Supplementary Information for

Comprehensive screening of quaternary ammonium surfactants and ionic liquids in wastewater effluents and lake sediments

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Contents

S1 Chemicals **2**

S2 Wastewater effluent samples **3**

S3 Analytical method **3**

S4 Target and suspect screening in wastewater effluent samples **9**

S5 Target and suspect screening in lake sediments **13**
S5.1 Lake Winona surface sediments . . . 14
S5.2 Lake Pepin core . . . 15
S5.3 Duluth Harbor core . . . 18
S5.4 Lake Winona core . . . 21
S5.5 Little Wilson Lake core . . . 24

S6 References **24**

S1 Chemicals

Compounds used as target, surrogate, or internal standard are listed in Table S1. Methanol and acetonitrile (HPLC-grade, Sigma-Aldrich), ultrapure water (18.2 MΩ·cm, EMD Millipore Corp.), formic acid (88%, Fisher Scientific), hydrochloric acid (TraceMetal Grade, Fisher Scientific), citric acid monohydrate (99%, Mallinckrodt), sodium citrate dihydrate (99%, Macron Fine Chemicals), and sodium thiosulfate pentahydrate (99%, Mallinckrodt) were used for sample preparation. Acetonitrile, water, formic acid, and ammonium acetate (all Optima LC/MS grade, Fisher Scientific) were used to prepare mobile phases for mass spectrometry analysis.

Table S1 Name, supplier, CAS number, and purity of target, surrogate, and internal standards (ISTD).

compound	abbreviation	type	supplier	CAS no. [a]	purity [b]
1-ethyl-3-methylimidazolium	C_2-IMI	target	Acros Organics	65039-09-0	99.3%
1-butyl-3-methylimidazolium	C_4-IMI	target	Acros Organics	79917-90-1	99.8%
1-butylpyridinium	C_4-PYR	target	Alfa Aesar	1124-64-7	100%
1-butyl-1-methylpyrrolidinium	C_4-MPY	target	TCI America	479500-35-1	98.9%
1-butyl-1-methylpiperidinium	C_4-PIP	target	TCI America	94280-72-5	98.7%
1-hexyl-3-methylimidazolium	C_6-IMI	target	Sigma-Aldrich	171058-17-6	98.0%
1-octyl-3-methylimidazolium	C_8-IMI	target	Acros Organics	64697-40-1	99.0%
1-decyl-3-methylimidazolium	C_{10}-IMI	target	Sigma-Aldrich	171058-18-7	98.0%
decyltrimethylammonium	C_{10}-ATMAC	target	TCI America	2082-84-0	100%
decyldimethylbenzylammonium	C_{10}-BAC	target	Sigma-Aldrich	965-32-2	99.0%
dodecyltrimethylammonium	C_{12}-ATMAC	target	Alfa Aesar	1119-94-4	99.5%
dodecyldimethylbenzylammonium	C_{12}-BAC	target	Alfa Aesar	139-07-1	98.0%
didodecyldimethylammonium	C_{12}-DADMAC	target	Santa Cruz	3282-73-3	99.9%
tetradecyltrimethylammonium	C_{14}-ATMAC	target	Acros Organics	1119-97-7	99.7%
tetradecyldimethylbenzylammonium	C_{14}-BAC	target	TCI America	139-08-2	90.1%
dihexadecyldimethylammonium	C_{16}-DADMAC	target	Santa Cruz	70755-47-4	99.3%
1-hexadecylpyridinium	C_{16}-PYR	target	TCI America	6004-24-6	94.6%
octadecyltrimethylammonium	C_{18}-ATMAC	target	Alfa Aesar	112-03-8	95.3%
octadecyldimethylbenzylammonium	C_{18}-BAC	target	Santa Cruz	122-19-0	98.5%
dioctadecyldimethylammonium	C_{18}-DADMAC	target	Acros Organics	3700-67-2	100%
benzethonium		target	TCI America	121-54-0	94.4%
domiphen		target	Alfa Aesar	538-71-6	99.5%
tetraoctylammonium	C_8-TAA	surrogate	Sigma-Aldrich	14866-33-2	100%
decyltrimethylammonium-d9	C_{10}-ATMAC-d9	surrogate	Santa Cruz	10108-87-9 [d]	99.2% [c]
tetradecyldimethylbenzylammonium-d7	C_{14}-BAC-d7	surrogate	Santa Cruz	139-08-2 [d]	99.3% [c]
tetraethylammonium	C_2-TAA	ISTD	TCI America	71-91-0	100%
tetrapropylammonium	C_3-TAA	ISTD	Acros Organics	1941-30-6	99.2%
tetrabutylammonium	C_4-TAA	ISTD	Acros Organics	37451-68-6	92.6%
tetrahexylammonium	C_6-TAA	ISTD	Sigma-Aldrich	4328-13-6	99.8%

[a] For the purchased compounds, includes counter-anion information; [b] According to certificate of analysis, accounts for water content if provided; [c] Isotopic purity; [d] CAS number of unlabeled compound.

S2 Wastewater effluent samples

Table S2 provides an overview of general water chemistry parameters of the 13 wastewater effluent samples as well as of the size and biological treatment of the sampled wastewater treatment plants.

Table S2 Sample ID and type, pH, total non-purgeable organic carbon (TOC), and total inorganic carbon (TIC) of wastewater effluent samples as well as properties of the corresponding treatment plant.

ID	type [a]	pH	TOC [b]	TIC [b]	plant size [c]	biological treatment
1	24-h	7.5	5.8	44	4.5 mgd	activated sludge
2	24-h	7.6	8.8	35	2.7 mgd	aeration tanks
3	24-h	7.7	8.7	58	38 mgd	activated sludge
4	24-h	7.8	7.2	65	32 mgd	activated sludge
5	24-h	7.6	7.7	49	12 mgd	activated sludge
6	24-h	7.8	9.1	42	29 mgd	activated sludge
7	24-h	7.7	9.6	48	314 mgd	activated sludge
8	24-h	8.1	8.7	56	0.5 mgd	membrane bioreactor
9	grab	7.3	7.0	58	5.2 mgd	aerated filter
10	grab	7.5	12	46	0.9 mgd	activated sludge
11	grab	8.1	6.3	133	1.1 mgd	rotating surfaces
12	grab	7.4	7.8	84	4.8 mgd	activated sludge with air
13	grab	6.3	6.2	74	19 mgd	activated sludge with O_2

[a] 24-hour composite or grab sample; [b] As mg C L^{-1} determined with a Shimadzu TOC-L analyzer; [c] Wastewater treatment plant capacity in million gallons per day.

S3 Analytical method

Samples were analyzed by liquid chromatography high-resolution mass spectrometry (LC-HRMS). For LC, a linear gradient with 0.1% formic acid in acetonitrile (B) and 0.1% formic acid in an aqueous solution of 5 mM ammonium acetate (A) was used. Initial gradient conditions were 98% B, which was held for 5.5 min at a flow rate of 1 μL/min. The flow rate was subsequently lowered to 0.3 μL/min in 0.5 min, after which the solvent composition was changed from 98% to 80% B in 20 min and from 80% to 2% B in 4 min. Final gradient conditions were held for 2 min before returning to 98% B and 1 μL/min flow rate in 1 min and equilibrating for 12 min. HRMS was performed with nanoflow positive electrospray ionization (5 kV spray voltage, 275°C source temperature), full scan acquisition (m/z: 70 − 700, resolution: 30,000), and data-dependent MS/MS scans for the top 5 most intense ions from a candidate list (HCD fragmentation, resolution: 15,000, normalized collision energy: 60, isolation width: 3 m/z units). Mass spectrometry parameters including retention time, accurate mass, and the two most intense MS/MS fragments are listed in Table S3 for targets and surrogate standards and in Table S4 for detected suspects and internal standards. In Table S5, a summary of the settings used in the enviMass workflow is given.

Limits of detection and quantification (LOD and LOQ) were calculated for each measurement sequence from peak areas of target compounds found in solvent blanks containing only surrogate and internal standards ($n = 4 - 6$) as shown in eqs S1 and S2,

$$\mathrm{LOD} = \mathrm{AR_{mean}} + 3 \times \mathrm{AR_{stdev}} \tag{S1}$$

$$\mathrm{LOQ} = \mathrm{AR_{mean}} + 10 \times \mathrm{AR_{stdev}} \tag{S2}$$

where $\mathrm{AR_{mean}}$ and $\mathrm{AR_{stdev}}$ are the mean and standard deviation of area ratios of target compounds to surrogate/internal standards in blank samples. For compounds with very small peak areas in blank samples, the LOQ was set to 50% of the smallest calibration standard. The presence of target compounds quantified above LOQ was manually verified by comparing MS/MS spectra of samples and standards. The presence of the two most intense MS/MS fragments (see Table S3 in the ESI[†]) was used for a positive identification. Recoveries, QAC concentrations in unspiked effluent and sediment samples, and accumulation rates of QACs in sediments were calculated with eqs. S3–S6,

$$\mathrm{R}_a = \frac{\left(\mathrm{AR^{SP}_{a/i}} - \mathrm{AR^{NS}_{a/i}}\right) \cdot \mathrm{RF_{a/i}}}{\mathrm{C_{SP}}} \tag{S3}$$

$$\mathrm{R}_r = \frac{\left(\mathrm{AR^{SP}_{a/s}} - \mathrm{AR^{NS}_{a/s}}\right) \cdot \mathrm{RF_{a/s}}}{\mathrm{C_{SP}}} \tag{S4}$$

$$\mathrm{C} = \frac{\left(\mathrm{AR^{NS}_{a/i}} - \mathrm{AR^{MB}_{a/i}}\right) \cdot \mathrm{RF_{a/i}}}{\mathrm{R}_a} = \frac{\left(\mathrm{AR^{NS}_{a/s}} - \mathrm{AR^{MB}_{a/s}}\right) \cdot \mathrm{RF_{a/s}}}{\mathrm{R}_r} \tag{S5}$$

$$\mathrm{ACR} = \frac{\mathrm{C}}{\mathrm{FF}} \cdot \mathrm{SAR} \tag{S6}$$

where R_a and R_r are absolute and relative total method recoveries, $\mathrm{AR_{a/i}}$ and $\mathrm{AR_{a/s}}$ are area ratios of analyte vs. ISTD and analyte vs. surrogate, respectively, for non-spiked samples (NS), spiked samples (SP), and method blanks (MB), RF_x are response factors (slope of calibration curve of AR_x vs. spiked concentrations), $\mathrm{C_{SP}}$ are nominal concentrations added to spiked samples, C are final QAC concentrations in ng/L or ng/g for effluent and sediment samples, respectively, FF is the lake-specific focusing factor,[1] SAR is the lake-specific sediment accumulation rate,[2] and ACR is the accumulation rate of QACs in ng $\mathrm{cm^{-2}\ year^{-1}}$.

Table S3 Molecular formula, corresponding surrogate and internal standards (ISTD), retention time (RT), accurate mass (m/z), and two most intense MS/MS fragments of targets and surrogate standards.

compound	abbreviation	type	ISTD	surrogate	formula	RT (min)	m/z	fragments
1-ethyl-3-methylimidazolium	C_2-IMI	target	C_2-TAA	C_{10}-ATMAC-d9	$C_6H_{11}N_2$	29.4 – 31.2	111.0917	83.06/111.09
1-butyl-3-methylimidazolium	C_4-IMI	target	C_3-TAA	C_{10}-ATMAC-d9	$C_8H_{15}N_2$	25.7 – 27.3	139.1230	83.06/139.12
1-butylpyridinium	C_4-PYR	target	C_2-TAA	C_{10}-ATMAC-d9	$C_9H_{14}N$	26.8 – 28.4	136.1121	80.05/136.11
1-butyl-1-methylpyrrolidinium	C_4-MPY	target	C_2-TAA	C_{10}-ATMAC-d9	$C_9H_{20}N$	27.1 – 29.0	142.1590	86.10/142.16
1-butyl-1-methylpiperidinium	C_4-PIP	target	C_2-TAA	C_{10}-ATMAC-d9	$C_{10}H_{22}N$	26.8 – 28.5	156.1747	100.11/156.17
1-hexyl-3-methylimidazolium	C_6-IMI	target	C_3-TAA	C_{10}-ATMAC-d9	$C_{10}H_{19}N_2$	23.9 – 24.9	167.1543	83.06/167.15
1-octyl-3-methylimidazolium	C_8-IMI	target	C_3-TAA	C_{10}-ATMAC-d9	$C_{12}H_{23}N_2$	23.3 – 24.2	195.1856	83.06/195.19
1-decyl-3-methylimidazolium	C_{10}-IMI	target	C_3-TAA	C_{10}-ATMAC-d9	$C_{14}H_{27}N_2$	22.8 – 23.9	223.2169	83.06/223.22
decyltrimethylammonium	C_{10}-ATMAC	target	C_3-TAA	C_{10}-ATMAC-d9	$C_{13}H_{30}N$	23.1 – 24.2	200.2373	85.09/200.24
decyldimethylbenzylammonium	C_{10}-BAC	target	C_4-TAA	C_{14}-BAC-d7	$C_{19}H_{34}N$	21.8 – 23.1	276.2686	91.05/184.21
dodecyltrimethylammonium	C_{12}-ATMAC	target	C_3-TAA	C_{10}-ATMAC-d9	$C_{15}H_{34}N$	22.9 – 24.0	228.2686	85.09/228.27
dodecyldimethylbenzylammonium	C_{12}-BAC	target	C_4-TAA	C_{14}-BAC-d7	$C_{21}H_{38}N$	21.7 – 23.0	304.2999	91.05/212.24
didodecyldimethylammonium	C_{12}-DADMAC	target	C_6-TAA	C_8-TAA	$C_{26}H_{56}N$	20.9 – 22.3	382.4407	214.25/382.44
tetradecyltrimethylammonium	C_{14}-ATMAC	target	C_3-TAA	C_{10}-ATMAC-d9	$C_{17}H_{38}N$	22.7 – 23.8	256.2999	85.09/256.30
tetradecyldimethylbenzylammonium	C_{14}-BAC	target	C_4-TAA	C_{14}-BAC-d7	$C_{23}H_{42}N$	21.5 – 22.9	332.3312	91.05/240.27
1-hexadecylpyridinium	C_{16}-PYR	target	C_4-TAA	C_{14}-BAC-d7	$C_{21}H_{38}N$	22.5 – 23.7	304.2999	80.05/304.30
dihexadecyldimethylammonium	C_{16}-DADMAC	target	C_6-TAA	C_8-TAA	$C_{34}H_{72}N$	20.8 – 22.1	494.5659	270.32/494.57
octadecyltrimethylammonium	C_{18}-ATMAC	target	C_4-TAA	C_{14}-BAC-d7	$C_{21}H_{46}N$	22.3 – 23.6	312.3625	85.09/312.36
octadecyldimethylbenzylammonium	C_{18}-BAC	target	C_4-TAA	C_8-TAA	$C_{27}H_{50}N$	21.3 – 22.7	388.3938	91.05/296.33
dioctadecyldimethylammonium	C_{18}-DADMAC	target	C_6-TAA	C_8-TAA	$C_{38}H_{80}N$	21.0 – 22.3	550.6285	298.35/550.63
benzethonium		target	C_4-TAA	C_{14}-BAC-d7	$C_{27}H_{42}NO_2$	22.1 – 23.5	412.3210	91.05/320.26
domiphen		target	C_4-TAA	C_{14}-BAC-d7	$C_{22}H_{40}NO$	21.6 – 23.1	334.3104	91.05/121.07
tetraoctylammonium	C_8-TAA	surrogate	C_6-TAA	n.a. [a]	$C_{32}H_{68}N$	20.3 – 21.7	466.5346	156.17/254.28
decyltrimethylammonium-d9	C_{10}-ATMAC-d9	surrogate	C_3-TAA	n.a.	$C_{13}H_{21}D_9N$	23.2 – 24.2	209.2929	85.09/209.29
tetradecyldimethylbenzylammonium-d7	C_{14}-BAC-d7	surrogate	C_4-TAA	n.a.	$C_{23}H_{35}D_7N$	21.6 – 22.8	339.3751	98.10/240.27

[a] Not applicable.

Table S4 Molecular formula, corresponding surrogate and internal standards (ISTD), retention time (RT), accurate mass (m/z), and two most intense MS/MS fragments of detected suspects and internal standards.

compound	abbr.	type	ISTD	reference [a]	formula	RT (min)	m/z	fragments
ethylbutyldimethylammonium	$C_{2/4}$-DADMAC	suspect	C_4-TAA	C_{12}-DADMAC	$C_8H_{20}N$	22.3 – 23.6	130.1590	74.10/130.16
butyldimethylbenzylammonium	C_4-BAC	suspect	C_3-TAA	C_{10}-BAC	$C_{13}H_{22}N$	24.2 – 25.5	192.1747	91.05/100.11
dibutyldimethylammonium	C_4-DADMAC	suspect	C_4-TAA	C_{12}-DADMAC	$C_{10}H_{24}N$	22.8 – 23.8	158.1903	102.13/158.19
butylhexyldimethylammonium	$C_{4/6}$-DADMAC	suspect	C_4-TAA	C_{12}-DADMAC	$C_{12}H_{28}N$	21.7 – 22.3	186.2216	130.16/186.22
hexyldimethylbenzylammonium	C_6-BAC	suspect	C_3-TAA	C_{10}-BAC	$C_{15}H_{26}N$	22.8 – 23.8	220.2060	91.05/128.14
dihexyldimethylammonium	C_6-DADMAC	suspect	C_4-TAA	C_{12}-DADMAC	$C_{14}H_{32}N$	22.3 – 23.6	214.2529	130.16/214.25
1-hexylpyridinium	C_6-PYR	suspect	C_3-TAA	C_4-PYR	$C_{11}H_{18}N$	24.3 – 24.5	164.1434	80.05/164.14
octyldimethylbenzylammonium	C_8-BAC	suspect	C_4-TAA	C_{10}-BAC	$C_{17}H_{30}N$	22.0 – 23.5	248.2373	91.05/156.17
dioctyldimethylammonium	C_8-DADMAC	suspect	C_4-TAA	C_{12}-DADMAC	$C_{18}H_{40}N$	21.3 – 22.8	270.3155	158.19/270.32
1-octylpyridinium	C_8-PYR	suspect	C_3-TAA	C_4-PYR	$C_{13}H_2N$	23.7 – 24.4	192.1747	80.05/192.17
didecyldimethylammonium	C_{10}-DADMAC	suspect	C_4-TAA	C_{12}-DADMAC	$C_{22}H_{48}N$	21.1 – 22.5	326.3781	186.22/326.38
ditetradecyldimethylammonium	C_{14}-DADMAC	suspect	C_6-TAA	C_{12}-DADMAC	$C_{30}H_{64}N$	20.7 – 22.0	438.5033	242.28/438.50
hexadecyltrimethylammonium	C_{16}-ATMAC	suspect	C_4-TAA	C_{14}-ATMAC	$C_{19}H_{42}N$	22.5 – 23.8	284.3312	85.09/284.33
hexadecyldimethylbenzylammonium	C_{16}-BAC	suspect	C_4-TAA	C_{14}-BAC	$C_{25}H_{46}N$	21.3 – 22.8	360.3625	91.05/268.30
docosyltrimethylammonium	C_{22}-ATMAC	suspect	C_4-TAA	C_{18}-ATMAC	$C_{25}H_{54}N$	22.1 – 23.5	368.4251	85.09/368.43
tetraethylammonium	C_2-TAA	ISTD	n.a. [b]	n.a.	$C_8H_{20}N$	30.0 – 31.7	130.1590	86.10/130.16
tetrapropylammonium	C_3-TAA	ISTD	n.a.	n.a.	$C_{12}H_{28}N$	23.4 – 24.4	186.2216	114.13/186.22
tetrabutylammonium	C_4-TAA	ISTD	n.a.	n.a.	$C_{16}H_{36}N$	21.6 – 23.0	242.2842	142.16/242.28
tetrahexylammonium	C_6-TAA	ISTD	n.a.	n.a.	$C_{24}H_{52}N$	20.7 – 22.0	354.4094	128.14/198.22

[a] Reference target compound, whose response factor was used for calculating concentrations; [b] Not applicable.

Table S5 enviMass v4.0 settings.

topic	parameter	setting
Peak picking	Filter RT range	yes
	Lower RT bound	15 min
	Upper RT bound	30 min
	Filter mass range	no
	Include parameter estimation	yes
	Max RT gap in an EIC	300 sec
	Min data points per peak...	5
	...within a given RT window	20 sec
	Max RT gap length	10 sec
	Max RT width of single peak	120 sec
	Min signal/noise	5
	Min signal/base	2
	Max number of peaks per EIC	5
	Peak intensity given as	peak area (sum intensity)
	Peak mass definition	Mean
Mass recalibration	Include for positive ionization	yes
	Reference compounds	ISTD and targets
	m/z tolerance	±5 ppm
	Max m/z correction	2 ppm
	RT tolerance	60 sec
	Include for negative ionization	no
Blind	Blank/blind intensity threshold	5
	m/z tolerance	±5 ppm
	RT tolerance	60 sec
	Subtract sample files with	method blank
Screening [a]	RT tolerance vs expected	60 sec
	RT tolerance (isotope pattern)	10 sec
	m/z tolerance	±8 ppm
	Intensity tolerance	30%
	Scoring	0.8
	Exclude matches below cutoff score	FALSE
	Screen only most intense isotopologue peak	FALSE
	Restrict screening to latest files	FALSE
	Adducts	M+
Profiles	Maximum number of files	100
	Peak deviation m/z tolerance	12 ppm
	Peak deviation RT tolerance	60 sec
Homolog series	Homolog units	C_2H_4, C_2H_4O, C_4H_8
	Charges	1
	Min change in RT	−60 sec
	Max change in RT	60 sec
	RT tolerance for homolog pairs	20 sec
	m/z tolerance	±10 ppm
	Min number of homologs in a series	5
	Filter by sample-vs-blind intensity ratio	yes
	Sample-vs-blind intensity ratio threshold:	5

[a] Same settings for ISTD and targets.

Table S6 Absolute and relative recoveries of target compounds spiked into matrix-free control samples.

target	absolute recovery		relative recovery	
compound	**in ultrapure water [a]**	**in citrate buffer [b]**	**in ultrapure water**	**in citrate buffer**
C_2-IMI	77%	1%	95%	2%
C_4-IMI	86%	13%	96%	1%
C_4-PYR	75%	7%	92%	5%
C_4-MPY	73%	7%	91%	7%
C_4-PIP	69%	9%	84%	8%
C_6-IMI	68%	102%	76%	91%
C_8-IMI	82%	103%	91%	94%
C_{10}-IMI	86%	96%	95%	88%
C_{10}-ATMAC	81%	105%	90%	96%
C_{10}-BAC	74%	103%	105%	160%
C_{12}-ATMAC	84%	93%	93%	86%
C_{12}-BAC	73%	94%	104%	150%
C_{12}-DADMAC	66%	35%	83%	97%
C_{14}-ATMAC	78%	86%	86%	79%
C_{14}-BAC	66%	61%	93%	94%
C_{16}-DADMAC	78%	50%	97%	136%
C_{16}-PYR	65%	62%	91%	96%
C_{18}-ATMAC	61%	43%	86%	67%
C_{18}-BAC	58%	30%	81%	105%
C_{18}-DADMAC	76%	46%	94%	127%
benzethonium	68%	78%	90%	120%
domiphen	77%	83%	109%	131%

[a] Matrix-free control for SPE of effluent samples; [b] Matrix-free control for SPE of sediment samples.

S4 Target and suspect screening in wastewater effluent samples

Table S7 lists absolute and relative recoveries determined in spiked effluent samples, method detection and quantification limits, and concentrations measured in method blanks. Recoveries were determined from effluent samples ($n = 13$) spiked with 1000 ng/L targets either vs. the corresponding internal standard (absolute recoveries) or surrogate standard (relative recoveries), see Table S3 for surrogate and internal standard assignment. Results of qualitative suspect screening (detected peaks of targets and suspects with enviMass and summary of homolog screening) are given in Table S9. Final QAC concentrations in effluent samples are shown in Tables S8 and S10 for targets and suspects, respectively.

Table S7 Limits of detection and quantification (LOD and LOQ), average concentrations in method blanks (MB), absolute and relative recoveries of all targets as well as number of effluent samples with target levels determined above LOD and LOQ, respectively, average concentration of targets across all 13 samples, and maximum concentrations quantified for each target in the 13 effluent samples.

target compound	LOD (ng/L)	LOQ (ng/L)	MB (ng/L)	absolute recovery	relative recovery	no. of samples [a] >LOD	>LOQ	average (ng/L)	maximum (ng/L)
C_2-IMI	11	26	10	46 ± 16%	79 ± 32%	0	0		
C_4-IMI	3.6	15	3.9	82 ± 25%	128 ± 25%	0	0		
C_4-PYR	7.1	22	7.1	54 ± 13%	94 ± 8%	13	10	53	102
C_4-MPY	3.6	27	3.6	50 ± 10%	77 ± 10%	0	0		
C_4-PIP	2.0	24	2.1	55 ± 15%	85 ± 9%	0	0		
C_6-IMI	1.6	19	2.9	69 ± 17%	120 ± 15%	1	0		
C_8-IMI	1.8	20	2.9	58 ± 22%	103 ± 4%	0	0		
C_{10}-IMI	1.3	20	2.1	61 ± 22%	104 ± 14%	0	0		
C_{10}-ATMAC	1.4	22	2.8	55 ± 23%	92 ± 3%	13	2	3.0	20
C_{10}-BAC	0.9	12	1.4	81 ± 13%	127 ± 27%	1	0		
C_{12}-ATMAC	15	26	19	55 ± 19%	91 ± 12%	1	0		
C_{12}-BAC	4.0	19	12	74 ± 14%	116 ± 24%	12	9	23	143
C_{12}-DADMAC [b]	179	237	89	16 ± 8%	n.a.	6	5	117	627
C_{14}-ATMAC	6.0	28	4.8	46 ± 22%	72 ± 12%	0	0		
C_{14}-BAC	5.1	30	15	47 ± 16%	73 ± 16%	13	11	216	1386
C_{16}-DADMAC [b]	49	311	43	7.0 ± 4%	n.a.	11	3	71	384
C_{16}-PYR	6.6	54	11	23 ± 7%	40 ± 10%	5	0		
C_{18}-ATMAC	6.7	102	27	13 ± 5%	20 ± 6%	13	1	7.1	93
C_{18}-BAC [c]	7.2	100	14	12 ± 6%	19 ± 8%	12	6	107	459
C_{18}-DADMAC [b]	146	338	260	5.8 ± 4%	n.a.	13	11	1025	2715
benzethonium	1.6	25	4.7	53 ± 15%	81 ± 23%	13	2	6.9	70
domiphen	2.4	21	4.7	65 ± 15%	100 ± 19%	0	0		

[a] Only counted with positive MS/MS spectra match; [b] Results calculated with absolute recoveries due to uncertain surrogate results; [c] Relative recovery and results calculated with C_{14}-BAC-d7 as surrogate standard instead of C_8-TAA.

Table S8 Concentrations of targets quantified in effluent samples given in ng/L, corrected for levels quantified in method blank and for mean relative (or absolute) recoveries with samples below LOQ shown as "<(LOQ-MB)" and samples below LOD as well as samples without MS/MS confirmation set to zero.

	WWTP												
target	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
C_2-IMI	0	0	0	0	0	0	0	0	0	0	0	0	0
C_4-IMI	0	0	0	0	0	0	0	0	0	0	0	0	0
C_4-PYR	53	98	< 15	102	98	87	58	55	< 15	76	< 15	45	21
C_4-MPY	0	0	0	0	0	0	0	0	0	0	0	0	0
C_4-PIP	0	0	0	0	0	0	0	0	0	0	0	0	0
C_6-IMI	0	0	0	0	0	0	0	< 16	0	0	0	0	0
C_8-IMI	0	0	0	0	0	0	0	0	0	0	0	0	0
C_{10}-IMI	0	0	0	0	0	0	0	0	0	< 17	0	0	0
C_{10}-ATMAC	< 19	< 19	< 19	< 19	< 19	< 19	20	< 19	< 19	< 19	< 19	< 19	19
C_{10}-BAC	< 11	< 11	< 11	< 11	< 11	< 11	< 11	< 11	< 11	< 11	< 11	< 11	< 11
C_{12}-ATMAC	0	0	< 7.3	0	0	0	0	0	0	0	0	0	0
C_{12}-BAC	4.6	24	7.2	13	8.7	< 6.3	29	< 6.3	39	0	143	27	< 6.3
C_{12}-DADMAC [a]	297	0	627	< 147	243	171	0	0	0	0	0	189	0
C_{14}-ATMAC	0	0	0	0	0	0	0	0	0	< 17	0	0	0
C_{14}-BAC	23	91	109	10	25	18	92	< 15	557	222	1386	279	< 15
C_{16}-DADMAC [a]	< 268	< 268	240	0	< 268	< 268	< 268	0	< 268	< 268	< 268	384	297
C_{16}-PYR [a]	0	< 43	< 43	< 43	0	0	< 43	0	< 43	0	< 43	0	0
C_{18}-ATMAC [a]	< 75	93	< 75	< 75	< 75	< 75	< 75	< 75	< 75	< 75	< 75	< 75	< 75
C_{18}-BAC [a]	< 86	139	181	< 86	< 86	< 86	95	0	320	196	< 86	459	< 86
C_{18}-DADMAC [a]	642	1054	746	< 78	1066	1452	486	< 78	1839	1094	661	2715	1570
benzethonium	< 20	20	< 20	< 20	< 20	70	< 20	< 20	< 20	< 20	< 20	< 20	< 20
domiphen	< 17	< 17	0	< 17	< 17	0	< 17	0	0	< 17	0	0	0

[a] Semi-quantitative results.

Table S9 Number of peaks, targets, suspects, and homolog series picked/detected by enviMass workflow and comparison with manual target screening for all 13 effluent samples, both method blanks (MB), and the highest level standard (Std).

				false[d]			homolog series[e]		
WWTP	**peaks**[a]	**in MB**[b]	**targets** [c]	**pos.**	**neg.**	**suspects** [c]	C_2H_4	C_2H_4O	C_4H_8
1	5328	1265	7	0	5	11	75	50	8
2	6658	1358	9	0	3	11	368	123	22
3	5761	1519	8	0	5	11	104	33	16
4	6074	1344	3	0	9	7	92	35	5
5	6186	1337	8	0	4	12	258	85	10
6	6426	1402	8	0	3	16	176	156	13
7	6247	1404	11	1	2	12	162	61	6
8	6512	1396	4	0	5	6	78	357	4
9	7421	1042	10	0	1	14	256	193	20
10	8551	869	4	0	8	15	666	112	10
11	4483	949	10	0	1	16	362	19	1
12	6153	950	10	1	2	12	553	82	18
13	6073	959	8	1	3	17	360	63	39
Std	1310	487	20	0	2	11	5	0	1
MB-1	3067		17			16			
MB-2	4694		19			16			

[a] Total number of peaks picked by enviMass workflow; [b] number of peaks also present in method blank;
[c] number of targets/suspects detected by enviMass workflow above method blank;
[d] false positive and false negative targets picks by enviMass (all positive hits) compared to manual target screening (all detections >LOD);
[e] number of homolog series detected by enviMass workflow (see restriction settings in Table S5).

Table S10 Semi-quantitative concentrations in ng/L of suspects detected in wastewater effluent samples (for details see main manuscript) confirmed by expected MS/MS fragments. Samples below LOQ are shown as "<(LOQ-MB)" and samples below LOD are set to zero.

		WWTP												
suspect	**recovery** [a]	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
$C_{2/4}$-DADMAC	30%	254	79	261	246	248	183	139	201	220	0	93	303	23
C_4-BAC	100%	< 15	< 15	< 15	< 15	< 15	< 15	< 15	< 15	< 15	< 15	< 15	< 15	< 15
C_4-DADMAC	30%	< 67	< 67	0	0	< 67	0	< 67	0	0	< 67	< 67	< 67	< 67
$C_{4/6}$-DADMAC	30%	0	0	< 67	0	0	< 67	< 67	0	< 67	< 67	0	0	0
C_6-BAC	100%	< 15	< 15	< 15	< 15	< 15	< 15	< 15	< 15	< 15	< 15	< 15	< 15	< 15
C_6-DADMAC	25%	< 83	0	0	< 83	0	0	0	< 83	0	0	0	0	0
C_6-PYR	50%	121	127	119	96	157	115	112	124	61	127	45	68	86
C_8-BAC	100%	< 15	0	0	0	0	0	0	< 15	0	0	< 15	0	0
C_8-DADMAC	25%	0	< 81	0	0	< 81	< 81	0	< 81	0	< 81	0	0	0
C_8-PYR	45%	0	0	0	0	0	< 45	0	< 45	< 45	55	0	0	0
C_{10}-DADMAC	20%	112	95	102	0	133	< 101	< 101	< 101	1009	< 101	348	771	< 101
C_{14}-DADMAC	12%	299	0	220	0	213	169	< 168	0	0	0	0	370	291
C_{16}-ATMAC	28%	< 73	< 73	< 73	< 73	< 73	< 73	< 73	< 73	< 73	< 73	< 73	< 73	< 73
C_{16}-BAC	31%	69	294	222	< 70	78	85	87	< 70	701	67	888	1015	87
C_{22}-ATMAC	13%	489	1298	853	422	905	1216	420	< 144	1430	189	817	1704	854

[a] Absolute recovery used for concentration calculations, based on linear interpolations of results from target compounds of same QAC group.

S5 Target and suspect screening in lake sediments

Average recoveries, detection and quantification limits for measured sediment samples are shown in Table S11. Recoveries were determined from spiked sediment samples ($n = 11$) either vs. the corresponding internal standard (absolute recoveries) or surrogate standard (relative recoveries). Table S12 lists qualitative suspect screening results. Focus-corrected concentrations and accumulation rates for target and suspect QACs are listed in Tables S13-S27.

Table S11 Average limits of detection and quantification (LOD and LOQ), concentrations in method blanks (MB), absolute and relative recoveries, and maximum concentrations measured in the 4 sediment cores (LP: Lake Pepin, LW: Lake Winona, DH: Duluth Harbor, LWL: Little Wilson Lake) and Lake Winona surface (LWS) sediments.

target compound	LOD (ng/g)	LOQ (ng/g)	MB (ng/g)	absolute recovery	relative recovery	LP (ng/g)	LW (ng/g)	DH (ng/g)	LWL (ng/g)	LWS (ng/g)
C_{10}-ATMAC	7.8	25	6.3	$67 \pm 11\%$	$99 \pm 6\%$	< 23	< 27	< 56	0	< 25
C_{10}-BAC	2.8	12	6.6	$79 \pm 9\%$	$123 \pm 17\%$	< 13	< 1.8	72	< 7.1	< 7.1
C_{12}-ATMAC	53	118	68	$68 \pm 11\%$	$98 \pm 17\%$	7.6	175	55	0	< 161
C_{12}-BAC	7.1	22	28	$60 \pm 9\%$	$101 \pm 22\%$	894	34	2471	< 6.1	127
C_{12}-DADMAC	36	75	70	$15 \pm 8\%$	$125 \pm 32\%$	170	1260	726	447	434
C_{14}-ATMAC	14	34	13	$51 \pm 7\%$	$77 \pm 15\%$	< 15	< 40	< 21	0	0
C_{14}-BAC	14	41	24	$46 \pm 14\%$	$95 \pm 10\%$	1599	144	4302	0	211
C_{16}-DADMAC	10	44	21	$7.5 \pm 6\%$	$60 \pm 12\%$	835	1227	1564	< 16	527
C_{16}-PYR	18	42	27	$34 \pm 14\%$	$69 \pm 18\%$	< 26	< 19	46	0	0
C_{18}-ATMAC	19	54	29	$16 \pm 10\%$	$42 \pm 17\%$	242	191	385	0	21
C_{18}-BAC	5.5	18	14	$12 \pm 7\%$	$127 \pm 27\%$	1101	449	2749	0	126
C_{18}-DADMAC	32	86	97	$5.1 \pm 4\%$	$48 \pm 20\%$	1927	5427	3815	1203	2599
benzethonium	6.5	24	28	$65 \pm 12\%$	$110 \pm 11\%$	154	39	1221	19	30
domiphen	6.9	24	15	$57 \pm 14\%$	$109 \pm 22\%$	< 17	28	18	< 20	0

Table S12 Number of peaks, targets, suspects, and homolog series picked/detected by enviMass workflow and comparison with manual target screening for sediment samples averaged for each sampling location.

				false[d]			homolog series[e]		
location	peaks[a]	in MB[b]	targets [c]	pos.	neg.	suspects [c]	C_2H_4	C_2H_4O	C_4H_8
Lake Pepin	7016	1653	10	2	2	10	437	116	41
Duluth Harbor	6592	2724	10	1	3	12	494	144	37
Lake Winona	9823	1372	8	1	4	9	1268	347	136
LW surface	10199	2603	11	4	1	15	2315	997	278

[a] Total number of peaks picked by enviMass workflow; [b] number of peaks also present in method blanks; [c] number of targets/suspects detected by enviMass workflow above method blank; [d] false positive and false negative targets picks by enviMass (all positive hits) compared to manual target screening (all detections >LOD); [e] number of homolog series detected by enviMass workflow (see restriction settings in Table S5).

S5.1 Lake Winona surface sediments

Table S13 Sediment concentrations in ng/g of all target compounds in surface sediment samples from Lake Winona with corresponding distance from the wastewater treatment plant outlet into the lake.

target QAC	distance (km) [a]					
	0.15	0.48 [b]	0.93	1.41	1.90	2.19
C_{10}-ATMAC	< 25	< 27	0	0	0	0
C_{10}-BAC	< 7.1	< 1.8	0	< 7.1	0	< 7.1
C_{12}-ATMAC	< 161	0	0	0	0	0
C_{12}-BAC	95	15	65	58	88	127
C_{12}-DADMAC	313	366	436	254	231	238
C_{14}-ATMAC	0	0	0	0	0	0
C_{14}-BAC	123	73	82	76	145	211
C_{16}-DADMAC [c]	496	525	529	354	259	307
C_{16}-PYR [c]	0	0	0	0	0	0
C_{18}-ATMAC [c]	8.4	21	< 21	0	0	0
C_{18}-BAC	129	103	< 6.1	< 6.1	< 6.1	< 6.1
C_{18}-DADMAC [c]	2655	2044	1840	1153	959	900
benzethonium	14	0	< 12	< 12	< 12	30
domiphen	0	< 18	0	0	0	0

[a] See Kerrigan *et al.*[3] for details; [b] Sample from Lake Winona core at 0 − 2 cm depth;
[c] Semi-quantitative results.

Table S14 Semi-quantitative sediment concentrations in ng/g of detected suspects in surface sediment samples from Lake Winona with corresponding distance from the wastewater treatment plant outlet into the lake.

suspect	recovery [a]	distance (km) [b]					
		0.15	0.48 [c]	0.93	1.41	1.90	2.19
$C_{2/4}$-DADMAC	30%	0	0	0	0	0	0
C_4-BAC	100%	< 15	< 19	< 15	< 15	< 15	< 15
C_4-DADMAC	30%	< 63	< 84	< 63	< 63	< 63	< 63
$C_{4/6}$-DADMAC	30%	126	159	189	214	172	161
C_6-BAC	100%	0	0	0	0	0	0
C_6-DADMAC	25%	263	105	185	166	188	156
C_6-PYR	50%	0	0	0	0	0	0
C_8-BAC	100%	< 15	< 19	0	< 15	< 15	< 15
C_8-DADMAC	25%	0	0	0	0	0	0
C_8-PYR	45%	< 47	< 60	< 47	< 47	< 47	< 47
C_{10}-DADMAC	20%	409	277	288	156	202	215
C_{14}-DADMAC	11%	< 172	< 874	200	< 172	< 172	< 172
C_{16}-ATMAC	33%	< 61	< 55	0	0	< 61	< 61
C_{16}-BAC	29%	163	131	109	85	114	123
C_{22}-ATMAC	16%	87	236	66	< 65	< 65	< 65

[a] Absolute recovery used for concentration calculations, based on linear interpolations of results from target compounds of same QAC group; [b] See Kerrigan *et al.*[3] for details;
[c] Sample from Lake Winona core at 0 − 2 cm depth.

S5.2 Lake Pepin core

Table S15 Focus-corrected sediment concentrations in ng/g of all target compounds in Lake Pepin with corresponding core section depth (top and bottom), average year of accumulation, and focusing factor.

top (cm)	0	10	20	36	52	64	80	104	116	128	144
bottom (cm)	6	14	24	40	56	68	84	108	120	136	152
year [a]	2010	1997	1990	1980	1969	1960	1949	1929	1919	1897	1870
focusing factor [b]	0.25	0.25	0.59	0.66	0.66	0.66	0.93	1.26	1.26	1.19	1.29
C_{10}-ATMAC	< 28	0	0	< 28	0	0	0	0	0	0	0
C_{10}-BAC	< 16	< 16	< 16	< 16	< 16	< 16	< 16	< 16	< 16	94	< 16
C_{12}-ATMAC	< 3.7	< 3.7	< 3.7	12	0	0	0	< 3.7	0	0	0
C_{12}-BAC	1680	1862	360	881	1354	747	139	< 10	< 10	< 10	< 10
C_{12}-DADMAC	250	244	192	222	258	40	98	23	< 1.5	0	< 1.5
C_{14}-ATMAC	0	0	0	< 18	< 18	< 18	0	0	0	0	0
C_{14}-BAC	2068	1926	598	1837	2422	886	80	< 17	< 17	< 17	< 17
C_{16}-DADMAC [c]	0	0	415	1185	1265	671	< 45	< 45	< 45	< 45	< 45
C_{16}-PYR [c]	0	0	0	< 32	< 32	< 32	0	0	0	0	0
C_{18}-ATMAC [c]	70	73	98	362	366	114	< 46	0	< 46	0	< 46
C_{18}-BAC	439	367	309	1358	1669	822	107	17	< 17	< 17	< 17
C_{18}-DADMAC [c]	559	1092	770	2920	2859	1385	435	175	246	78	42
benzethonium	< 21	< 21	< 21	64	233	208	66	< 21	< 21	< 21	< 21
domiphen	< 21	< 21	< 21	< 21	< 21	< 21	< 21	< 21	< 21	< 21	< 21

[a] Determined in Kerrigan *et al.*[2]; [b] From Anger *et al.*[1]; [c] Semi-quantitative results.

Table S16 Focus-corrected sediment accumulation rates in ng cm^{-2} yr^{-1} of all target compounds in Lake Pepin with corresponding core section depth (top and bottom), average year of accumulation, and sediment accumulation rate (SAR).

top (cm)	0	10	20	36	52	64	80	104	116	128	144
bottom (cm)	6	14	24	40	56	68	84	108	120	136	152
year [a]	2010	1997	1990	1980	1969	1960	1949	1929	1919	1897	1870
SAR [a]	0.25	0.25	0.59	0.66	0.66	0.66	0.93	1.26	1.26	1.19	1.29
C_{10}-ATMAC	< 13	0	0	< 13	0	0	0	0	0	0	0
C_{10}-BAC	< 7.2	< 7.2	< 7.2	< 7.2	< 7.2	< 7.2	< 7.2	< 7.2	< 7.2	29	< 7.2
C_{12}-ATMAC	< 1.7	< 1.7	< 1.7	6.4	0	0	0	< 1.7	0	0	0
C_{12}-BAC	316	350	256	493	718	456	90	< 4.5	< 4.5	< 4.5	< 4.5
C_{12}-DADMAC	47	46	136	124	137	24	64	13	< 0.7	0	< 0.7
C_{14}-ATMAC	0	0	0	< 8.6	< 8.6	< 8.6	0	0	0	0	0
C_{14}-BAC	389	362	425	1029	1284	541	52	< 8.1	< 8.1	< 8.1	< 8.1
C_{16}-DADMAC [b]	0	0	295	664	671	409	< 21	< 21	< 21	< 21	< 21
C_{16}-PYR [b]	0	0	0	< 15	< 15	< 15	0	0	0	0	0
C_{18}-ATMAC [b]	13	14	70	203	194	70	< 22	0	< 22	0	< 22
C_{18}-BAC	82	69	219	761	884	502	69	10	< 7.8	< 7.8	< 7.8
C_{18}-DADMAC [b]	105	205	547	1635	1516	845	283	98	121	24	14
benzethonium	< 9.6	< 9.6	< 9.6	36	124	127	43	< 9.6	< 9.6	< 9.6	< 9.6
domiphen	< 9.7	< 9.7	< 9.7	< 9.7	< 9.7	< 9.7	< 9.7	< 9.7	< 9.7	< 9.7	< 9.7

[a] In g cm^{-2} yr^{-1} from Kerrigan *et al.*[2]; [b] Semi-quantitative results.

Table S17 Semi-quantitative sediment concentrations (not focus-corrected) in ng/g of detected suspects in Lake Pepin samples from different depth.

suspect	recovery [a]	average sample depth (cm) 3	12	22	38	54	66	82	106	118	132	148
$C_{2/4}$-DADMAC	30%	0	0	< 267	0	0	0	0	< 267	< 267	0	0
C_4-BAC	100%	< 19	< 19	< 19	< 19	< 19	< 19	< 19	< 19	< 19	< 19	< 19
C_4-DADMAC	30%	< 84	< 84	< 84	< 84	< 84	0	0	0	0	0	0
$C_{4/6}$-DADMAC	30%	< 52	< 52	53	< 52	< 52	< 52	< 52	< 52	< 52	< 52	< 52
C_6-BAC	100%	< 19	< 19	< 19	< 19	0	0	< 19	< 19	< 19	< 19	< 19
C_6-DADMAC	25%	127	< 85	0	0	0	0	0	0	0	0	0
C_6-PYR	50%	< 54	< 54	< 54	< 54	< 54	< 54	< 54	< 54	< 54	< 54	< 54
C_8-BAC	100%	< 19	< 19	< 19	0	< 19	< 19	0	0	0	0	0
C_8-DADMAC	25%	0	< 94	< 94	96	0	0	0	0	0	0	0
C_8-PYR	45%	< 60	< 60	< 60	< 60	0	< 60	0	< 60	0	0	0
C_{10}-DADMAC	20%	< 123	256	254	452	< 123	< 123	0	< 123	0	0	0
C_{14}-DADMAC	11%	0	0	0	0	< 209	0	0	0	0	0	0
C_{16}-ATMAC	33%	75	< 68	< 68	190	142	102	0	0	0	0	0
C_{16}-BAC	29%	256	240	254	821	668	351	< 89	< 89	0	0	0
C_{22}-ATMAC	16%	0	0	0	0	0	0	0	0	< 88	0	0

[a] Absolute recovery used for concentration calculations, based on linear interpolations of results from target compounds of same QAC group.

Table S18 Focus-corrected semi-quantitative sediment accumulation rates in ng cm^{-2} yr^{-1} of detected suspects in Lake Pepin with corresponding core section depth (top and bottom) and average year of accumulation.

top (cm)	0	10	20	36	52	64	80	104	116	128	144
bottom (cm)	6	14	24	40	56	68	84	108	120	136	152
year [a]	2010	1997	1990	1980	1969	1960	1949	1929	1919	1897	1870
$C_{2/4}$-DADMAC	0	0	< 152	0	0	0	0	< 152	< 152	0	0
C_4-BAC	< 11	< 11	< 11	< 11	< 11	< 11	< 11	< 11	< 11	< 11	< 11
C_4-DADMAC	< 48	< 48	< 48	< 48	< 48	0	0	0	0	0	0
$C_{4/6}$-DADMAC	< 30	< 30	64	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30
C_6-BAC	< 11	< 11	< 11	< 11	0	0	< 11	< 11	< 11	< 11	< 11
C_6-DADMAC	95	< 48	0	0	0	0	0	0	0	0	0
C_6-PYR	< 31	< 31	< 31	< 31	< 31	< 31	< 31	< 31	< 31	< 31	< 31
C_8-BAC	< 11	< 11	< 11	0	< 11	< 11	0	0	0	0	0
C_8-DADMAC	0	< 53	< 53	81	0	0	0	0	0	0	0
C_8-PYR	< 34	< 34	< 34	< 34	0	< 34	0	< 34	0	0	0
C_{10}-DADMAC	< 70	193	306	384	< 70	< 70	0	< 70	0	0	0
C_{14}-DADMAC	0	0	0	0	< 119	0	0	0	0	0	0
C_{16}-ATMAC	57	< 39	< 39	161	114	94	0	0	0	0	0
C_{16}-BAC	192	181	306	696	537	324	< 51	< 51	0	0	0
C_{22}-ATMAC	0	0	0	0	0	0	0	0	< 50	0	0

[a] Determined in Kerrigan *et al.*[2].

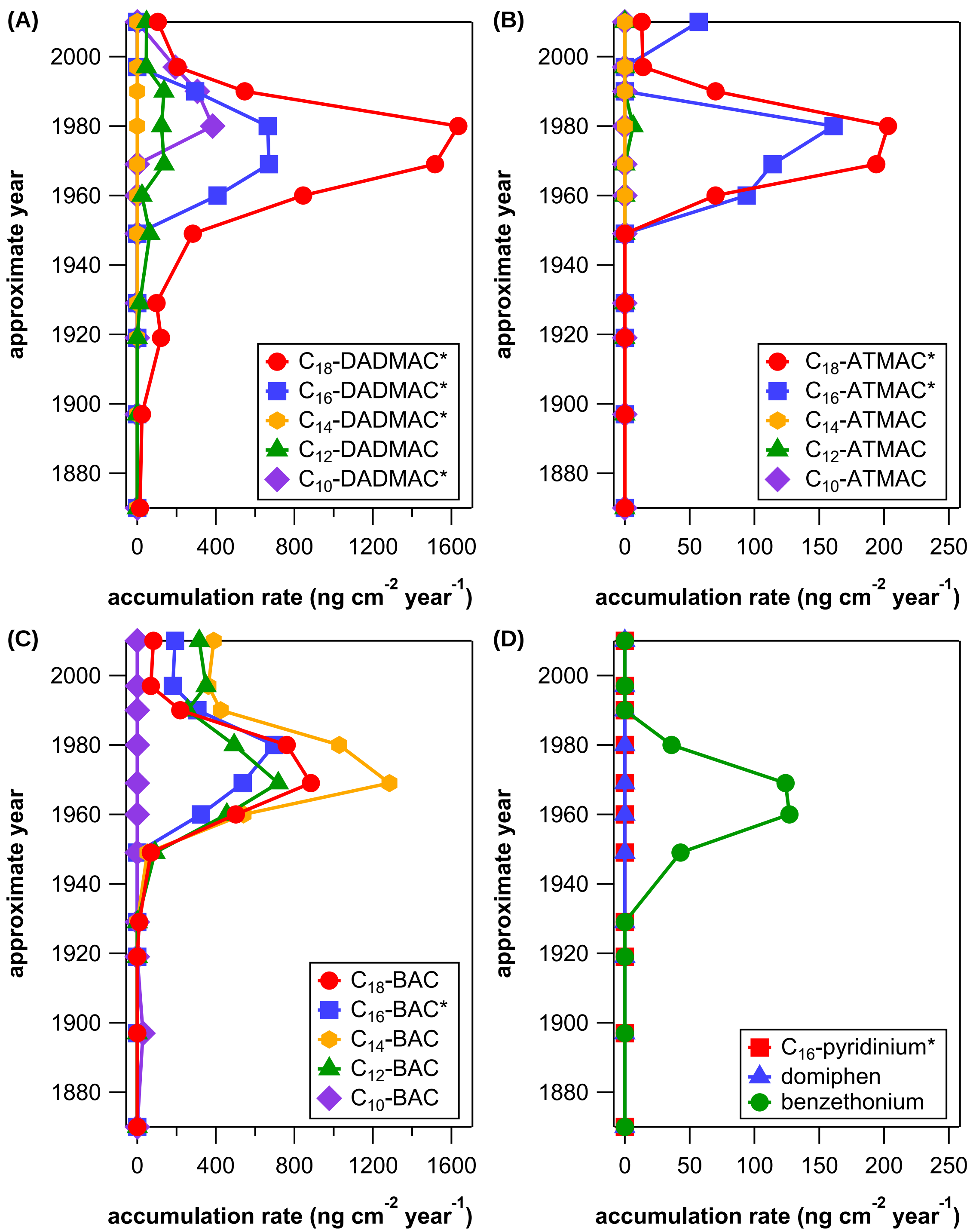

Fig. S1 Focus-corrected sediment accumulation rates of individual target compounds and suspect QACs measured in samples from the Lake Pepin sediment core. Compounds with an asterisk indicate semi-quantitative results. All targets and suspects not shown were below LOQ in all samples.

S5.3 Duluth Harbor core

Table S19 Focus-corrected sediment concentrations in ng/g of all target compounds in Duluth Harbor with corresponding core section depth (top and bottom), average year of accumulation, and focusing factor.

top (cm)	0	4	8	12	16	20	22	24
bottom (cm)	2	6	10	14	18	22	24	26
year [a]	2012	2003	1991	1980	1969	1958	1952	1942
focusing factor [b]	1.98	1.98	1.98	1.98	1.98	1.98	1.98	1.98
C_{10}-ATMAC	< 9.3	< 9.3	< 9.3	0	0	0	0	0
C_{10}-BAC	20	15	36	27	32	13	10	19
C_{12}-ATMAC	20	21	28	28	20	8.2	6.6	11
C_{12}-BAC	349	274	728	949	1248	1000	475	409
C_{12}-DADMAC	105	113	142	147	191	366	28	47
C_{14}-ATMAC	< 11	0	< 11	< 11	< 11	< 11	0	0
C_{14}-BAC	502	455	989	1548	2173	1196	484	251
C_{16}-DADMAC [c]	158	128	253	415	790	782	315	282
C_{16}-PYR [c]	< 7.6	< 7.6	< 7.6	10	23	8.3	< 7.6	12
C_{18}-ATMAC [c]	46	35	128	186	195	58	55	36
C_{18}-BAC	207	187	280	391	620	1389	156	164
C_{18}-DADMAC [c]	668	589	1086	1759	1927		855	1037
benzethonium	181	23	46	45	88	53	266	617
domiphen	< 6.3	< 6.3	6.5	< 6.3	9.3	< 6.3	< 6.3	< 6.3

[a] Determined in Kerrigan *et al.* [2]; [b] From Anger *et al.* [1]; [c] Semi-quantitative results.

Table S20 Focus-corrected sediment accumulation rates in ng cm^{-2} yr^{-1} of all target compounds in Duluth Harbor with corresponding core section depth (top and bottom), average year of accumulation, and sediment accumulation rate (SAR).

top (cm)	0	4	8	12	16	20	22	24
bottom (cm)	2	6	10	14	18	22	24	26
year [a]	2012	2003	1991	1980	1969	1958	1952	1942
SAR [a]	0.26	0.19	0.18	0.19	0.17	0.16	0.16	0.11
C_{10}-ATMAC	< 1.7	< 1.7	< 1.7	0	0	0	0	0
C_{10}-BAC	5.1	2.8	6.6	5.1	5.5	2.1	1.5	2.1
C_{12}-ATMAC	5.2	4.1	5.1	5.3	3.4	1.3	1.0	1.3
C_{12}-BAC	91	52	132	179	216	159	74	46
C_{12}-DADMAC	27	22	26	28	33	58	4.4	5.3
C_{14}-ATMAC	< 1.9	0	< 1.9	< 1.9	< 1.9	< 1.9	0	0
C_{14}-BAC	130	87	179	293	377	190	76	28
C_{16}-DADMAC [b]	41	24	46	79	137	124	49	32
C_{16}-PYR [b]	< 1.4	< 1.4	< 1.4	1.9	4.0	1.3	< 1.4	1.3
C_{18}-ATMAC [b]	12	6.7	23	35	34	9.2	8.5	4.1
C_{18}-BAC	54	36	51	74	107	220	24	18
C_{18}-DADMAC [b]	173	112	197	333	334	1073	133	117
benzethonium	47	4.4	8.3	8.5	15	8.3	42	70
domiphen	< 1.1	< 1.1	1.2	< 1.1	1.6	< 1.1	< 1.1	< 1.1

[a] In g cm^{-2} yr^{-1} from Kerrigan *et al.* [2]; [b] Semi-quantitative results.

Table S21 Semi-quantitative sediment concentrations (not focus-corrected) in ng/g of detected suspects in Duluth Harbor samples from different depth.

		average sample depth (cm)							
suspect	**recovery** [a]	1	5	9	13	17	21	23	25
$C_{2/4}$-DADMAC	30%	0	0	0	0	0	30	0	0
C_4-BAC	100%	< 19	0	< 19	< 19	< 19	< 19	< 19	< 19
C_4-DADMAC	30%	< 81	0	< 81	< 81	< 81	< 81	< 81	< 81
$C_{4/6}$-DADMAC	30%	0	0	0	0	0	0	0	0
C_6-BAC	100%	0	0	0	0	0	< 19	0	< 19
C_6-DADMAC	25%	123	124	209	283	398	0	476	< 72
C_6-PYR	50%	< 53	< 53	< 53	< 53	< 53	< 53	< 53	< 53
C_8-BAC	100%	< 19	< 19	< 19	< 19	< 19	< 19	< 19	< 19
C_8-DADMAC	25%	167	175	232	207	< 93	0	0	< 93
C_8-PYR	45%	< 59	< 59	< 59	< 59	< 59	< 59	< 59	< 59
C_{10}-DADMAC	20%	449	558	608	371	208	< 123	< 123	< 123
C_{14}-DADMAC	11%	< 213	< 213	0	< 213	0	0	< 213	0
C_{16}-ATMAC	33%	75	73	81	130	135	< 70	81	< 70
C_{16}-BAC	29%	271	303	328	476	482	212	147	< 85
C_{22}-ATMAC	16%	< 99	< 99	0	0	0	0	0	0

[a] Absolute recovery used for concentration calculations, based on linear interpolations of results from target compounds of same QAC group.

Table S22 Focus-corrected semi-quantitative sediment accumulation rates in ng cm^{-2} yr^{-1} of detected suspects in Duluth Harbor samples with corresponding core section depth (top and bottom) and average year of accumulation.

top (cm)	0	4	8	12	16	20	22	24
bottom (cm)	2	6	10	14	18	22	24	26
year [a]	2012	2003	1991	1980	1969	1958	1952	1942
$C_{2/4}$-DADMAC	0	0	0	0	0	2.4	0	0
C_4-BAC	< 1.7	0	< 1.7	< 1.7	< 1.7	< 1.7	< 1.7	< 1.7
C_4-DADMAC	< 7.3	0	< 7.3	< 7.3	< 7.3	< 7.3	< 7.3	< 7.3
$C_{4/6}$-DADMAC	0	0	0	0	0	0	0	0
C_6-BAC	0	0	0	0	0	< 1.7	0	< 1.7
C_6-DADMAC	16	12	19	27	35	31	37	< 6.5
C_6-PYR	< 4.8	< 4.8	< 4.8	< 4.8	< 4.8	< 4.8	< 4.8	< 4.8
C_8-BAC	< 1.7	< 1.7	< 1.7	< 1.7	< 1.7	< 1.7	< 1.7	< 1.7
C_8-DADMAC	22	17	21	20	< 8.3	0	0	< 8.3
C_8-PYR	< 5.3	< 5.3	< 5.3	< 5.3	< 5.3	< 5.3	< 5.3	< 5.3
C_{10}-DADMAC	59	54	56	35	18	< 11	< 11	< 11
C_{14}-DADMAC	< 19	< 19	0	< 19	0	0	< 19	0
C_{16}-ATMAC	10	7.0	7.4	12	12	< 6.3	6.4	< 6.3
C_{16}-BAC	35	29	30	45	42	17	12	< 7.6
C_{22}-ATMAC	< 8.8	< 8.8	0	0	0	0	0	0

[a] Determined in Kerrigan *et al.*[2].

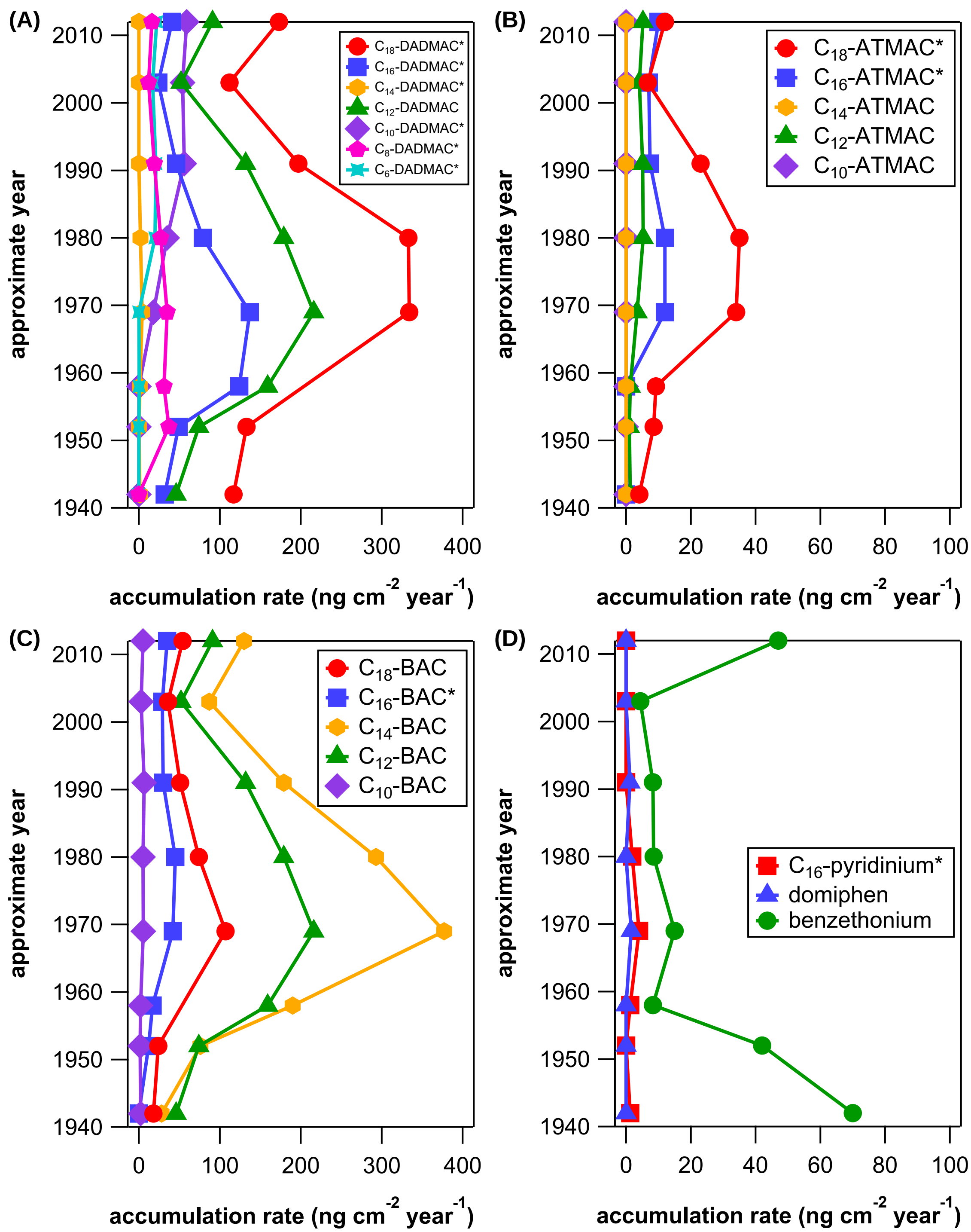

Fig. S2 Focus-corrected sediment accumulation rates of individual target compounds and suspect QACs measured in samples from the Duluth Harbor sediment core. Compounds with an asterisk indicate semi-quantitative results. All targets and suspects not shown were below LOQ in all samples.

S5.4 Lake Winona core

Table S23 Focus-corrected sediment concentrations in ng/g of all target compounds in Lake Winona with corresponding core section depth (top and bottom), average year of accumulation, and focusing factor.

top (cm)	0	8	16	28	36	40	48	52	56	60
bottom (cm)	2	10	18	30	38	42	50	54	58	62
year [a]	2014	2009	2002	1990	1978	1971	1957	1947	1935	1921
focusing factor [b]	1.35	1.35	1.35	1.35	1.35	1.35	1.35	1.35	1.35	1.35
C_{10}-ATMAC	< 20	< 20	< 20	< 20	< 20	< 20	< 20	0	0	< 20
C_{10}-BAC	< 1.3	< 1.3	< 1.3	< 1.3	< 1.3	< 1.3	< 1.3	< 1.3	< 1.3	< 1.3
C_{12}-ATMAC	0	130	16	128	2.6	53	59	59	56	49
C_{12}-BAC	11	14	15	21	12	25	20	< 1.0	< 1.0	< 1.0
C_{12}-DADMAC	271	453	226	934	37	133	< 6.6	< 6.6	90	< 6.6
C_{14}-ATMAC	0	0	0	0	0	0	< 30	0	0	0
C_{14}-BAC	54	107	65	71	79	66	41	< 13	< 13	< 13
C_{16}-DADMAC [c]	389	518	417	909	287	567	11	44	84	60
C_{16}-PYR [c]	0	0	0	0	0	0	< 14	0	0	0
C_{18}-ATMAC [c]	15	101	29	26	142	85	< 22	< 22	< 22	< 22
C_{18}-BAC	76	137	77	332	46	228	11	4.5	16	7.7
C_{18}-DADMAC [c]	1514	2679	1719	4020	845	2406	235	242	408	313
benzethonium	0	4.4	0	< 10	0	< 10	29	< 10	0	< 10
domiphen	< 13	< 13	< 13	< 13	< 13	< 13	25	< 13	< 13	< 13

[a] Determined in Kerrigan *et al.* [2]; [b] From Anger *et al.* [1]; [c] Semi-quantitative results.

Table S24 Focus-corrected sediment accumulation rates in ng cm^{-2} yr^{-1} of all target compounds in Lake Winona with corresponding core section depth (top and bottom), average year of accumulation, and sediment accumulation rate (SAR).

top (cm)	0	8	16	28	36	40	48	52	56	60
bottom (cm)	2	10	18	30	38	42	50	54	58	62
year [a]	2014	2009	2002	1990	1978	1971	1957	1947	1935	1921
SAR [a]	0.32	0.31	0.25	0.17	0.13	0.12	0.11	0.10	0.08	0.07
C_{10}-ATMAC	< 3.3	< 3.3	< 3.3	< 3.3	< 3.3	< 3.3	< 3.3	0	0	< 3.3
C_{10}-BAC	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
C_{12}-ATMAC	0	40	4.0	21	0.3	6.6	6.4	5.9	4.6	3.4
C_{12}-BAC	3.4	4.4	3.8	3.6	1.5	3.1	2.2	< 0.2	< 0.2	< 0.2
C_{12}-DADMAC	86	140	57	157	4.6	16	< 1.1	< 1.1	7.5	< 1.1
C_{14}-ATMAC	0	0	0	0	0	0	< 4.9	0	0	0
C_{14}-BAC	17	33	16	12	10	8.1	4.5	< 2.2	< 2.2	< 2.2
C_{16}-DADMAC [b]	123	161	104	152	36	70	1.2	4.4	6.9	4.2
C_{16}-PYR [b]	0	0	0	0	0	0	< 2.3	0	0	0
C_{18}-ATMAC [b]	4.9	31	7.2	4.3	18	10	< 3.6	< 3.6	< 3.6	< 3.6
C_{18}-BAC	24	43	19	56	5.7	28	1.2	0.5	1.3	0.5
C_{18}-DADMAC [b]	477	830	430	675	107	296	26	24	34	22
benzethonium	0	1.4	0	< 1.7	0	< 1.7	3.2	< 1.7	0	< 1.7
domiphen	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2	2.3	< 2.2	< 2.2	< 2.2

[a] In g cm^{-2} yr^{-1} from Kerrigan *et al.* [2]; [b] Semi-quantitative results.

Table S25 Semi-quantitative sediment concentrations (not focus-corrected) in ng/g of detected suspects in Lake Winona samples from different depth.

		average sample depth (cm)									
suspect	**recovery** [a]	1	9	17	29	37	41	49	53	57	61
$C_{2/4}$-DADMAC	30%	0	< 11	0	0	18	< 11	< 11	0	0	13
C_4-BAC	100%	< 19	< 19	< 19	< 19	< 19	< 19	< 19	< 19	< 19	< 19
C_4-DADMAC	30%	< 84	< 84	< 84	< 84	0	0	0	0	0	0
$C_{4/6}$-DADMAC	30%	159	< 63	142	145	230	146	112	229	191	259
C_6-BAC	100%	0	< 19	0	< 19	0	< 19	0	0	0	0
C_6-DADMAC	25%	105	< 96	154	144	170	135	< 96	174	222	236
C_6-PYR	50%	< 54	< 54	< 54	< 54	< 54	< 54	< 54	< 54	< 54	< 54
C_8-BAC	100%	0	< 19	< 19	0	< 19	< 19	< 19	< 19	< 19	< 19
C_8-DADMAC	25%	0	0	0	0	0	0	0	0	0	0
C_8-PYR	45%	< 60	< 60	0	< 60	< 60	0	0	0	< 60	< 60
C_{10}-DADMAC	20%	277	519	332	211	597	< 125	< 125	< 125	< 125	< 125
C_{14}-DADMAC	11%	< 874	< 874	< 874	0	0	0	0	0	0	0
C_{16}-ATMAC	33%	< 55	< 55	< 55	< 55	68	< 55	< 55	< 55	< 55	< 55
C_{16}-BAC	29%	131	204	152	138	207	104	< 65	0	< 65	< 65
C_{22}-ATMAC	16%	236	312	293	< 167	267	0	0	0	0	< 167

[a] Absolute recovery used for concentration calculations, based on linear interpolations of results from target compounds of same QAC group.

Table S26 Focus-corrected semi-quantitative sediment accumulation rates in ng cm^{-2} yr^{-1} of detected suspects in Lake Winona with corresponding core section depth (top and bottom) and average year of accumulation.

top (cm)	0	8	16	28	36	40	48	52	56	60
bottom (cm)	2	10	18	30	38	42	50	54	58	62
year [a]	2014	2009	2002	1990	1978	1971	1957	1947	1935	1921
$C_{2/4}$-DADMAC	0	< 1.4	0	0	1.7	< 1.4	< 1.4	0	0	0.6
C_4-BAC	< 2.4	< 2.4	< 2.4	< 2.4	< 2.4	< 2.4	< 2.4	< 2.4	< 2.4	< 2.4
C_4-DADMAC	< 10	< 10	< 10	< 10	0	0	0	0	0	0
$C_{4/6}$-DADMAC	37	< 7.8	26	18	22	13	9.1	17	12	13
C_6-BAC	0	< 2.4	0	< 2.4	0	< 2.4	0	0	0	0
C_6-DADMAC	25	< 12	29	18	16	12	< 12	13	14	12
C_6-PYR	< 6.6	< 6.6	< 6.6	< 6.6	< 6.6	< 6.6	< 6.6	< 6.6	< 6.6	< 6.6
C_8-BAC	0	< 2.4	< 2.4	0	< 2.4	< 2.4	< 2.4	< 2.4	< 2.4	< 2.4
C_8-DADMAC	0	0	0	0	0	0	0	0	0	0
C_8-PYR	< 7.3	< 7.3	0	< 7.3	< 7.3	0	0	0	< 7.3	< 7.3
C_{10}-DADMAC	65	119	61	26	56	< 15	< 15	< 15	< 15	< 15
C_{14}-DADMAC	< 107	< 107	< 107	0	0	0	0	0	0	0
C_{16}-ATMAC	< 6.7	< 6.7	< 6.7	< 6.7	6.4	< 6.7	< 6.7	< 6.7	< 6.7	< 6.7
C_{16}-BAC	31	47	28	17	19	9.5	< 8.0	0	< 8.0	< 8.0
C_{22}-ATMAC	55	72	54	< 20	25	0	0	0	0	< 20

[a] Determined in Kerrigan *et al.*[2].

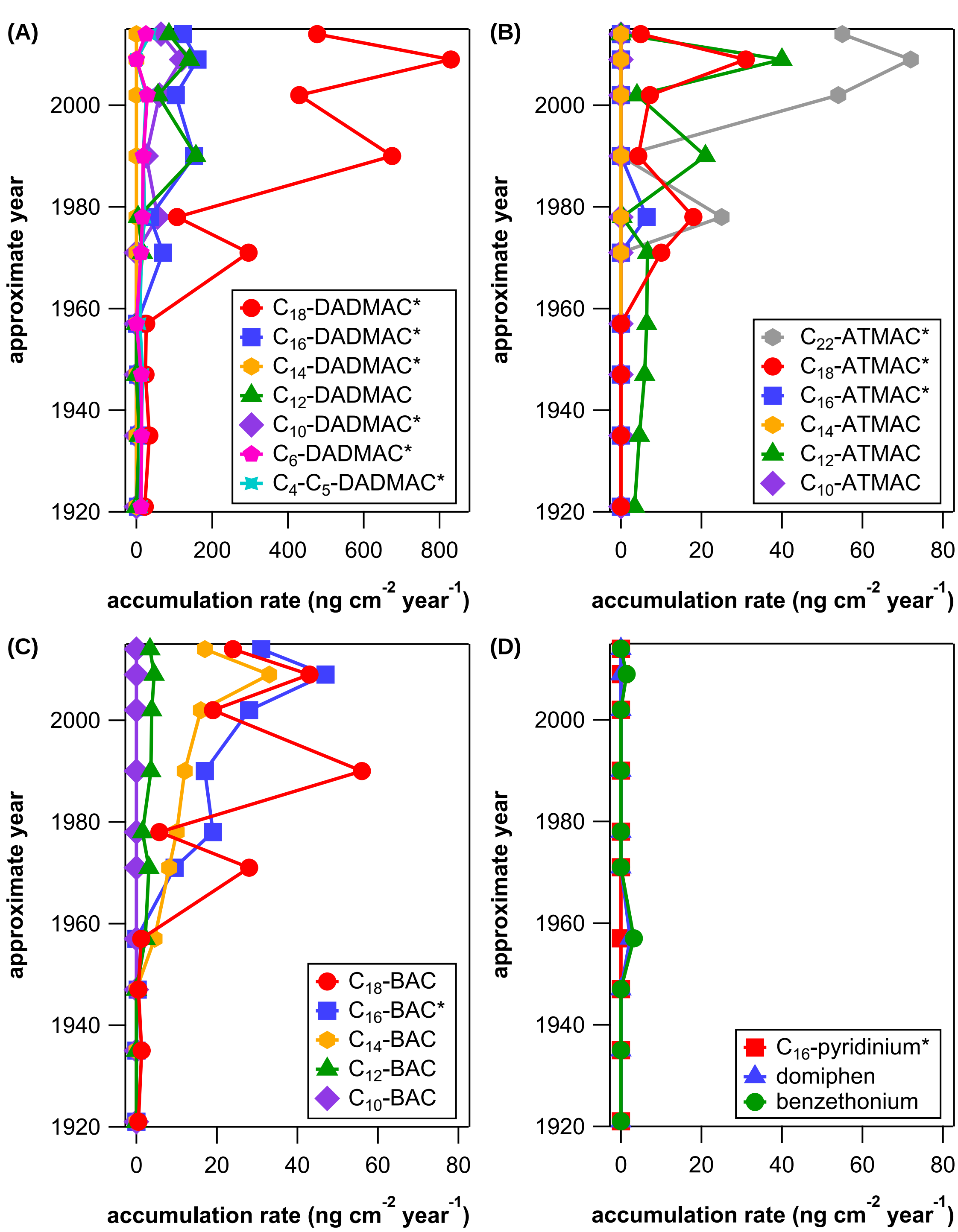

Fig. S3 Focus-corrected sediment accumulation rates of individual target compounds and suspect QACs measured in samples from the Lake Winona sediment core. Compounds with an asterisk indicate semi-quantitative results. All targets and suspects not shown were below LOQ in all samples.

S5.5 Little Wilson Lake core

Table S27 Focus-corrected sediment concentrations in ng/g (left) and sediment accumulation rates in ng cm^{-2} yr^{-1} (right) of all target compounds in Little Wilson Lake with corresponding core section depth (top and bottom), average year of accumulation, focusing factor, and sediment accumulation rate (SAR).

top (cm)	0	16	24	0	16	24
bottom (cm)	2	18	26	2	18	26
year [a]	2013	1990	1970	2013	1990	1970
focusing factor [b]	2.36	2.36	2.36			
SAR [c]				0.04	0.03	0.04
C_{10}-ATMAC	0	0	0	0	0	0
C_{10}-BAC	0	< 3.0	0	0	< 0.1	0
C_{12}-ATMAC	0	0	0	0	0	0
C_{12}-BAC	0	< 2.6	0	0	< 0.1	0
C_{12}-DADMAC	189	< 16	< 16	7.4	< 0.6	< 0.6
C_{14}-ATMAC	0	0	0	0	0	0
C_{14}-BAC	0	0	0	0	0	0
C_{16}-DADMAC [d]	0	< 6.7	0	0	< 0.2	0
C_{16}-PYR [d]	0	0	0	0	0	0
C_{18}-ATMAC [d]	0	0	0	0	0	0
C_{18}-BAC	0	0	0	0	0	0
C_{18}-DADMAC [d]	510	48	< 23	20	1.3	< 0.8
benzethonium	0	8.0	< 5.0	0	0.2	< 0.2
domiphen	< 8.6	< 8.6	< 8.6	< 0.3	< 0.3	< 0.3

[a] Determined in Kerrigan *et al.*[2]; [b] From Anger *et al.*[1];
[c] In g cm^{-2} yr^{-1} from Kerrigan *et al.*[2]; [d] Semi-quantitative results.

S6 References

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[3] J. F. Kerrigan, K. D. Sandberg, D. R. Engstrom, T. M. LaPara and W. A. Arnold, *Environ. Sci.: Processes Impacts*, 2018, **20**, 1167–1179.