Supplementary Information

Characterisation of water-soluble synthetic polymeric substances in wastewater using LC-HRMS/MS

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Table S13: HS detected in the secondary clarifier and/or after ozonation using envihomolog and analysed by RPLC-(-)-APPI-HRMS/SMS. Data evaluation and mining was done according to the workflow described in Figure 1…….xls sheet “S13_APPI_negative_HS”

Sample preparation

In case of centrifugation, approximately 10 mL of sample were transferred to glass centrifuge tubes and centrifuged at 4160 x g, at 4 °C for 30 min (Megafuge 1.0R, Hereaus instruments). After adjusting an aliquot of the supernatant to the starting condition of the chromatographic separation the sample was stored at 4 °C until subjected to LC-HRMS/MS analysis. In case of vacuum- assisted evaporative concentration , the optimized conditions of Mechelke et al. (Mechelke et al., 2019) were employed (55 °C, 20 mbar and 200 to 300 orbital movements per minute using a vacuum-assisted evaporation system). Briefly, after evaporation of 10 mL until an approximate residual volume of 0.3 mL using the vacuum-assisted evaporation system (Syncore Analyst, BÜCHI Labortechnik AG, Switzerland), samples were centrifuged for 15 min at 2320 x g at 4 °C (5427 R, Eppendorf, Switzerland), transferred into a glass vial and visually adjusted to a final volume of 1 mL. This resulted to a pre-concentration factor of 10.

Table S2: Optimized parameters for the analysis of homologous series in wasterwater using a C18 Xbridge column (2.1x50 mm, 3.5 µm), coupled to a ThermoScienfitic QExactive mass spectrometer. For the APPI source a Photomate Light Source from Synagen and the employed vacuum ultraviolet lamp is filled with krypton gas. a) Shows chromatographic separation parameters adjusted according to the different ionization sources employed. b) depicts optimized source conditions for ESI, APPI and APCI and c) lists MS and DD-MS2 parameters of the QExactive. Information on quality control can be found in e)

a)

	ESI	**APPI**	**APCI**
Mobile phase A	H_2O, 2% MeOH, 1 mM NH_4FA, 0.01% FA (pH 3.5)	H_2O, 2% MeOH, 5% IPA	H_2O, 2% MeOH
Mobile phase B	MeOH, 2% H_2O, 1 mM NH_4FA, 0.01% FA	MeOH, 2% H_2O, 5% IPA	MeOH, 2% H_2O
Gradient	0.0 min 2% 1.0 min 2% 3.0 min 40 % 20.0 min 100% 25.0 min 100% 25.5 min 2% 30.0 min 2%	0.0 min 0% 1.0 min 0% 20.0 min 100% 25.0 min 100% 25.5 min 0% 30.0 min 0%	0.0 min 2% 1.0 min 2% 3.0 min 40 % 20.0 min 100% 25.0 min 100% 25.5 min 2% 30.0 min 2%
Flow rate/ mL min^{-1}	0.200		
Column oven T/ °C	40		
Injection volume/ µL	20		

b)

	ESI	**APPI**	**APCI**
Auxiliary gas heater T/ °C	120	-	-
Spray voltage/ V	pos: 4 neg: 3	-	-
Discharge current/ V	-	-	5
Vaporizer T/ °C	-	350	400
Sheath gas flow rate	40	40	40
Aux gas flow rate	10	15	15
Sweep gas flow rate	0	0	0

Capillary T/ °C	300	300	300

c)

Parameter	**Settings**
S-Lens Level/ arbitrary	70
Mass range/ m/z	200 -3000
Resolution MS1	140 K @ m/z 200
Microscans	1
AGC target	5.00E+5
Maximum IT/ ms	100
MS2 settings	
Resolution MS2	17.5 K @ m/z 200
Chrom peak width (FWHM)	12s
AGC target	1.00E+5
Maximum IT/ ms	70
Isolation window/ m/z	1.5
Stepped (N)CE	50, 100, 150
Data- dependent MS2 settings	
Minimum AGC target	1.00E+3
Exclude isotopes	On
Dynamic exclusion/ s	5
If idle	pick others

e) For quality control, a composite sample was prepared by mixing the three different samples in the same ratio and additionally adding a mixture of five isotopically labelled standards (diazonon D10 (CIL Cambridge Isotope Laboratories, MA, US), oxazepam D5 (Lipomed, Switzerland), sitaglipdin D4, sulpirid D3, bezafibrat D4 (TRC-Canada)). The compound selection was based on RT, covering a wide elution range of the employed chromatographic method. To check mass accuracy over the course of the measurement sequence, one aliquot of each sample type (primary clarifier, secondary clarifier, after ozonation *and* blank sample) was spiked with the aforementioned isotopically labelled standard mixture to a final concentration of 250 ng mL^{-1}.

Table S3: Settings for enviMass v4.2beta (Loos 2018)

Parameters in enviMass	Settings
Instrument Resolution	QExactive, QExactivePlus_R140000@200
Workflow section: **Pre-processing** Mass recalibration: **Yes**, RT alignment: **No**; Median Intensity normalization: **No**; Blank/ Blind detection: detect: **Yes**, remove: **No**; Replicate Filter: include: **Yes**, use in profiling: **Yes**; LOD interpolation: **No**	
Peak picking	RT filter range: **1 – 25min**; Parameter estimation: Yes; maximum RT gap in an EIC: **118 s**; maximum m/z deviation of a centroid data point from its EIC mean: **8 ppm**; minimum number of centroid data points per peak: 5 within a given RT window: **7 s**; Maximum RT gap width to be interpolated: **6 s**; maximum RT width of a single peak, +/- from apex: **50 s**; minimum log10(intensity) threshold: **4**; minimum S/N: **5**; minimum Signal/Base: **3**; maximum possible number of peaks within a single EIC: **5**; Peak intensity: **intensoid(max int.)**; Peak mass definition: **weighted mean**
Mass recalibration	Reference compounds: target compounds; +/- m/z tolerance for peak matches: **8 mmu**, maximum permissible m/z correction: **4 mmu**; RT tolerance: **30 s**
Blind	No subtraction, use specified blind/blank samples per sample type

Replicates	+/- m/z tolerance: **3 ppm**; RT tolerance window of peak caused by the same analyte across replicate sample: **3 s**
Workflow section: **Targets** Screen internal standards: **No**; Screen Target Compounds: **Yes**; Intensity normalization using IS-profiles: No	
Screening	IS, Targets& suspects: RT tolerance of peaks relative to their expected RT: **30 s**; RT tolerance of peaks within an isotope pattern: **1.5 s**; mass tolerance: **3 ppm** Adducts: (+): M+H, M+NH4, M+Na, M+K, M+, M+3H, M+2H+Na, M+H+2Na, M+3Na, M+2H, M+H+NH4, M+H+Na, M+H+K, M+2Na (-): M-H, M-2H, M-3H, M-, M+FA-H, M-H2O-H, M+Cl
Workflow section: **Nontargets** Peakshape correlation: **Yes**; File-wise componentization: include: isotopologue grouping: **Yes**; adduct grouping: **Yes**; homologous series detection: **Yes**; Profile componentization: **Yes**; Blacklist screening: **No**	
Profiles	Peak Mass deviation within profiles: +/- m/z tolerance: **3 ppm**; peak deviation within profiles: RT tolerance: **30 s**
Componentization	
File-wise componentization: Isotopologue/ Adduct grouping	+/- m/z tolerance: **3 ppm**; RT tolerance of peaks within an isotope pattern: **1.5 s** Adducts: (+): M+H, M+NH4, M+Na, M+K, M+, M+3H, M+2H+Na, M+H+2Na, M+3Na, M+2H, M+H+NH4, M+H+Na, M+H+K, M+2Na (-): M-H, M-2H, M-3H, M-, M+FA-H, M-H2O-H, M+Cl
File-wise componentization: Homologous series detection	Homologous units: C2H7N, C4H13N3, C3H6N6, C10H21N2O, C7H13NO4S, C4H2O4, C8H10NO3S, C8H11O7, C20H11N4SO3, C22H18O8S2, C26H14N42O7S2, C3H5O5S1, C1H2, BH3, C2H2, CO, C2H4, H2Si, CH2O, C3H6, CO2, CH4Si, C2H4O, C2H3F, C1F2, C3H3N, C4H6, C4H8, C2H2O2, C2H6Si, C3H6O, CH4OSi, C2H3Cl, C2F2, C2H2F2, C4H3N, C4H2O, C4H5N, C5H8, C4H6O, C5H10, C3H5NO, C3H4O2, C3H8Si, C4H8O, C2H6OSi, C3H5Cl, C5H5N, C5H4O, C4H2S, C4H2O2, C6H10, C4H4O2, C5H8O, C6H12, C4H7NO, C3H6OSi, C4H6O2, C4H10Si, C5H10O, C4H9NO, C4H5Cl, C3H4O3, C4H8O2, C6H5N, C3H5ClO, C6H4O, C6H6O, C5H6N2, C2H2Cl2, C5H4S, C7H12, C4H2O3, C6H10O, C7H14, C5H9NO, C2F4, C4H4O3, C8H4, C5H8O2, C5H12Si, C6H12O, C4H6O3, C8H6, C3H4O2S, C4H5FO2, C8H8, C7H7N, C2H3Br, C4H7ClO, C6H6Si, C7H6O, C6H5NO, C2H5O3P, C6H4S, C7H8O, C6H8N2, C6H4FN, C8H14, C5H5NO2, C6H9NO, C5H4O3, C5H8O1N2, C8H16, C5H7NO2, C6H11NO, C6H10O2, C6H14Si, C6H14N2, C4H5N1O3, C5H7O3, C8H5N, C2ClF3, C4H4O4, C7H4N2, C5H8O3, C9H8, C6H14NO, C7H3NO, C9H9N, C9H10, C8H9N, C4H5ClO2, C7H4O2, C7H8Si, C8H8O, C7H7NO, C4H4F2O2, C6H6N2O, C8H7F, C6H5NO2, C9H16, C6H4ClN, C6H7N1O2, C9H18, C5H9NOSi, C4H4F4, C7H12O2, C7H16Si, C8H16O, C5H7O3N1, C6H10O3, C7H14O2, C5H7O4, C8H4O2, C5H8O4, C6H4N4, C10H12, C9H11N, C8H10Si, C9H10O, C8H10N2, C6H14O3, C8H9NO, C6H4N2O2, C7H8OSi, C7H7NO2, C8H7Cl, C8H10S, C10H18, C7H9NO2, C6H4O2S, C4H3F3O2, C8H12O2, C10H20, C5H11N5, C8H15NO, C6H6O4, C8H14O2, C8H18Si, C8H4N2O, C6H8O4, C7H12O3, C8H4O3, C7H8COSi, C9H8O2, C3F6, C9H10O2, C10H14O, C12H8, C9H12S, C8H11NO2, C5H8Cl2O, C11H22, C9H17NO, C4H7F3OSi, C7H8O4, C9H16O2, C9H20Si, C10H20O, C9H20N2, C8H15NO2, C10H6S, C9H18O2, C6H3NCl2, C9H5NO2, C4H2O4Na2, C6H11NO4, C8H6N2O2, C6H10O5, C10H10O2, C8H4S2, C4H2F6, C9H8O3, C13H8, C10H12S, C10H12O2, C12H7N, C3F6O, C10H14S, C12H9N, C9H4N4, C10H16O2, C10H20N2, C12H24, C6H2BrO, C6H4BrN, C10H19NO, C6H4NO3S, C11H6O2, C8H10O4, C10H18O2, C10H22Si, C8H12O4, C9H20OSi, C12H17N, C6H8O6, C11H14S, C10H13NO2, C13H8O, C12H8N2, C14H12, C11H16S, C8H7Br, C10H14SO, C12H10N2, C10H14O3, C12H22O, C13H26, C8H17N5, C11H21NO, C8H8O3S, C12H8O2, C12H12N2, C11H24Si, C10H8O4, C14H11N, C12H18S, C7H4N2SO3, C13H8O2, C13H12Si, C14H28, C12H23NO, C12H10OSi, C10H14O4, C12H22O2, C12H26Si, C10H16O4, C7H7NO4S, C10H18O4, C8H13NO5, C14H21N, C12H15NO2, C11H10O4, C14H22O, C14H8O2, C13H20S, C4F6O3, C15H14O, C15H30, C13H25NO, C11H20N2O2, C13H24O2, C13H28Si, C11H18O4, C6H4IN, C8H10O7, C12H13NO3, C12H12O4, C14H20O2, C15H10O2, C12H14O4, C14H22S, C14H22O2, C8H10NNaO3S, C15H16Si, C16H32, C14H10O3, C15H18N2, C12H22N2O2, C14H30Si, C12H20O4, C11H22O3Si, C12H8O3S, C14H8N4, C14H16O3, C16H24O, C14H6N2O2, C15H24S, C15H10O3, C14H10N2O2, C14H8O4, C15H12O3, C12H19NS2, C8H11O7Na, C14H10O4, C16H20NO, C5F8O2, C16H4O3, C13H8O3S, C18H12O, C16H20O2, C14H18N2O2, C6H3NBr2, C14H16O4, C16H24O2, C16H26S, C14H20O4, C14H24N2O2, C18H36, I2, C16H14O3, C14H26N2O2, C16H34Si, C10H10NSO5, C15H12O4, C16H16O3, C17H24O2, C7H4OSe2, C10H16O8, C5F10O, C14H6N2S2, C14H6N2O4, C12H10O7, C17H14O3, C19H38, C17H16O3,

	C15H28N2O2, C17H36Si, C18H36O, C16H18N2O2, C16H16O4, C18H28Si, C16H18O4, C18H29NO, C13H8O5S, C18H12O3, C15H19NO4, C6F10O, C16H23O4, C7H4SSe2, C18H16O3, C16H24O4, C20H40, C18H18O3, C16H30N2O2, C18H38Si, C13H17NO4S, C18H20O3, C16H28O4, C19H12O3, C12H16O8, C17H24N2O2, C19H28O2, C17H26N2O2, C19H18O3, C20H26Si, C20H40O, C21H32O, C18H26N2O2, C18H24O4, C15H8Cl2O3, C20H12N4, C22H44, C20H22O3, C18H34N2O2, C20H42Si, C21H16O3, C16H12Cl2O3, C19H36N2O2, C20H24O4, C22H37NO, C25H32, C24H18N2, C22H24O3, C24H48, C22H26O3, C20H38N2O2, C20H36O4, C21H20O5, C24H36O2, C23H18O4, C24H38O2, C16H8F6O3, C22H10N2O4, C22H22O5, C24H36OSi, C25H24O3, C26H18O3, C22H10N2O5, C29H40, C16H10Cl4O3, C26H16O4, C23H10N2O5, C24H16O4S, C26H16N4O Charges z: (+)-ESI: **1- 6**; (+)- APPI, (+)-APCI, (-)-ESI, (-)- APPI, (-)-APCI: **1- 3**; minimum change in RT from one homologue to next: **2 s**; maximum change in RT from one homologue to next: **240 s**; tolerance by which the RT differences between two adjacent homologue pairs are allowed to change: **5 s**; +/- m/z tolerance: **3 ppm**; minimum number of homologues in a series: **4**; filter peaks by sample-vs-blind intensity ratio: **yes**; sample-vs-blind intensity ratio: **3**; Check series smoothness with: **spline up to series of length 7**, maximum number of homologues in a series: **50**; Filter homologous series: **reduce redundant combinations, merge gapped series, only keep series with a majority of monoisotopic peaks, reduce co-eluting series to most intense one**
File-wise componentization: Peak shape correlation	RT tolerance window for candidate peak pairs: **1.5 s**; min number of MS1 scans over which peak pairs co-elute to check for their peak shape correlation: **8**; min. spearman correlation coefficient: **0.95**
Workflow section: **Concentration** Calibration: **No**; Quantification: **No**; Recovery: **No**	
Workflow section: **Profiling** Profile extraction: **Yes**; Profile filtering: **Yes**; subtract internal standard peaks: **No**, Substract target compound peaks: **No**; subtract peaks, which have also been detected in blind/blank samples: **No**, peaks from spiked files: **No**; Profile blind detection: **Yes**, Trend detection: **Yes**, Comparison: **No**	

Non-target HS detection: Advances on the embedded non-targeted HS extraction tool, envihomolog:

A first advance was to detect and merge sets of systematically gapped series that overlap in their peak composition. These are series which have multiples of RU mass differences of each other, and which share subsets of peaks in alternating series positions as set by their RU mass difference. Such gapping arises from decreasing peak intensities, e.g., at the end of series, with non-detected peak signals leading to overlapping but differently mass-spaced series. The series with the smallest RU mass difference was retained for each such merging. Second, another advance was made to reduce partly overlapping and redundant peak series combinations over isobaric and close-eluting peaks and based on all possible peak series combinations formed by the original envihomolog algorithm. For this purpose, series were selected by their decreasing intensity summed of their contained peaks, and in a way that the next selected series had no peaks in common with any of the previously selected series. Unselected HS peaks remaining after this procedure were represented by the most intense (again by intensity peak sum) series they were contained in, and even if such a series overlapped in its peak composition with previously selected series. Third, series can form over the different isotopologues of the same ion species of a homologous analyte, and are then redundant in representing this analyte. Therefore, the nontarget components of HS peaks were checked for non-monoisotopic series. The HS with the largest fraction of monoisotopic peaks was retained, and other series in the individual components discarded. Fourth, and despite the named reduction to monoisotopic series, HS redundancy can still arise over the different ion species of a homologous monoisotopic analyte. The simultaneous co-elution over several peaks between HS as a criterion for grouping and further reduction is an advantage over non-HS componentization, and can even be applied to differently charged and possibly yet unidentified HS ion species. Here, monoisotopic series which coeluted with at least four peaks were reduced to the most intense series to finally represent a homologous analyte.

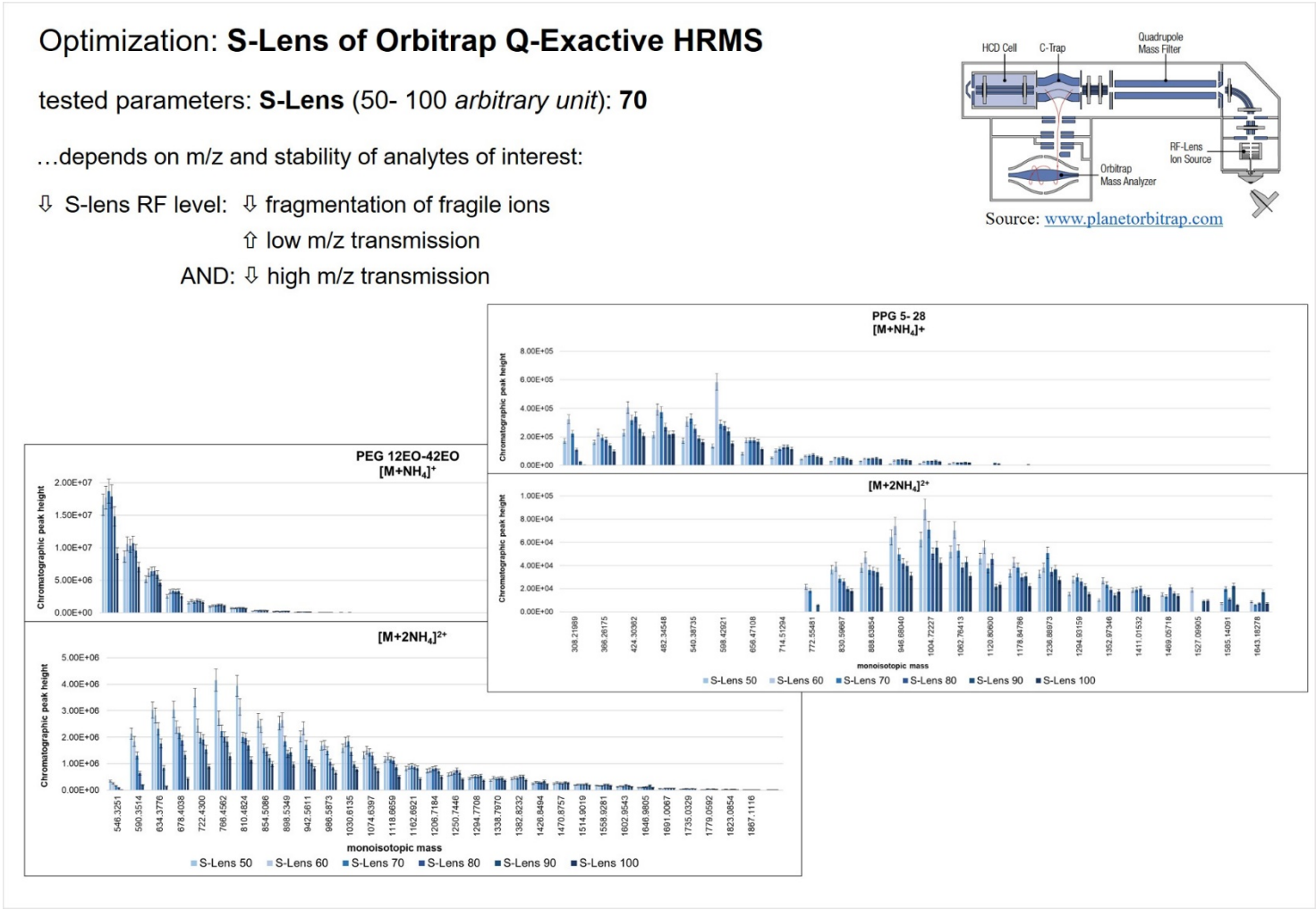


Figure S 1: Optimization of S-Lens of QExactive HRMS instrument using two model homologous series, that is polythethylene glycol (PEG) and polypropylene glycol (PPG). For the optimization a sample taken from the primary clarifier, diluted 1:5 with nanopure water was used. To account for repeatability, a rather over-estimated value of 15% relative standard deviation was applied.

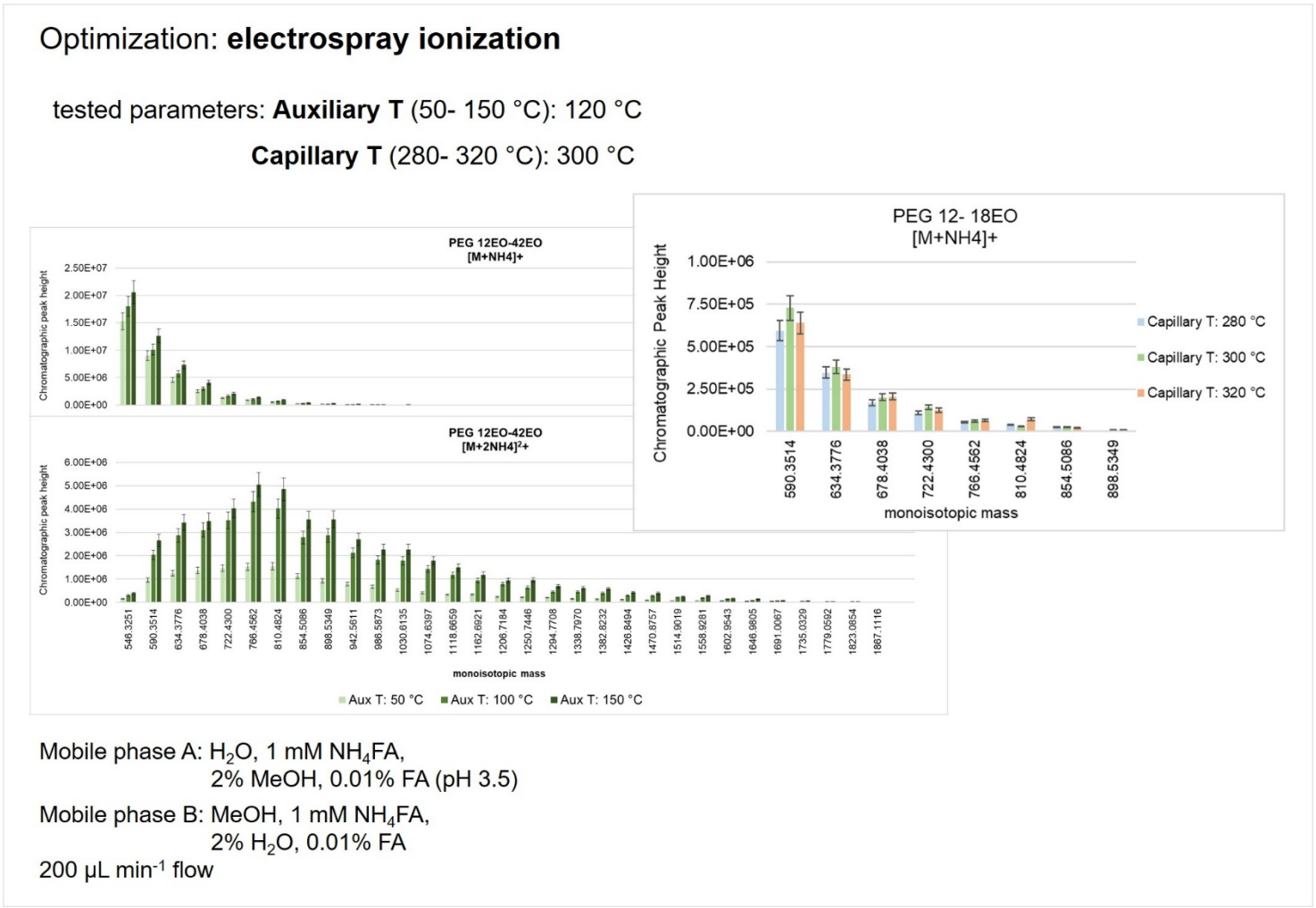


Figure S 2: Optimization of electrospray ionization interface using two model homologous series, that is polythethylene glycol (PEG) and polypropylene glycol (PPG). For the optimization a sample taken from the primary clarifier, diluted 1:5 with nanopure water was used. To account for repeatability, a rather over-estimated value of 15% relative standard deviation was applied. Tested parameters were the capillary temperature and the auxiliary temperature.

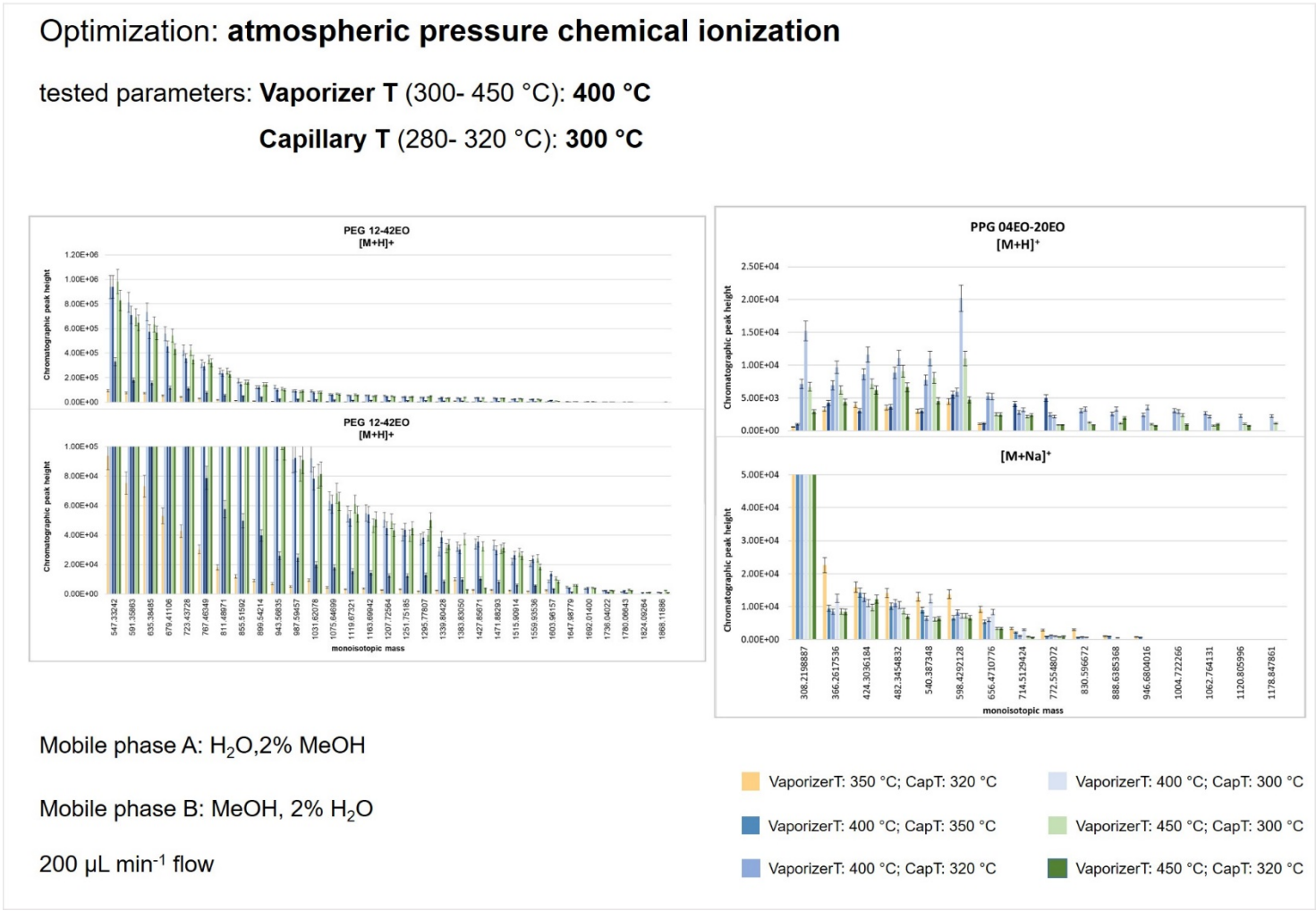


Figure S 3: Compared to ESI, in case of APCI, solvent is evaporated by heating after the sample solution is sprayed into a fine mist of droplets. By applying a high voltage to a needle close to the exit end of the tube and creating a corona discharge, reagent ions are formed through a series of chemical reactions, involving the sheath gas nitrogen and solvent molecules. Sample molecules are ionized by reacting with the formed reagent ions. Polarity, thermal stability and molecular weight of the analytes of interest are the key parameters responsible for ion formation (Gruendling et al., 2010).
Optimization of atmospheric pressure chemical ionization interface using two model homologous series, that is polythethylene glycol (PEG) and polypropylene glycol (PPG). For the optimization a sample taken from the primary clarifier, diluted 1:5 with nanopure water was used. To account for repeatability, a rather over-estimated value of 15% relative standard deviation was applied. Tested parameters were the capillary temperature and the vaporizer temperature.

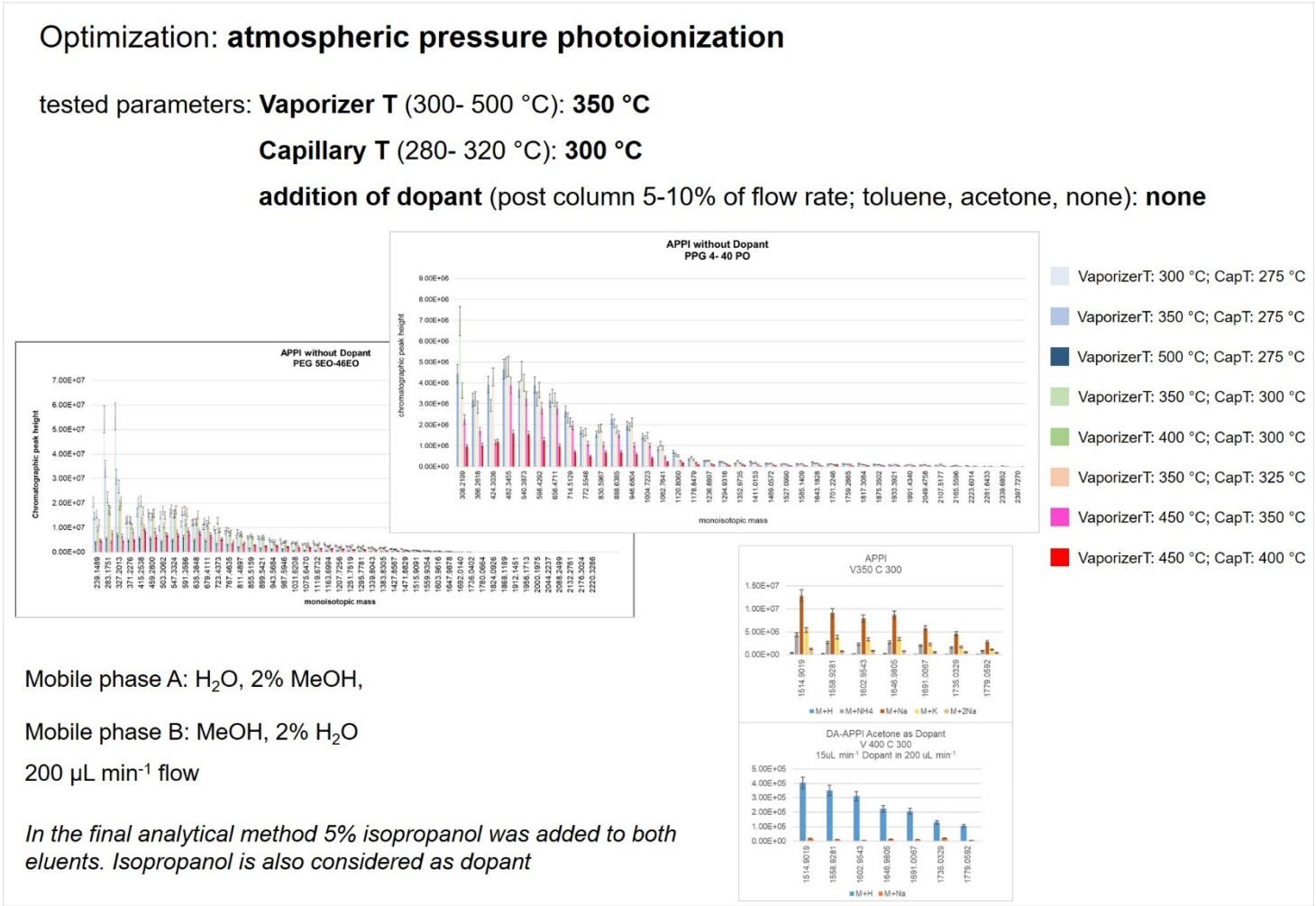
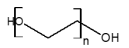
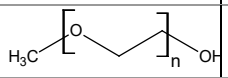
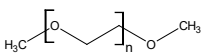
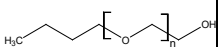
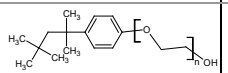
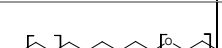
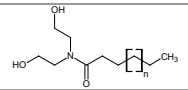
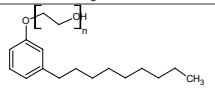
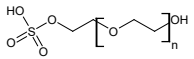
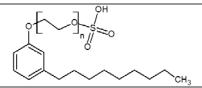
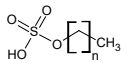
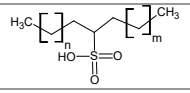
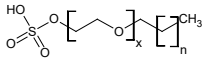
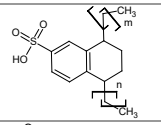
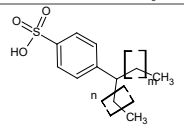
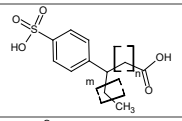
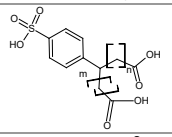
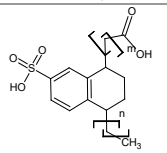


Figure S 4: Ion formation in APPI can be distinguished classified into either direct or indirect/ dopant assisted photoionization. A direct analyte photoionization occurs if the ionization potential of the analyte molecule is lower than the energy of the photon emitted by the light source. In the latter approachdopant-assisted photoionization, primary reagent ions are generated by using either dopant or appropriate solvents. This dopant or solvent is amenable to direct photoionization and produces thereby reagent ions which can subsequently ionize the analyte (Andrea and Alessandro, 2003), (Terrier et al., 2011).
Optimization of atmospheric pressure photoionization interface using two model homologous series, that is polythethylene glycol (PEG) and polypropylene glycol (PPG). For the optimization a sample taken from the primary clarifier, diluted 1:5 with nanopure water was used. To account for repeatability, a rather over-estimated value of 15% relative standard deviation was applied. Tested parameters were the capillary temperature, the vaporizer temperature and the post-column addition of the dopants toluene or acetone.

Table S8: Findings on suspect screening. Results are grouped depending on the ionization mode and polarity. Presence is defined by detecting at least 4 elements of the HS family defined in the suspect list. P indicates presence of the HS family in the composite sample of the primary clarifier, the secondary clarifier is abbreviated as S, O specifies findings after the Ozonation and sand filtration step and B corresponds to detections in the blind. The abbreviation Cent and VEC corresponds to the sample preparation steps, centrifugation and vacuum assisted evaporative concentration step. The notations “n”, ”m”, ”x” indicate the repeating unit that is present in the polymeric substance and indicate also the number of repeating units linked together. Level of confidence is indicated as described by (Schymanski et al., 2014a). For a level 2 identification for at least 2 elements of the HS family a MS2 spectrum needed to be available (and give a match).

Abbreviation ***of HS family***	**Name** ***of HS family***	**n, m**	**x**	**Molecular structure**	**Level of confidence**	**APCI**		**APPI**		**ESI**	
						(+)	**(-)**	**(+)**	**(-)**	**(+)**	**(-)**
PEG-EOn n= 2- **85**	polyethylene glycol	C_2H_4O			D (1)	Cent.: P,S,O,B VEC: P,S,O,B	Cent.: P VEC: P	Cent.: P,S,O,B VEC: P,S,O,B	Cent.: P VEC: P,S,O,B	Cent.: P,S,O,B VEC: P,S,O,B	Cent.: P VEC: P
PEG-MME-EOn n= 2- 80	PEG monomethyl ether	C_2H_4O			D (2)	Cent.: - VEC: P	Cent.: - VEC: P	Cent.: P VEC: P, O		Cent.: P VEC: P,O	Cent.: P VEC: P
PEG-DME-EOn n=2- 80	PEG dimethyl ether	C_2H_4O			D (2)		Cent.: P VEC: P		Cent.: - VEC: P	Cent.: P VEC: P,S,O	Cent.: P VEC: P
PEG-MB-EOn n=2 -80	PEG monobutyl ether	C_2H_4O			C (3)			Cent.: - VEC: P		Cent.: P VEC: P	Cent.: P VEC: P
PPG-POn n=2 -50	polypropylene glycol	C_3H_6O			D (2)			Cent.: P,S VEC: P	Cent.: - VEC: P	Cent.: P,S,O,B VEC: P,S,O,B	Cent.: P VEC: P
TMBP-EOn n= 1- 10	tetramethylbutyl phenol, ethoxylated	CH_2			C (3)						Cent.: - VEC: P
Cn- AEOx n= 10- 18, x= 1-20	alcohol ethoxylates	CH_2	C_2H_4O		D (2)	Cent.: P VEC: P		Cent.: P,S,O VEC: P,S,O,B	Cent.: P VEC: P	Cent.: P,S,O,B VEC: P,S,O,B	Cent.: P VEC: P
OPEOn n= 1- 30	octylphenol ethoxylates	C_2H_4O			D (2)						Cent.: P VEC: P
Cn - DEA, n= 7-17	coconut diethanolamide	CH_2			D (2)					Cent.: P VEC: P	
NPEOn n= 1- 20	nonylphenol polyethoxylates	C_2H_4O			D (2)			Cent.: S,O,B VEC: S,O			Cent.: - VEC: P
GES-n n= 2- 13	glycol ether sulfate	C_2H_4O			D (2)		Cent.: P VEC: P		Cent.: P VEC: P,O	Cent.: P VEC: P	Cent.: P VEC: P
NPEOn- SO4 n= 1- 15	nonylphenol ethoxylates sulfate	C_2H_4O			D (2)		Cent.: - VEC: P				Cent.: - VEC: P

Cn - AS n= 8- 16	alkyl sulfate	CH_2			D (2)						Cent.: P, B VEC: P
Cn- SAS n, m = 10- 21	secondary alkane sulfonate	CH_2			D (2)						Cent.: P VEC: P
Cn- AExS n= 12- 18; x= 1-12	alkyl ethoxy sulfates	CH_2	C_2H_4O		D (2)		Cent.: P VEC: P		Cent.: - VEC: P	Cent.: P VEC: P	Cent.: P VEC: P
Cn - DATS n, m= 4- 19	dialkyl tetralinsulfonates	CH_2			D (2)						Cent.: P VEC: P
Cn- LAS n, m = 8- 14	linear alkylbenzene sulfonate	CH_2			D (2)					Cent.: P VEC: P	Cent.: P, B VEC: P, B
SPA-Cn n, m = 1- 15	sulfophenyl carboxylic acids	CH_2			D (2)					Cent.: P,S,O,B VEC: P,S,O,B	Cent.: P,S,O VEC: P,S,O
SPA-nDC n, m = 1- 15	sulfophenyl alkyl dicarboxylated	CH_2			D (2)						Cent.: - VEC: P,S,O
STA-nC n, m = 1- 12	sulfotetralin alkyl carboxylated	CH_2			D (2)					Cent.: S,O VEC: S,O	Cent.: O VEC: P,O

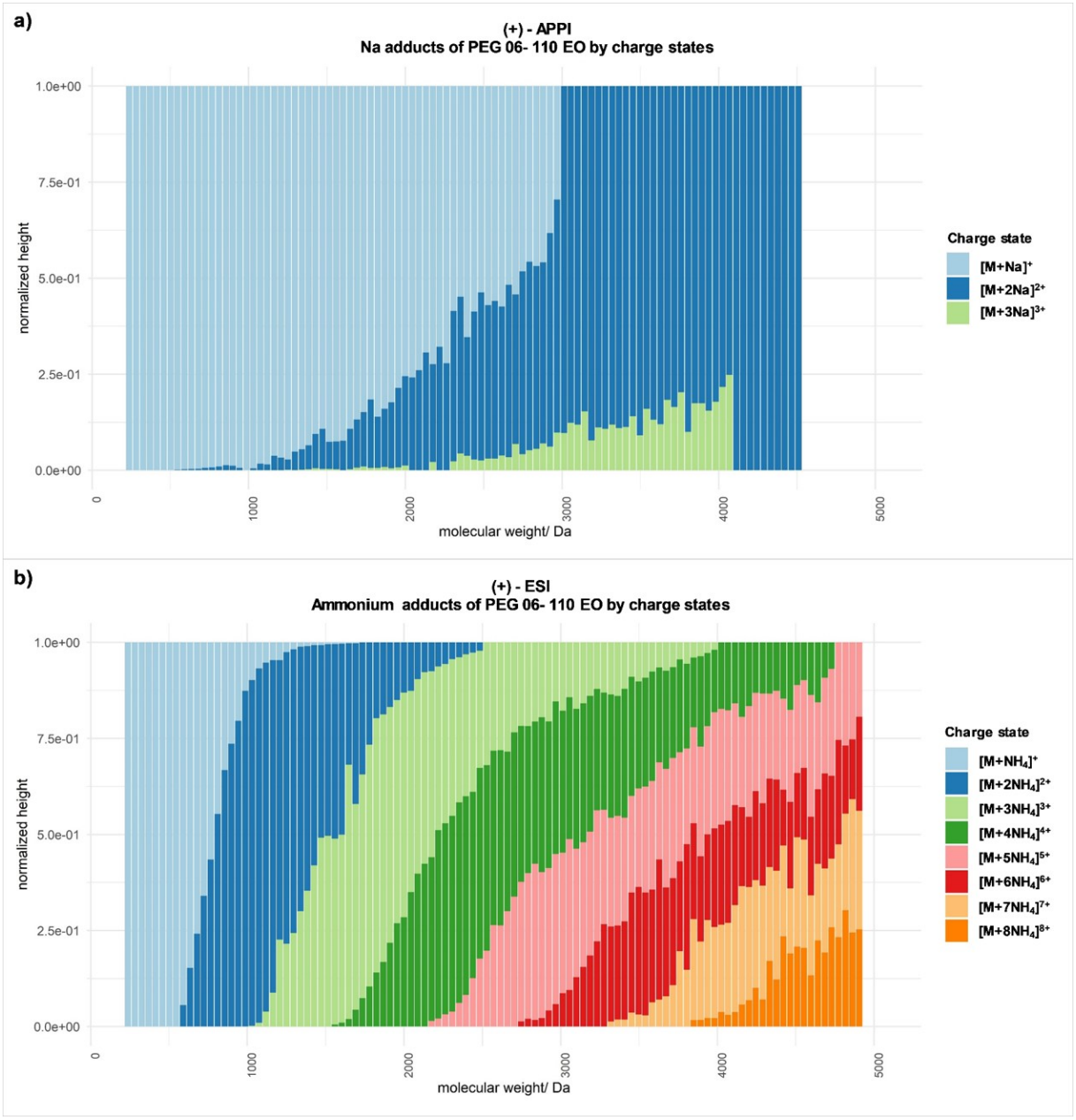


Figure S 5: Molecular weight dependent charge state distribution. The x-axis shows the moleucular weight of PEG, namely 06- 110 EO units, intensities are shown as normalized peak heights on the y-axis. Number of charges are color coded. For both ionization interfaces the most abundant ion specie, namely Na-adducts for APPI and NH_4-adducts for ESI are shown. a) Ionization performed using (+)-APPI: shows observed Na-adducts with charge states up to +3 for PEG 06- 110 EO. b) Ionization performed using (+)-ESI: shows observed NH_4-adducts with charge states up to +8 for PEG 06- 110 EO.

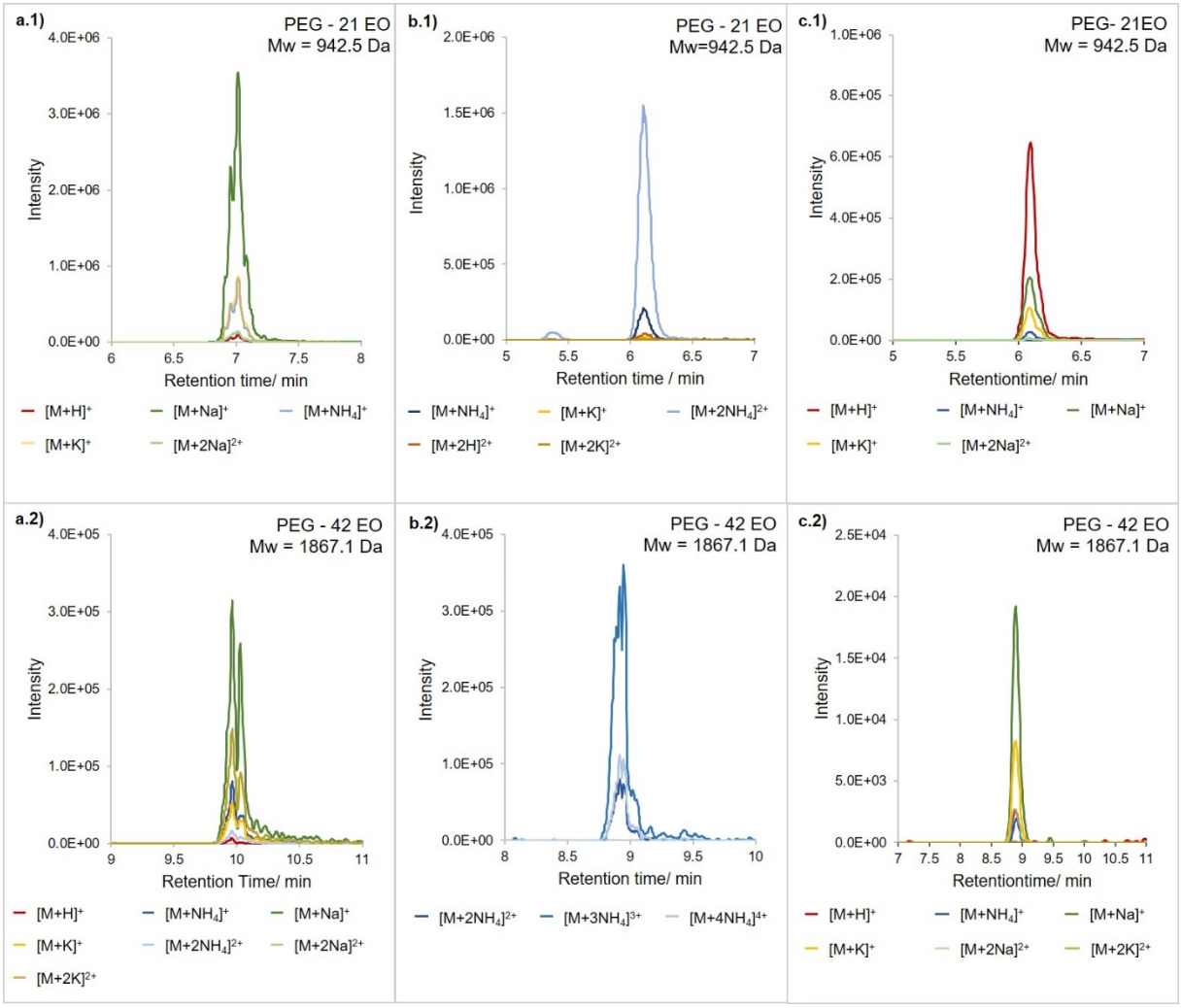


Figure S 6: Prevalent Ion species, depending on the employed ionization interface and molecular weight. a1) EIC of most abundant ion species for PEG-21EO, using (+) APPI as ionization source. a2) EIC of most abundant ion species for PEG-42EO, using (+) APPI as ionization source. b1) EIC of most abundant ion species for PEG-21EO, using (+) ESI as ionization source. b2) EIC of most abundant ion species for PEG-42EO, using (+) ESI as ionization source. c1) EIC of most abundant ion species for PEG-21EO, using (+) APCI as ionization source. c2) EIC of most abundant ion species for PEG-42EO, using (+) APCI as ionization source.

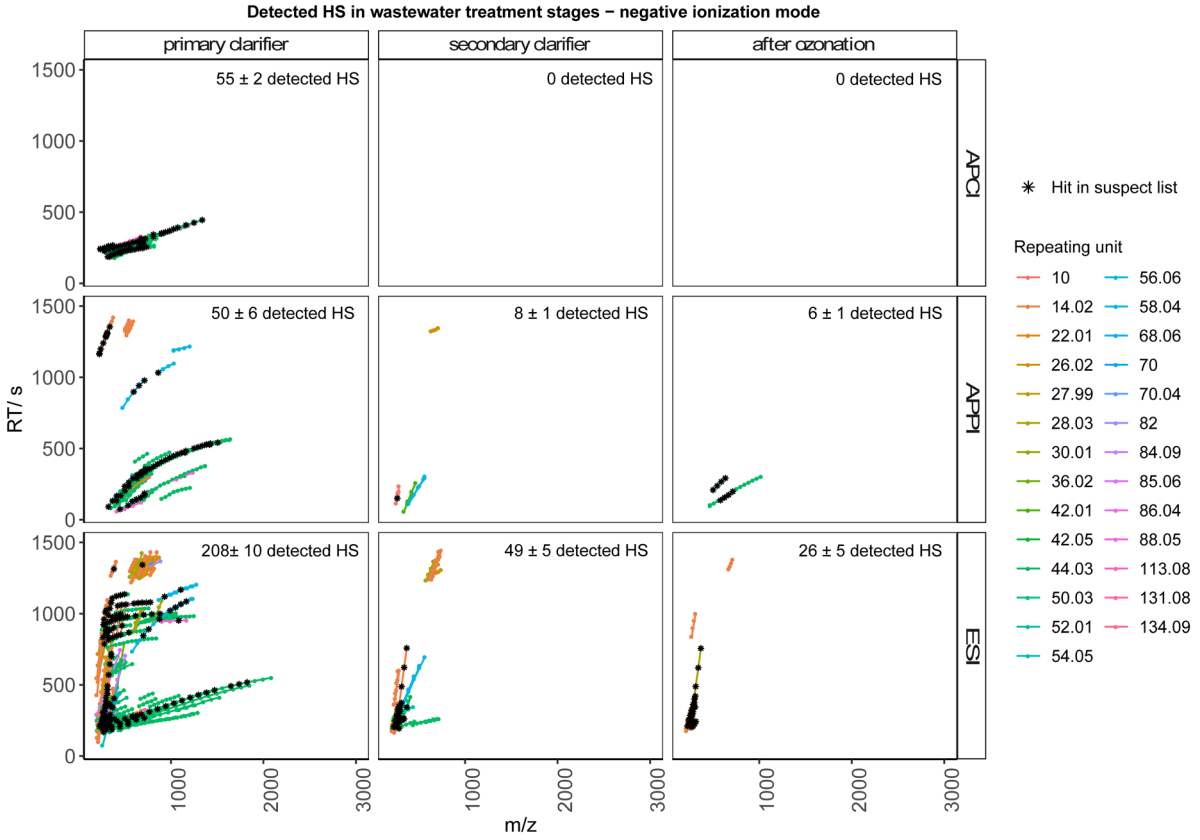


Figure S7: Detected HS in the different wastewater treatment stages. Samples were pre-concentrated using vacuum- assisted evaporative concentration. Ionization was performed with APCI, APPI or ESI in negative mode. RU are depicted as m/z and indicated in the respective color. Hits from the suspect list are highlighted by a black asterisk.