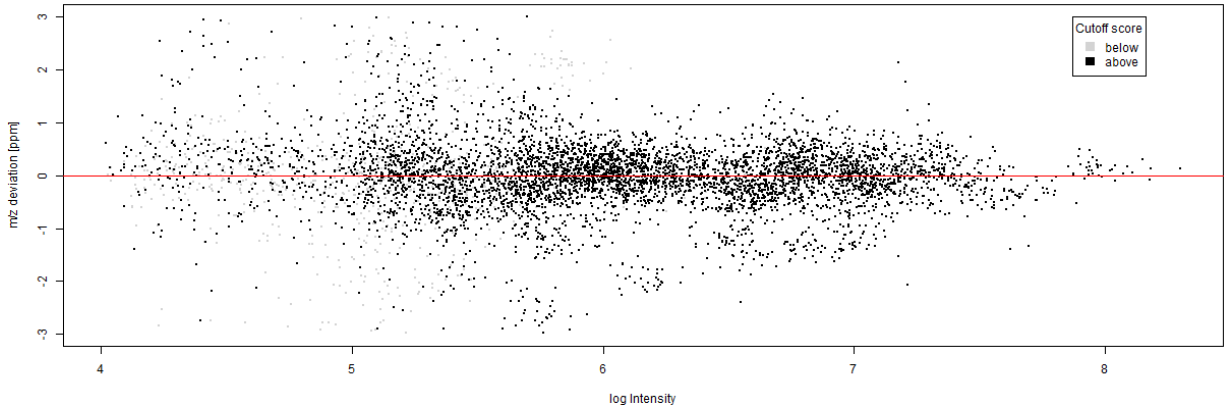

Table S-5.1. List of labelled internal standards screened in positive ionization mode, detected adduct, retention time and sample matches

Labelled-compound name	Adduct	Retention time	Sample matches
2,2-Difluoro-2-deoxyuridin-13C,15N2	M+H	2.8	27
2,4-D-D3	M+H	10.2	27
2,6-Dichlorobenzamide-3,4,5-D3	M+H	4.8	27
5-Metyhl-1H-benzotriazole-D6	M+H	7	27
Alachlor-D13	M+H	12.9	27
Aldicarb (N-methyl-13C-D3-carbamoyl-13C)	M+H	7.4	27
Amisulpride-D5	M+H	5	27
Atenolol acid-D5	M+H	4.7	27
Atenolol-D7	M+H	3.3	27
Atomoxetine-D3	M+H	9	27
Atorvastatin-D5	M+H	13.5	27
Atrazine-D5	M+H	9.7	27
Atrazine-2-Hydroxy-D5	M+H	5.7	27
Atrazine-desisopropyl-D5	M+H	5.5	27
Azithromycin-D3	M+H	7.3	27
Bentazon D6	M+H	8.7	27
Benzotriazole-D4	M+H	5.7	27
Bezafibrat-D4	M+H	11.7	27
Bicalutamid-D4	M+H	10.8	27
Caffeine-D9	M+H	5.2	27
Candesartan-D5	M+H	7.3	27
Carbamazepine-10,11-epoxide-13C, D2	M+H	10.6	27
Carbamazepine-D8	M+H	4	27
Carbendazim-D4	M+H	4.8	27
Cetirizin-D8	M+H	10.5	27
Chloridazon-D5	M+H	6	27
Chloridazon-desphenyl-15N2	M+H	2.2	27
Chloridazon-methyl-desphenyl-D3	M+H	3	27
Chlorotoluron-D6	M+H	9	27
Chlorpyrifos-D10	M+H	17	27
Chlorpyrifos-methyl D6	M+H	14.9	27
Chlothianidin-D3	M+H	5.7	27
Citalopram-D6	M+H	7.8	27
Clarithromycin-D3	M+H	11.1	27
Climbazol-D4	M+H	9.5	27
Clofibric acid-D4	M+H	11.2	27
Clopidogrel-(+/-)-D4	M+H	6.7	27
Clotrimazol-D5	M+H	10.2	27
Clozapine-D8	M+H	7.5	27
Codeine-13C,D3	M+H	3.9	27
Cyclophosphamid-D4	M+H	7.5	27
Cyprodinil-D5	M+H	10.3	27
Desethylatrazine-15N3	M+H	6.9	27
Diazepam-D5	M+H	11.4	27

Labelled-compound name	Adduct	Retention time	Sample matches
Diazinon-D10	M+H	14.3	27
Dicamba-D3	M+H	8.2	27
Dichlorprop-D6	M+H	11.8	27
Diclofenac-D4	M+H	14	27
Diflufenican-D3	M+H	15.7	27
Dimethenamid-D3	M+H	11.4	27
Dimethoate-D6	M+H	6.1	27
Diuron-D6	M+H	10.3	27
Eprosartan-D3	M+H	7.3	27
Erythromycin-13C2	M+H	9.6	27
Fenofibrate-D6	M+H	16.8	27
Fluconazol-D4	M+H	6.6	27
Fluoxetine-D5	M+H	10.6	27
Furosemid-D5	M+H	8	27
Gabapentin-D4	M+H	4.8	27
Gemcitabine-13C,15N2	M+H	2.2	27
Hydrochlorothiazide-C13, D2	M+H	3.2	27
Hydromorphone-D3	M+H	2.9	27
Ibuprofen-D3	M+H	14.5	27
Imidacloprid D4	M+H	5.7	27
Indomethacin-D4	M+H	14.1	27
Irbesartan-D3	M+H	10.4	27
Irgarol-D9	M+H	10.5	27
Isoproturon-D6	M+H	10	27
Lamotrigine-13C3,D3	M+H	6.6	27
Levetiracetam-D3	M+H	4.2	27
Lidocaine-D10	M+H	5.5	27
MCPA-D3	M+H	10.8	27
Mecl0zine-D8	M+H	12.3	27
Mecoprop-D6	M+H	12	27
Mefenamic acid-D3	M+H	15.7	27
Mesotrion-D3	M+H	7.5	25
Metformin-D6	M+H	2	25
Methiocarb-D3	M+H	11.2	21
Methylprednisolon-D3	M+H	10.6	14
Metolachlor-D6	M+H	13.1	14
Metolachlor-ESA D11	M+H	9	13
Metoprolol-D7	M+H	6.4	9
Metronidazol-D4	M+H	3.4	6
Metsulfuron-methyl-D3	M+H	8.1	5
Morphine-D3	M+H	2.4	4
N,N-diethyl-3-methylbenzamide-D10	M+H	9.9	4
N4-Acetyl-Sulfamethoxazol-D5	M+H	6.8	2
N4-Acetyl-Sulfathiazol-D4	M+H	5.3	2
Naproxen-D3	M+H	11.4	2

Labelled-compound name	Adduct	Retention time	Sample matches
Nelfinavir-D3	M+H	10.8	1
Octilinone-D17	M+H	12.8	0
O-Desmethylvenlafaxin-D6	M+H	6	0
Oxazepam-D5	M+H	10	0
Oxcarbazepine-D4	M+H	7.8	0
Paracetamol-D4	M+H	3.3	0
Phenazon-D3	M+H	5.9	0
Pirimicarb-D6	M+H	5.8	0
Pravastatin-D3	M+H	10.4	0
Primidon-D5	M+H	6.6	0
Prochloraz-D7	M+H	13.6	0
Propazin-D6	M+H	11	0
Propiconazol D5	M+H	14.4	0
Propranolol-D7	M+H	8	0
Ranitidin-D6	M+H	3.3	0
Ritalinic acid-D10	M+H	6	0
Ritonavir-D6	M+H	14.8	0
Simazin-D5	M+H	8.2	0
Sotalol-D6	M+H	2.9	0
Sulcotrion-D3	M+H	8.1	0
Sulfadiazine-D4	M+H	3.4	0
Sulfadimethoxin-D4	M+H	7	0
Sulfamethazine-13C6	M+H	5.1	0
Sulfamethoxazole-D4	M+H	5.8	0
Sulfapyridin-D4	M+H	4.2	0
Sulfathiazol-D4	M+H	4	0
Tebuconazole-D6	M+H	14.3	0
Tebutam-D4	M+H	13	0
Terbutryn-D5	M+H	9.9	0
Terbutylazin-D5	M+H	11.5	0
Thiamethoxam-D3	M+H	4.9	0
Tramadol-D6	M+H	6.3	0
Triclosan-D3	M+H	16.1	0
Trimethoprim-D9	M+H	5.2	0
Valsartan-13C5,15N	M+H	12.3	0
Valsartan acid-D4	M+H	8.2	0
Venlafaxin-D6	M+H	7.5	0
Venlafaxine-N,O-didesmethyl-D3	M+H	6.1	0
Verapamil-D6	M+H	8.7	0

Table S-5.2. List of labelled internal standards screened in negative ionization mode, detected adduct, retention time and sample matches

Labelled-compound name	Adduct	Retention time	Sample matches
2,2-Difluoro-2-deoxyuridin-13C,15N2	M-H	2.8	27
2,4-D-D3	M-H	10.2	27
2,6-Dichlorbenzamide-3,4,5-D3	M-H	4.8	0
5-Metyhl-1H-benzotriazole-D6	M-H	7	27
Alachlor-D13	M-H	12.9	0
Aldicarb (N-methyl-13C-D3-carbamoyl-13C)	M-H	7.4	0
Amisulpride-D5	M-H	5	12
Atenolol acid-D5	M-H	4.7	0
Atenolol-D7	M-H	3.3	0
Atomoxetine-D3	M-H	9	0
Atorvastatin-D5	M-H	13.5	27
Atrazine-D5	M-H	9.7	0
Atrazine-2-Hydroxy-D5	M-H	5.7	19
Atrazine-desisopropyl-D5	M-H	5.5	0
Azithromycin-D3	M-H	7.3	0
Bentazon D6	M-H	8.7	27
Benzotriazole-D4	M-H	5.7	27
Bezafibrat-D4	M-H	11.7	27
Bicalutamid-D4	M-H	10.8	27
Caffeine-D9	M-H	5.2	27
Candesartan-D5	M-H	7.3	0
Carbamazepine-10,11-epoxide-13C, D2	M-H	10.6	0
Carbamazepine-D8	M-H	9	0
Carbendazim-D4	M-H	4.8	0
Cetirizin-D8	M-H	10.5	27
Chloridazon-D5	M-H	6	15
Chloridazon-desphenyl-15N2	M-H	2.2	27
Chloridazon-methyl-desphenyl-D3	M-H	3	0
Chlorotoluron-D6	M-H	9	0
Chlorpyrifos-D10	M-H	17	0
Chlorpyrifos-methyl D6	M-H	14.9	27
Chlothianidin-D3	M-H	5.7	0
Citalopram-D6	M-H	7.8	0
Clarithromycin-D3	M-H	11.1	0
Climbazol-D4	M-H	9.5	27
Clofibric acid-D4	M-H	11.2	0
Clopidogrel-(+/-)-D4	M-H	6.7	0
Clotrimazol-D5	M-H	10.2	0
Clozapine-D8	M-H	7.5	0
Codeine-13C,D3	M-H	3.9	0
Cyclophosphamid-D4	M-H	7.5	0
Cyprodinil-D5	M-H	10.3	0

Labelled-compound name	Adduct	Retention time	Sample matches
Desethylatrazine-15N3	M-H	6.9	0
Diazepam-D5	M-H	11.4	0
Diazinon-D10	M-H	14.3	0
Dicamba-D3	M-H	8.2	1
Dichlorprop-D6	M-H	11.8	27
Diclofenac-D4	M-H	14	27
Diflufenican-D3	M-H	15.7	0
Dimethenamid-D3	M-H	11.4	0
Dimethoate-D6	M-H	6.1	0
Diuron-D6	M-H	10.3	27
Eprosartan-D3	M-H	7.3	0
Erythromycin-13C2	M-H	9.6	0
Fenofibrate-D6	M-H	16.8	0
Fluconazol-D4	M-H	6.6	27
Fluoxetine-D5	M-H	10.6	0
Furosemid-D5	M-H	8	27
Gabapentin-D4	M-H	4.8	0
Gemcitabine-13C,15N2	M-H	2.2	27
Hydrochlorothiazide-C13, D2	M-H	3.2	27
Hydromorphone-D3	M-H	2.9	0
Ibuprofen-D3	M-H	14.5	21
Imidacloprid D4	M-H	5.7	27
Indomethacin-D4	M-H	14.1	27
Irbesartan-D3	M-H	10.4	0
Irgarol-D9	M-H	10.5	0
Isoproturon-D6	M-H	10	0
Lamotrigine-13C3,D3	M-H	6.6	0
Levetiracetam-D3	M-H	4.2	0
Lidocaine-D10	M-H	5.5	0
MCPA-D3	M-H	10.8	27
Mecl0zine-D8	M-H	12.3	0
Mecoprop-D6	M-H	12	27
Mefenamic acid-D3	M-H	15.7	27
Mesotrion-D3	M-H	7.5	27
Metformin-D6	M-H	2	0
Methiocarb-D3	M-H	11.2	0
Methylprednisolon-D3	M-H	10.6	0
Metolachlor-D6	M-H	13.1	0
Metolachlor-ESA D11	M-H	9	27
Metoprolol-D7	M-H	6.4	0
Metronidazol-D4	M-H	3.4	0
Metsulfuron-methyl-D3	M-H	8.1	27
Morphine-D3	M-H	2.4	0

Labelled-compound name	Adduct	Retention time	Sample matches
N,N-diethyl-3-methylbenzamide-D10	M-H	9.9	0
N4-Acetyl-Sulfamethoxazol-D5	M-H	6.8	27
N4-Acetyl-Sulfathiazol-D4	M-H	5.3	27
Naproxen-D3	M-H	11.4	12
Nelfinavir-D3	M-H	10.8	0
Octilinone-D17	M-H	12.8	0
O-Desmethylvenlafaxin-D6	M-H	6	0
Oxazepam-D5	M-H	10	27
Oxcarbazepine-D4	M-H	7.8	0
Paracetamol-D4	M-H	3.3	27
Phenazon-D3	M-H	5.9	0
Pirimicarb-D6	M-H	5.8	0
Pravastatin-D3	M-H	10.4	27
Primidon-D5	M-H	6.6	0
Prochloraz-D7	M-H	13.6	0
Propazin-D6	M-H	11	0
Propiconazol D5	M-H	14.4	0
Propranolol-D7	M-H	8	0
Ranitidin-D6	M-H	3.3	8
Ritalinic acid-D10	M-H	6	0
Ritonavir-D6	M-H	14.8	0
Simazin-D5	M-H	8.2	0
Sotalol-D6	M-H	2.9	0
Sulcotrion-D3	M-H	8.1	27
Sulfadiazine-D4	M-H	3.4	27
Sulfadimethoxin-D4	M-H	7	27
Sulfamethazine-13C6	M-H	5.1	27
Sulfamethoxazole-D4	M-H	5.8	27
Sulfapyridin-D4	M-H	4.2	27
Sulfathiazol-D4	M-H	4	27
Tebuconazole-D6	M-H	14.3	0
Tebutam-D4	M-H	13	0
Terbutryn-D5	M-H	9.9	0
Terbutylazin-D5	M-H	11.5	0
Thiamethoxam-D3	M-H	4.9	0
Tramadol-D6	M-H	6.3	0
Triclosan-D3	M-H	16.1	27
Trimethoprim-D9	M-H	5.2	0
Valsartan-13C5,15N	M-H	12.3	27
Valsartan acid-D4	M-H	8.2	27
Venlafaxin-D6	M-H	7.5	0
Venlafaxine-N,O-didesmethyl-D3	M-H	6.1	0
Verapamil-D6	M-H	8.7	0

S-6: Overview on the data from the 15 most populated clusters

Table S-6.1. Feature population of the prioritised clusters in positive ESI mode, number of prioritised features and associated HRMS2 data.

Top populated cluster	Features in cluster	Intensity-prioritised	Triggered HRMS2
1	974	487	158
2	834	417	111
3	804	402	188
4	763	382	83
5	728	364	84
6	682	341	148
7	632	316	77
8	514	257	78
9	466	233	74
10	238	119	98
11	231	116	45
12	190	95	60
13	185	93	60
14	160	80	31
15	124	62	53

Table S-6.2. Feature population of the prioritised clusters in negative ESI mode, number of prioritised features and associated HRMS2 data.

Top populated cluster	Features in cluster	Intensity-prioritised	Triggered HRMS2
1	651	488	89
2	640	480	98
3	473	355	82
4	460	345	64
5	454	341	76
6	427	320	73
7	426	320	90
8	415	311	69
9	398	299	71
10	286	215	100
11	129	97	49
12	106	80	46
13	100	75	20
14	96	72	34
15	62	47	22

S-7: List of (tentatively) identified substances

Table S-7.1. Details of (tentatively) identified substances prioritised from positive data.

Please double-click embedded .xlsx file icon to open the table

(tentatively)identifid-pos.xlsx

Table S-7.2. Details of the (tentatively) identified substances prioritised from negative ESI data.

Please double-click embedded .xlsx file icon to open the table

(tentatively)identifid-neg.xlsx