Supplement of

Dissolved organic matter signatures in urban surface waters: spatio-temporal patterns and drivers

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Details of DOM absorbance and fluorescence analyses

DOM absorbance and fluorescence were measured simultaneously on an Aqualog (Horiba Ltd, Kyoto, Japan) using a 1 cm quartz cuvette and ultrapure water as a blank. We produced excitation-emission-matrices (EEMs) at 5 nm increments along the excitation range (250 to 550 nm) and 1.77 nm increments along the emission range (250-600 nm). Triplicate samples for each site and season were each measured three times, yielding a total of nine measurements per site and season, which were averaged after deletion of any obvious outliers resulting from erroneous readings. EEMs were corrected for (i) the water Raman scatter, (ii) the Rayleigh-Tyndall effect, and (iii) the inner filter effect (Mcknight et al., 2001; Parlanti et al., 2000). We interpolated EEMs to a 1 nm grid from the recorded grid (1.77 x 5 nm cells) to allow computation of the various indices exactly as defined in Table A2.

EEMs were also used for parallel factor analysis (PARAFAC), a multivariate 3-way modeling strategy decomposing the EEM into individual components which additively produce the overall fluorescence signal (Stedmon and Bro, 2008; Bro, 1997). Prior to PARAFAC, missing data in Rayleigh scatter regions were interpolated to expedite the modeling process (Bro, 1997). PARAFAC was conducted using Matlab (version 7.11.0, MathWorks) and the DOMFluor Toolbox (1.7) following Stedmon & Bro (2008). We limited the number of components to 10, rigorously assessed residual EEM plots and validated final models by split-half validation and random initialization as recommended (Stedmon and Bro, 2008). We finally modelled eight fluorescent components from 116 EEMs. We compared our excitation-emission loading spectra and maxima with fluorophore data published in the OpenChrom/OpenFluor database (http://www.openfluor.org) (Murphy et al., 2014).

Details of FT-ICR-MS methods

We looked for molecular masses between 150 and 1000 Da. We carried out the internal mass calibration and exported the raw mass lists for further data processing using previously established R code (Del Campo et al., 2019). Briefly, we first chose data above a method detection threshold before alignment of peaks across samples. Next we assigned molecular formulae to m/z values assuming single-charged deprotonated molecular ions and Cl-adducts for a maximum elemental combination of $C_{100}H_{250}O_{80}N_4P_2S_2$. In addition, to eliminate doubtful formula assignments, we performed (i) an accurate assessment of mass error and its partitioning into random and systematic components(Savory et al., 2011), (ii) an exploration for stable isotope validation by daughter peaks (Koch et al., 2007), and (iii) homologous series assessment based on CH_2, CO_2 and H_2O as chemical building blocks for aliphatic, acid-based and alcohol-based elongation (Koch et al., 2007). We grouped formulae into 12 non-overlapping molecular groups (Lesaulnier et al., 2017) based on elemental composition to condense the mass-spectrometric information. For each group, we calculated the average molecular mass, the number of formulae (molecular richness) and the total intensity. Finally, we used van Krevelen plots to present the sum formulae derived from the FT-ICR-MS data in a space defined by O:C (oxygen richness) and H:C (saturation) ratios. To avoid bias due to systematic overplotting of thousands of compounds with identical O:C and H:C ratios, we used a random order of plotting.

40 **Table S1: Site coordinates and land cover. Longitude is given in decimal degrees East and latitude in decimal degrees North. Land cover was calculated for 50-m strips around water bodies using QGIS (QGIS Development Team, 2009) and data provided by the Senate Administration for Environment, Transport and Climate Protection of Berlin (Senate Administration for Environment, 2017) .**

Site ID	Site name	Water body type	Latitude	Longitude	Agri-culture (%)	Forest (%)	Urban pavement (%)	Urban green space (%)
H1	Teltowkanal	River	52.44239	13.32454	0	0	60	30
H2	Teltowkanal	River	52.42642	13.52039	0	0	100	0
H3	Wuhle	Stream	52.52562	13.57913	50	0	50	0
H4	Tegeler Fliess	Stream	52.63442	13.38013	50	0	10	40
L1	Biesdorfer See	Lake	52.50331	13.54970	0	0	50	50
L2	Obersee	Lake	52.54856	13.48972	0	0	50	50
L3	Ploetzensee	Lake	52.54380	13.33049	0	0	0	100
L4	Gross Glienicker	Lake	52.46417	13.11489	0	10	0	90
L5	Havel	Lake	52.44310	13.14453	0	0	100	0
L6	Schlachtensee	Lake	52.44066	13.21183	0	60	30	10
L7	Müggelsee	Lake	52.43837	13.64510	0	70	30	0
P1	Hoheheideteich	Pond	52.57694	13.16428	0	100	0	0
P2	Hamburger Teich	Pond	52.56738	13.44549	0	0	30	70
P3	Ruhwaldteich	Pond	52.52573	13.25998	0	0	50	50
P4	Kienhorstbecken	Pond	52.57724	13.34556	0	0	0	100
P5	Mittelfeldteich	Pond	52.61208	13.23045	0	100	0	0
P6	Neurandteich	Pond	52.63883	13.27377	0	0	65	35
P7	Möwensee	Pond	52.55282	13.33545	0	0	30	70
R1	Müggelspree	River	52.42985	13.68912	0	0	100	0
R2	Landwehrkanal	River	52.51935	13.31959	0	0	80	20
R3	Spree	River	52.53613	13.21622	0	0	100	0
R4	Kuhlake	River	52.57817	13.16509	0	100	0	0
R5	Neukölln Canal	River	52.48936	13.43949	0	0	30	70
R6	Spree	River	52.47137	13.49683	0	0	100	0
R7	Panke	River	52.53690	13.36759	0	0	60	40
S1	Zingergraben	Stream	52.58209	13.38594	0	0	95	5
S2	Schwarzer Graben	Stream	52.56488	13.34918	0	0	50	50
S3	Graben 1 Buch	Stream	52.62384	13.46883	0	100	0	0
S4	Graben 73 Buchholz	Stream	52.62881	13.45315	100	0	0	0
S5	Erpe	Stream	52.45888	13.61245	0	50	50	0
S6	Koppelgraben	Stream	52.62065	13.41089	50	0	30	20
S7	Plumpengraben	Stream	52.41513	13.5628	0	0	100	0

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