SUPPORTING INFORMATION:

Unravelling Contaminants in the Anthropocene Using Statistical Analysis of Liquid Chromatography-High-Resolution Mass Spectrometry Nontarget Screening Data Recorded in Lake sediments

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Standards and reagents

Ethylacetate (≥ 99.7%) was purchased from Sigma Aldrich (Steinheim, Germany). Acetone (≥ 99.8 %) and formic acid (≥ 98 %) from Merck (Darmstadt, Germany). Isopropanol (≥ 99.5%) and methanol (≥ 99.9%) were purchased from Acros Organics (New Jersey, USA) and Fisher Scientific (Wohlen, Switzerland), respectively. Nano-pure water was obtained from a Barnstead Nanopure stationary laboratory water system (Barnstead Nanopure Thermo Scientific, San Jose, U.S.). The internal standards (purity ≥97%) used for quality control, mass recalibration and intensity normalization were purchased from the following suppliers: Sigma Aldrich (Steinheim, Germany), TRC Canada (Toronto, Canada), TCI Europe (Antwerpen, Belgium), Dr. Ehrenstorfer (Augsburg, Germany), Novartis (Basel, Switzerland), ReseaLIFEchem GmbH (Burgdorf, Switzerland), CDN Isotopes Inc. (Augsburg, Germany), and Lipomed AG (Arlesheim, Switzerland). For confirmation of imazalil a standard was purchased from Sigma Aldrich (Steinheim, Germany).

Table S1. Morphology and hydrological characteristics of Greifensee and Lake Lugano

	Greifensee	Lake Lugano (Southern basin)
Lake basin		
Lake area (km^2)	8.5	20
Maximun depth (m)	32	95
Mean depth (m)	18	55
Lake volumen (km^3)	0.15	1
Mean residence time (years)	1.1	1.4
Watershed		
Land area (km^2)		290
Total area (km^2)	160	608

Physico-chemical Analysis of lake sediments

Sediment cores were dated using ^{210}Pb and ^{137}Cs signals from Chernobyl (1986) and the atomic bomb tests (1963) using gamma spectroscopy (HPGe GCW 3523) with sedimentation rates of 0.3 cm/year and 0.5 cm/year for Greifensee and Lake Lugano, respectively as reported elsewhere.[1] Additional counting of annual laminations was performed since individual layers can easily be identified because of the oxic and anoxic seasonal periods of the lake represented by different colours. Total carbon (TC) content was measured using an elemental analyser (EURO EA 3000). Total inorganic carbon (TIC) was obtained from a titration Coulometer(CM5015). Total organic carbon (TOC) was calculated as TOC = TC – TIC. TOC values from Lake Lugano were taken from a core in close proximity (< 47 m, 45°57'30.2"N, 8°53'40.2"E) to the one used in this study presenting the same physicochemical characteristics (e.g., age model) than the one retrieved two years earlier in 2012.[2] TOC values are reported in Table S2. Based on the TOC values in Greifensee and the clusters obtained in our work, the change of TOC within both lakes do not influence the outcomes of this work strongly since similar clusters are observed in both lakes even though TOC values are very different. Furthermore, TOC values are in close proximity in both lakes until early 1980s, indicating that TOC is not the only factor responsible for the accumulation of organic contaminants observed. Moreover, although, one of the clusters in Lake Lugano shows similar pattern as the TOC values, perhaps reflecting the pattern of the most hydrophobic compounds, there are additional clusters that shown constant increasing concentration over time and different patterns over time.

Table S2. Total organic content (TOC) measured in Greifensee and Lake Lugano sediments

Greifensee		Lake Lugano	
Year	%TOC	Year	%TOC
2014-2004	3.7	2014	8.5
2004-1995	3.3	2004	3.8
1995-1984	3.1	1995	6.0
1984-1974	3.7	1990	8.4
1974-1964	3.9	1982	5.4
1964-1954	3.2	1976	4.6
1954-1944	3.0	1968	4.7
1944-1934	1.7	1952	4.3
1934-1918	1.6	1936	1.8
1918-1902	1.4	1902	1.6
1902-1886	1.4	1876	2.0
1889-1870	1.5		

LC-HRMS analyses

Freeze-dried sediments from Greifensee were extracted by pressurized liquid extraction (PLE) using an in-cell cleanup technique that employed Florisil as a sorbing phase, as described in detail elsewhere.[3, 4] Briefly, the extraction was performed with 10-mL stainless steel cells prepared by placing, from bottom to top, a 27-mm glass fiber filter, a 16.2-mm cellulose filter (Dionex, Olten, Switzerland), ~1 g of activated Florisil (60/100 mesh, Supelco, Bellefonte, USA), and an additional cellulose filter. Furthermore, ~6 g of previously freeze-dried, homogenized and weighed sediment mixed with 500 mg of hydromatrix (diatomaceous earth, Restek, Bellefonte, PA) to increase solvent channeling was added to the cell. Extraction of the cells was then carried out on an ASE 350 system (Dionex, Sunnyvale, U.S.A.) using ethyl acetate and acetone at a ratio of 70:30 (% v/v) as extraction solvents. Two static extraction cycles of 5 min at 80°C and a rinsing volume of 60% were implemented, each followed by 100 s of purging with N_2. The Lake Lugano sediment samples were freeze-dried, extracted by pressurized liquid extraction, and cleaned up by liquid-liquid partitioning using a combination of acetonitrile, $MgSO_4$, and NH_4Cl. Details in the extraction method used for both sediment cores have been previously reported and validated with 180 target compounds having a broad range of physical-chemical properties in earlier studies.[3] Although Greifensee and Lake Lugano sediments were extracted by different

techniques, the range of compounds studied is comparable in both extraction methods and should not affect the results as illustrated in Figure S1 where the distribution of predicted Log K_{ow} is obtained from measured RT. The extracts from both lakes were spiked with 60 µL of 2.0 mg/L of a mixed solution containing 98 internal standards with an absolute amount of 120 ng each for quality control, mass calibration and normalization procedures. The extracts were then gently evaporated to approximately 1 mL at a temperature of 45°C with an automated evaporator system (Syncore® Polyvap from Büchi, Flawil, Switzerland). Additional evaporation with a gentle stream of N_2 at 40°C was performed to adjust the final volume to 500 µL. The final extracts were filtered into 2-mL auto sampler vials using 0.2-µm PTFE filters (BGB Analytics, Boeckten, Switzerland).

Detection of analytes was performed on an LC system connected to a Q Exactive™ Hybrid Quadrupole-Orbitrap Mass Spectrometer (Thermo Fisher Scientific, San Jose, U.S.A.) equipped with an electrospray ionization (ESI) source, as described by Chiaia et al.[5] Data dependent and data independent acquisition (DIA) measurements were performed separately in the positive and negative ionization modes. Full range mass spectra were recorded over a mass range of 100 to 1100 *m/z* with a nominal resolving power of 140,000 referenced to *m/z* 400 and with a mass accuracy of ±5 ppm. High resolution product ion spectra were acquired in MS/MS experiments with a nominal resolving power of 17,500. MS/MS measurements for Greifensee were conducted using data independent acquisition (DIA) with the following overlapping mass isolation windows: 95-155 *m/z*, 150-190 m/z, 185-225 *m/z*, 220-260 m/z, 255-295 m/z, 290-330 m/z, 325-365 *m/z*, 360-400 m/z and 395-1005 *m/z*. A small overlap of neighboring windows was chosen to ensure the inclusion of all parent ions. For the generation of product ions by higher energy collision dissociation (HCD), the normalized collision energies were set to 95%, 100% and 105%.

The electrospray, source fragmentation and capillary voltage were set to 5 kV, 15 V and 25 V in positive ion mode, and to -4 kV, -15 V and -20 V in negative mode. The capillary temperature and tube lens were set at 300°C and 60 V in positive mode and 350°C and -70 V in negative mode. The sheath and auxiliary gas flow were set at 50 and 20 arbitrary units, respectively, for both ionization modes.

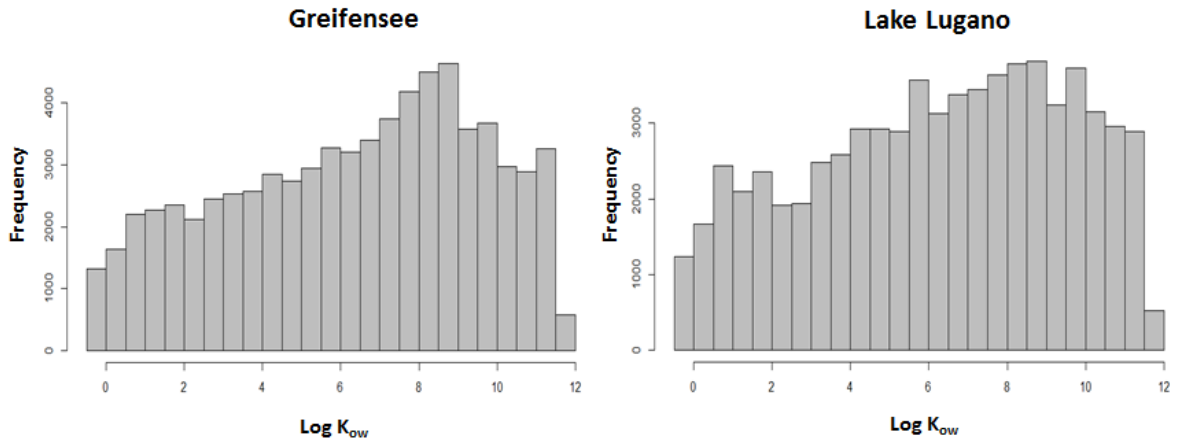

Figure S1. Distribution of predicted Log K_{ow} values obtained from measured RT from Greifensee and Lake Lugano. The Log K_{ow} values were predicted using164 reference standards.[3]

Table S3. Compounds detected in sediments of Greifensee and Lake Lugano

Compound Name	CAS No.	Application	Location
Acetochlor	34256-82-1	Pesticide	Lake Lugano
Alachlor	15972-60-8	Pesticide	Lake Lugano
Benzotriazole	95-14-7	Corrosion Inhibitor	Greifensee
Bromochlorophen	15435-29-7	Antimicrobial	Greifensee, Lake Lugano
Chlorophen	120-32-1	Pesticide/Pharma	Greifensee, Lake Lugano
Dichlorocarbanilide		Transformation Product of Triclocarban	Greifensee, Lake Lugano

Compound Name	CAS No.	Application	Location
Dichlorophen	97-23-4	Pesticide/Antimicrobial	Greifensee, Lake Lugano
Flucofuron	370-50-3	Pesticide	Greifensee, Lake Lugano
Fludioxonil	131341-86-1	Pesticide	Lake Lugano
Flufenamic acid	530-78-9	Pharmaceutical	Lake Lugano
Galaxolidon		PCP	Greifensee, Lake Lugano
Hexachlorophen	70-30-4	Antimicrobial	Greifensee, Lake Lugano
Irgarol	28159-98-0	Pesticide	Greifensee, Lake Lugano
Lufenuron	103055-07-8	Pesticide	Greifensee, Lake Lugano
Octocrylene	6197-30-4	PCP	Greifensee, Lake Lugano
Prochloraz	67747-09-5	Pesticide	Greifensee
Prometryn	7287-19-6	Pesticide	Greifensee, Lake Lugano
Propiconazol	60207-90-1	Pesticide	Greifensee, Lake Lugano
Terbutryn	886-50-0	Pesticide	Greifensee, Lake Lugano
Tonalide	1506-02-1	PCP	Greifensee, Lake Lugano
Triclocarban	101-20-2	Antimicrobial	Greifensee, Lake Lugano
Triclosan	3380-34-5	Antimicrobial	Greifensee, Lake Lugano

Quality control and quantification

Quality control accounted for about 40% of the samples. Method blank samples were prepared by performing the exact same extraction and clean up procedure using sediment from the deepest part of the core, because contamination was not likely to be present in these layers. This procedure allows identifying any contamination during the whole work-up procedure. Pure methanol samples were used as instrument blanks to control contamination within the instrument. Additional two standard mixes in methanol with 250 µg/L and 450 µg/L concentrations in vial were used to control the stability of the instrument during the measuring time. The instrumental

blanks and standard mixes were run before and after a batch of seven samples. Additional sample duplicates were randomly measured accounting for about 20% of the total samples measured. Estimated concentrations of imazalil (C_{ised}) were obtained by using climbazole-D4 (RT 7.9 min) as internal standard.

Trend detection

The detection of profiles was conducted in two steps. First, the enviMass picks the peaks obtained from the mzXML files and groups them into components. A minimum of five scans within 20s were needed to define a peak and the intensity threshold of a peak was set to 10^4 to avoid picking instrumental noise. Individual peaks were partitioned to one signal if they had a maximal mass deviation of 5 ppm from their mean and were within a 60 s retention time (RT) window. Then, two quality controls and data pre-processing to align systematic deviations including mass recalibration, intensity correction and RT alignment are performed. The first quality check compares the intensity distribution between the samples and highlights samples with extreme deviations. The mass recalibration was performed to improve mass accuracy in which the software uses the mass differences between the theoretical and measured internal standard masses to recalibrate all masses. The global (overall) intensity correction and the RT alignment were also corrected by the internal standards to reduce intensity differences and RT shifts between samples, respectively. The internal standards shown in Table S3 and S4 were detected within a tolerance window of 5 ppm and RT of 60 s. Only the main adducts $[M+H]^+$ and $[M-H]^-$ in negative mode were considered. Finally, a second quality check was conducted to find mismatches between the corrected and uncorrected data. The recalibrated and normalized masses from different LC-HRMS experiments were grouped into time series. Profiles were extracted with a peak to peak deviation tolerance of 5 ppm and 60 s RT. Additionally a blank subtraction

was performed if the intensity ratio of sample to blank was smaller than 100. Finally, a trend was reported if the maximal intensity exceeds a predefined threshold that is depending on all intensities in the profile. Detailed parameters and the most important settings during the workflow are given in Table S5.

All trends from exact masses that were detected in the blind were excluded and a minimum intensity threshold of 10^4 was set for the maximum intensity. Therefore, very low intensity substances are excluded in this work. The RT window was chosen from 3.76 min to 23.5 min to account for the settings chosen in the liquid chromatography, where the first minutes (0-3.76) were sent to waste and the last minutes (23.5-35 min) were used to re-calibrate the column. Therefore, this time period was excluded from the analysis since no organic contaminants are expected.[6-9] A table with the profiles fulfilling all criteria described above was exported containing the exact masses, RTs and intensities of the different samples.

Table S4. Internal standards in positive ionization used for Mass recalibration, intensity correction and RT alignment

Name	Formula	Exact Mass	M+H	M+H	RT (min)
5-Methyl-Benzotriazol-D6	C7H1D6N3	139.1011	140.1089	TRUE	5.96
Atomoxetin-D3	C17H18D3NO	258.1811	259.1884	TRUE	7.79
Atorvastatin-d5	C33H30D5FN2O5	563.2843	564.2922	TRUE	12.09
Atrazin-2-Hydroxy-D5	C8H10D5N5O	202.1596	203.1663	TRUE	4.36
Atrazin-D5	C8H9D5ClN5	220.1246	221.1324	TRUE	8.28
Atrazin-Desethyl-15N3	C6H10ClN2[15]N3	190.0536	191.0609	TRUE	5.8
Atrazin-Desethyl-D6	C6H4D6ClN5	193.0996	194.1074	TRUE	9.71
Azoxystrobin-d4	C22H13D4N3O5	407.1419	408.1492	TRUE	9.75
Benzotriazol-D4	C6H1D4N3	123.0729	124.0807	TRUE	4.55
Bezafibrat-D4	C19H16D4ClNO4	365.1326	366.1404	TRUE	10.33

Name	Formula	Exact Mass	M+H	M+H	RT (min)
Candesartan-D5	C24H15D5N6O3	445.1905	446.1983	TRUE	9.19
Carbamazepin-10,11-epoxid- 13C, D2	C14H10D2N2O2[13]C	255.1058	256.1131	TRUE	6.33
Carbamazepin-D8	C15H4D8N2O	244.1446	245.1525	TRUE	7.65
Cetirizin-D8	C21H17D8ClN2O3	396.2056	397.2129	TRUE	9.08
Chloridazon-D5	C10H3D5ClN3O	226.067	227.0742	TRUE	5.39
Chloridazon-methyl-desphenyl-D3	C5H3D3ClN3O	162.0387	163.046	TRUE	5.34
Chlorpyrifos-D10	C9HD10Cl3NO3PS	358.9885	359.9963	TRUE	15.47
Chlorpyrifos-methyl D6	C7HD6Cl3NO3PS	326.9328	327.9401	TRUE	13.67
Chlortoluron-D6	C10H7D6ClN2O	218.1088	219.1166	TRUE	8.18
Citalopram-D6	C20H15D6FN2O	330.2015	331.2087	TRUE	6.65
Clarithromycin-D3	C38H66D3NO13	750.4952	751.503	TRUE	9.35
Climbazol-D4	C15H13D4ClN2O2	243.1259	297.1302	TRUE	7.9
Clopidogrel-(+/-)-D4	C15H10D4ClNO2S	280.1576	312.0758	TRUE	5.77
Clothianidin-D3	C6H5D3ClN5O2S	252.0275	253.0348	TRUE	5.1
Clotrimazol-D5	C22H12D5ClN2	349.1389	350.1467	TRUE	8.58
Clozapin-D8	C18H11D8ClN4	334.18	335.1873	TRUE	6.35
Coffein-D9	C8H1N4O2D9	203.1363	204.1441	TRUE	3.97
Cyclophosphamid-D4	C7H11Cl2N2O2PD4	264.0499	265.0572	TRUE	6.35
Diazepam-D5	C16H8Cl1N2O1D5	289.103	290.1103	TRUE	9.89
Diazinon-D10	C12H11D10N2O3PS	314.1633	315.1711	TRUE	12.61
Diclofenac-D4	C14H7D4Cl2NO2	418.0571	300.0490	TRUE	12.5
Diflufenican-D3	C19H8D3F5N2O2	397.0924	398.1002	TRUE	14.17
Dimethenamid-D3	C12H15D3ClNO2S	278.093	279.1008	TRUE	9.94
Diuron-D6	C9H4D6Cl2N2O	238.0541	239.062	TRUE	8.9
Eprosartan-D3	C23H21D3N2O4S	427.1645	428.1718	TRUE	6.28
Erythromycin-13C2	C35H67NO13[13]C2	735.468	736.4752	TRUE	7.97
Fenofibrate-D6	C20H15D6ClO4	366.1511	367.1578	TRUE	15.1
Fluconazol-D4	C13H8F2N6O1D4	310.1292	311.1364	TRUE	5.55
Fluoxetine-D5	C17H13F3N1O1D5	314.1654	315.1727	TRUE	8.93
Imidacloprid D4	C9H6D4ClN5O2	259.0775	260.0848	TRUE	5.0
Indomethacin-D4	C19H12Cl1N1O4D4	361.1019	362.1092	TRUE	12.5
Irbesartan-D3	C25H25D3N6O	431.2513	432.2586	TRUE	9.14
Irgarol-D9	C11H10D9N5S1	262.1932	263.1999	TRUE	9.03
Isoproturon-D6	C12H12D6N2O	212.179	213.1869	TRUE	8.65
Lamotrigin-13C3,d3	C6[13]C3H4D3Cl2N5	261.0367	262.044	TRUE	5.51
Mefenaminsäure-D3	C15H12D3N1O2	274.1933	245.1364	TRUE	14.23

Name	Formula	Exact Mass	M+H	M+H	RT (min)
Mephedron-D3	C11H12D3NO	180.1342	181.1415	TRUE	12.13
Mesotrion-D3	C14H10D3NO7S	342.0607	343.0674	TRUE	6.35
Methiocarb D3	C11H12D3NO2S	258.0471	229.1084	TRUE	10.15
Methylprednisolon-D3	C22H27O5D3	377.2282	378.2354	TRUE	9.12
Metolachlor-D6	C15H16D6ClNO2	289.1716	290.1788	TRUE	11.49
Metoprolol-D7	C15H18D7NO3	274.2268	275.2347	TRUE	5.22
Metsulfuron-methyl D3	C14H12D3N5O6S	384.0926	385.1004	TRUE	7.16
N,N-diethyl-3-methylbenzamid-D10 (DEET-D10)	C12H7D10NO	201.1932	202.2011	TRUE	8.44
N,O-Didesvenlafaxin-D3	C15H20D3NO2	252.1917	253.199	TRUE	5.12
N4-Acetyl-Sulfamethoxazol-D4	C12H9D4N3O4S	299.0878	300.0951	TRUE	5.72
Naproxen-d3	C14H11O3D3	233.1131	234.1204	TRUE	9.96
Nelfinavir-D3	C32H42D3N3O4S	570.3319	571.3392	TRUE	9.47
Octhilinon-D17 (2-n-Octyl-4-isothiazolin-3-on-D17 (OI-D17))	C11H2D17NOS	230.226	231.2327	TRUE	11.4
O-Desvenlafaxin-D6	C16H19D6NO2	269.2262	270.2335	TRUE	5.1
Oxazepam-D5	C15H6ClD5N2O2	291.0823	292.0896	TRUE	8.85
Oxcarbazepin-D4	C15H8D4N2O2	202.0783	257.1223	TRUE	6.72
Phenazon-D3 (Antipyrin-d3)	C11H9D3N2O	191.1143	192.1211	TRUE	4.78
Pirimicarb D6	C11H12D6N4O2	244.1808	245.1881	TRUE	5.02
Primidon-D5	C12H9D5N2O2	223.1375	224.1442	TRUE	5.55
Prochloraz D7	C15H9D7Cl3N3O2	288.1029	383.082	TRUE	12.02
Propazin-D6	C9H10D6ClN5	235.1465	236.1544	TRUE	9.68
Propiconazol-D5	C15H12D5Cl2N3O2	346.1006	347.1084	TRUE	12.92
Propranolol-D7	C16H14D7NO2	289.1678	267.2084	TRUE	6.56
Ritalinsäure-D10	C13H7N1O2D10	229.1887	230.196	TRUE	4.8
Ritonavir-D6	C37H42N6O5S2D6	726.3504	727.3577	TRUE	13.17
Simazin-D5	C7H7D5ClN5	206.109	207.1168	TRUE	6.97
Sulcotrion-D3	C14H10D3ClO5S	331.0366	332.0433	TRUE	6.9
Sulfadimethoxin-D4	C12H10D4N4O4S	314.0981	315.106	TRUE	5.91
Sulfamethoxazol-D4	C10H7D4N3O3S	257.0767	258.0845	TRUE	4.88
Tebuconazole D6	C16H16D6ClN3O	313.1824	314.1901	TRUE	12.68
Tebutam-D4	C15H19D4NO	237.2025	238.2103	TRUE	11.49
Terbutryn-D5	C10H14D5N5S1	246.1681	247.1748	TRUE	8.51

Name	Formula	Exact Mass	M+H	M+H	RT (min)
Terbutylazin-D5	C9H11D5ClN5	234.1403	235.1481	TRUE	9.99
Tramadol-D6	C16H19N1O2D6	269.2262	270.2335	TRUE	5.1
Valsartan-13C5,15N	[13]C5C19H29[15]N1N4O3	441.2403	442.2481	TRUE	10.83
Valsartansäure-D4	C14H6D4N4O2	202.0783	271.1128	TRUE	6.86
Venlafaxin-D6	C17H21N1O2D6	283.2418	284.2491	TRUE	6.19
Verapamil-D6	C27H32N2O4D6	460.3208	461.3281	TRUE	7.16

Table S5. Internal standards in negative ionization used for Mass recalibration, intensity correction and RT alignment

Name	Formula	Exact Mass	M-H	M-H	RT (min)
2,4-D 6C13	C2[13]C6H6Cl2O3	225.9933	224.9823	TRUE	9.03
Bentazon-D6	C10H6D6N2O3S	246.0951	245.0872	TRUE	7.51
Bezafibrat-D4	C19H16D4ClNO4	365.1326	364.12592	TRUE	10.14
Bicalutamid-D4	C18H10D4F4N2O4S	434.0855	433.0789	TRUE	9.33
Clofibrinsäure-D4	C10H7D4ClO3	218.0648	217.0575	TRUE	9.72
Dicamba-D3	C8H3D3Cl2O3	222.9888	221.981	TRUE	9.02
Dichlorprop-D6	C9H2D6Cl2O3	240.0227	239.0154	TRUE	10.37
Diclofenac-D4	C14H7D4Cl2NO2	418.0571	298.0345	TRUE	12.29
Furosemid-D5	C12H6Cl1N2O5S1D5	335.0391	334.0318	TRUE	6.68
MCPA-D3	C9H6D3ClO3	203.0429	202.0356	TRUE	9.35
Mecoprop-D3	C10H8D3ClO3	217.0591	216.0512	TRUE	9.74
Mefenaminsäure-D3	C15H12D3N1O2	274.1933	243.12183	TRUE	13.98
Mesotrion-D3	C14H10D3NO7S	342.0607	341.0528	TRUE	6.31
Metolachlor-ESA D11	C15H12D11N1O5S1	548.064	339.1917	TRUE	7.78
Metsulfuron-methyl D3	C14H12D3N5O6S	384.0926	383.0858	TRUE	7.07
PFOS-13C4	C4[13]C4F17HSO3	503.9509	502.9436	TRUE	13.47
Pravastatin-D3	C23H33D3O7	427.2649	426.2577	TRUE	8.91
Sulcotrion-D3	C14H10D3ClO5S	331.0366	330.0288	TRUE	6.83

Name	Formula	Exact Mass	M-H	M-H	RT (min)
Triclosan-13C6	C6H7Cl3O2[13]C6	293.9718	292.96401	TRUE	14.32
Triclosan-D3	C12H4D3Cl3O2	290.97	289.9627	TRUE	14.32

Table S6. enviMass setting used for the identification and extraction of trends in a sediment cores.

*Detailed description of each parameter can be found in reference 10.

enviMass step	**Settings**
Peak picking	- Minimum number of measurements per peak: 5 - Within a given RT window: 20 s - Maximum RT gap length to be interpolated: 10 s - Peak definition – Maximum RT length of a single peak: 120 s - Minimum log10(intensity threshold: 4 - Minimum Signal/Noise: 5 - Minimum Signal/Base: 2 - Maximum possible number of peaks within a single EIC: 5 - Maximum retention time gap in an EIC: 300 - Maximum deviation of a measurement from its EIc mean: 5 ppm
Adducts	- Positive ions: M+H, M+ - Negative ions: M-H
Resolution	Q-Exactive, ExactivePlus/R140000@200
Recalibration	- Reference compounds: Internal Standards - m/z tolerance: 5 ppm - RT tolerance: 60 s
Screening IS	- RT tolerance of peaks in sample relative to their expected RT: 60 s - RT tolerance of peaks within an isotope pattern: 10 s - RT tolerance of peaks in blank/blind relative to their expected RT: 60 s - Scoring weight for mass matching: 0.5 - Scoring weight for relative intensity matching: 0.2 - Score weight for occurrence blank/blind: 0 - m/z tolerance: 5 ppm - Intensity tolerance: 80% - lower intensity threshold: 50000
Normalization	- Minimum of files covered by ach IS profile: 90% - Screening threshold: 0.8 - Minimum number of Is profiles: 15 - Number of blank profiles in subsampling: 100 - Number of sample profiles in subsamples: 100
Profiling	- Maximum number of newest samples to be processed: 100 - Peak-to-Peak deviation within profiles: 5 ppm - RT tolerance: 60 s
Trends	- Time lag of trends (days): 3,6,12 - Trend vs. mean + variance intensity threshold: 2 - Show maximum intensity above blind: TRUE

Blind	Run a blind subtraction if intensity ratio sample/blind < 100

Table S7. Confusion matrix for the selected Spearman's rank correlation cutoff.

Anthropocene	ρ < 0.5	ρ ≥ 0.5	
No	175	6	181
Yes	1	18	19
	176	24	200

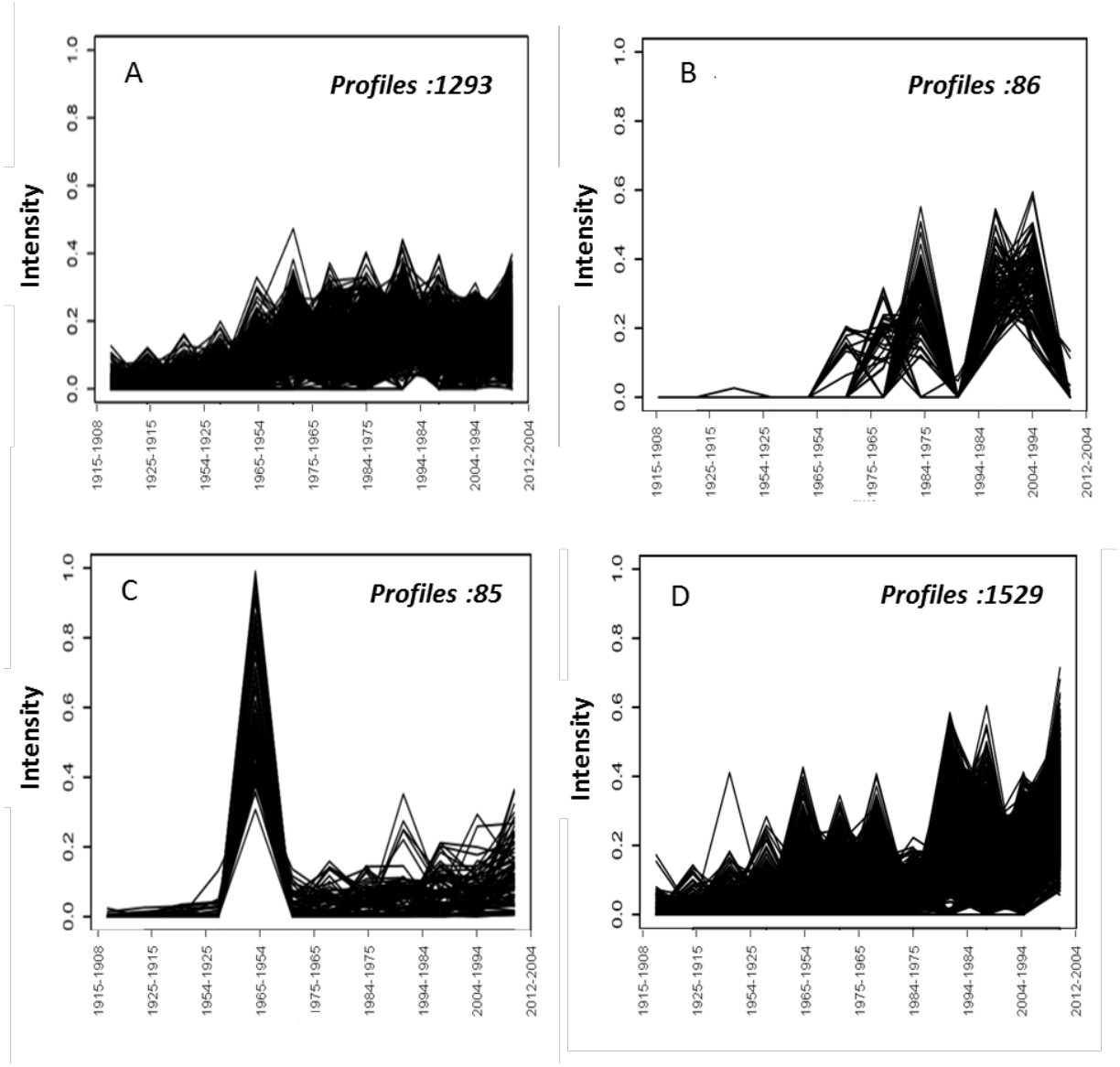

Figure S2. Examples of clusters attributed to natural organic matter (A and B), instrument sparks B and C) or to a missing spill event (C) recorded in Greifensee and eliminated from the analysis. The number of profiles in each cluster is also shown.

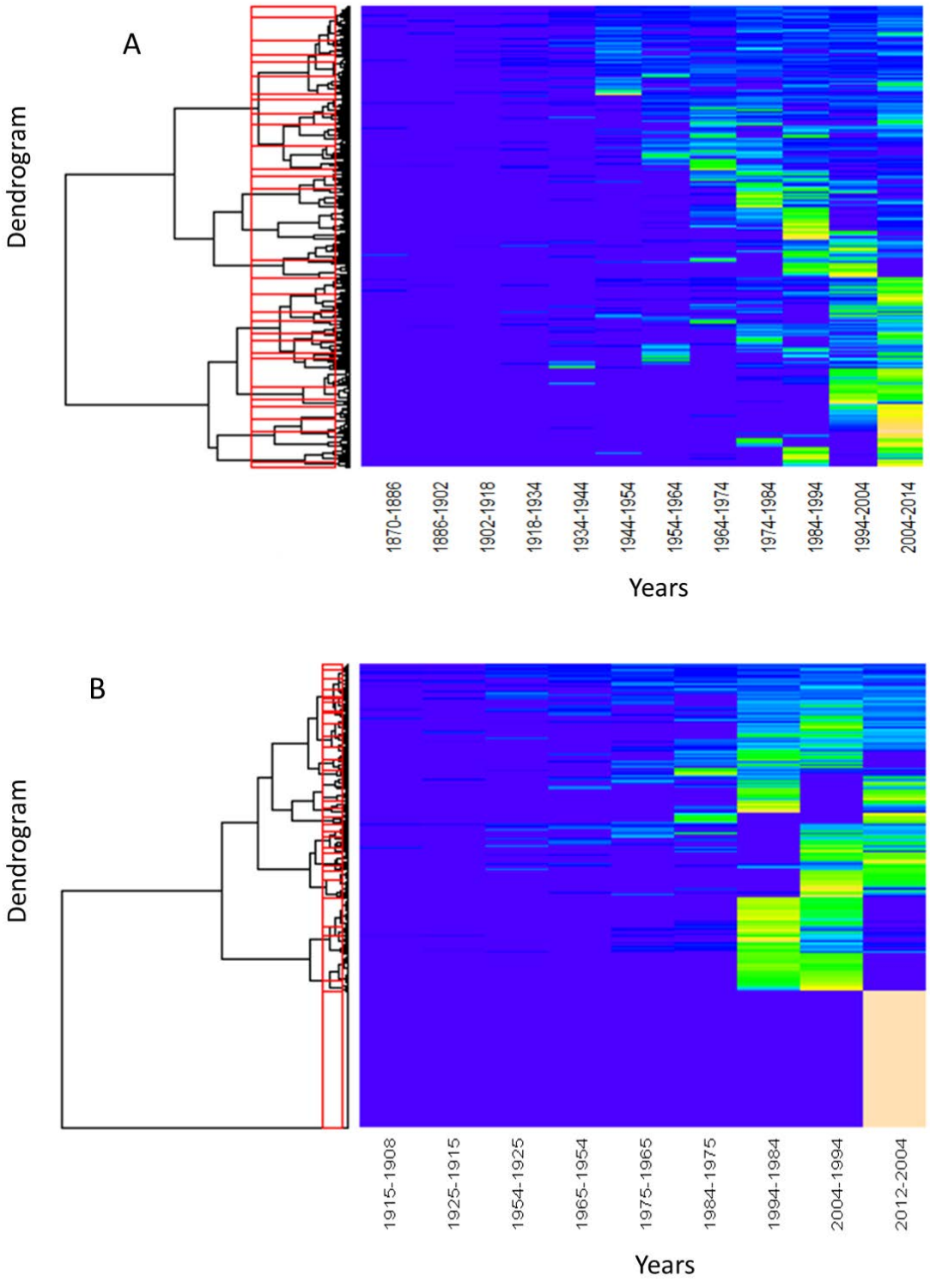

Figure S3. Heatmaps of dendograms of the hierarchical cluster analysis for Greifensee (A) and Lake Lugano (B) in positive ionization. The red lines indicate the differentiated clusters with the chosen cluster number k=29.

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