Supporting Information

Riedel et al. 10.1073/pnas.1221487110

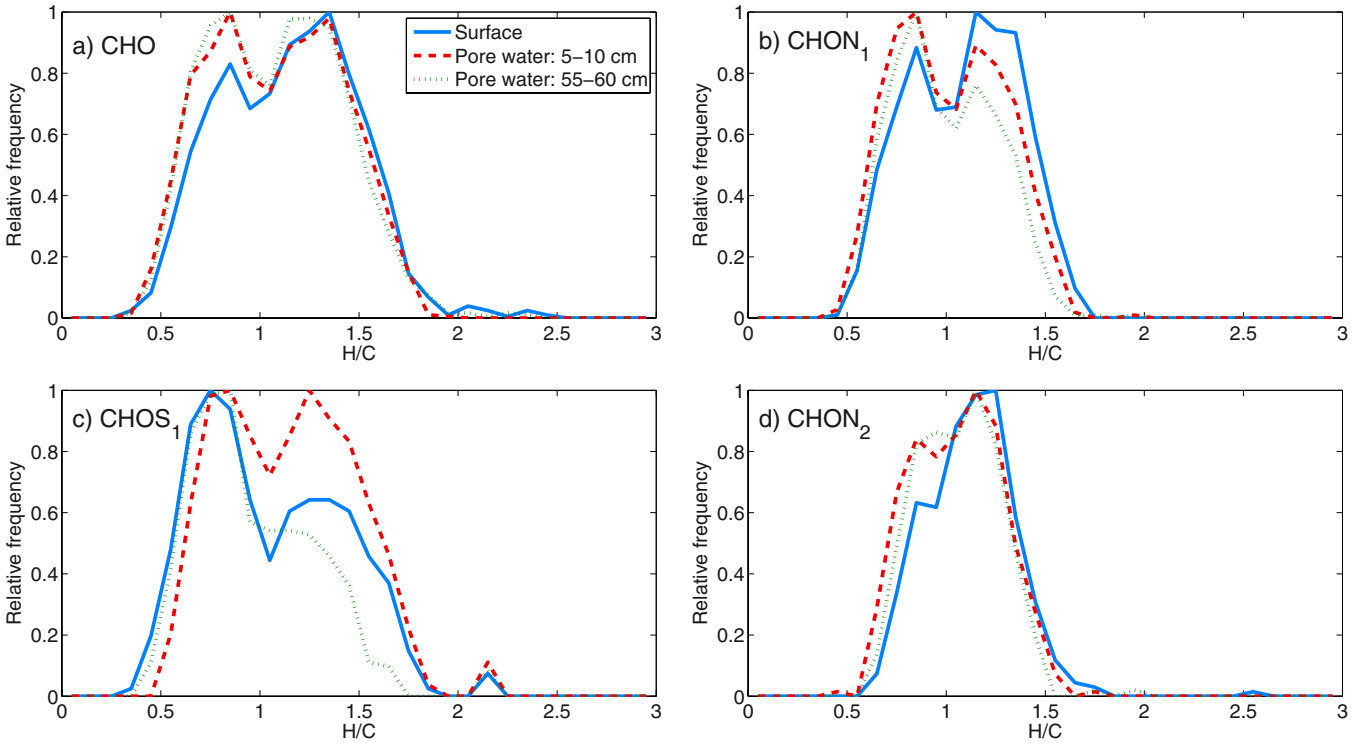

Fig. S1. Normalized distribution of elemental hydrogen-to-carbon (H/C) ratios of the surface and pore water samples, respectively, from the "Wendewiesen" site. Compound classes are sorted as in Table 2 and Fig. 1. The bimodal distribution of the H/C ratio relative frequency indicates the predominance of two distinct compound groups at Wendewiesen, one aromatic (low H/C ratio) and one aliphatic (high H/C ratio). Aromatic compounds were preferentially removed at the redox interface. Elemental ratios of all formulas not shared between pore and surface waters are further illustrated in Fig. S3.

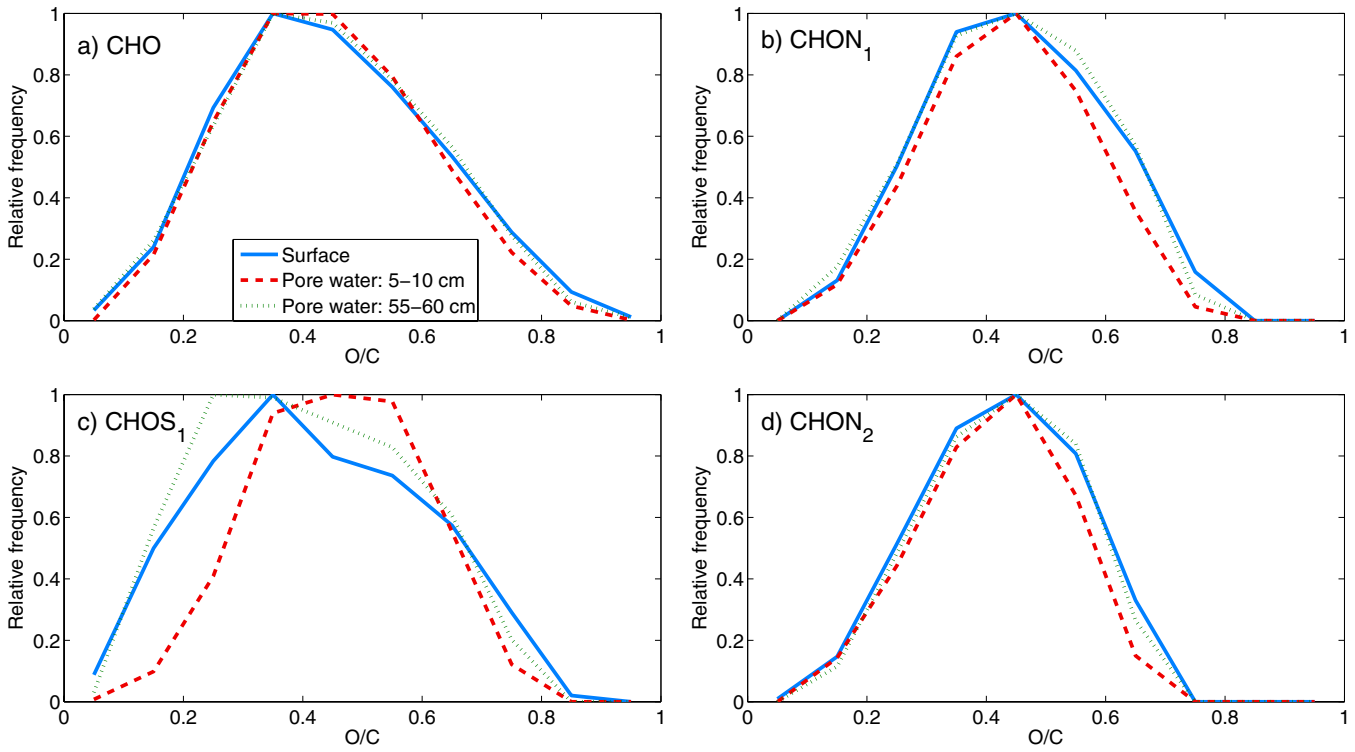

Fig. S2. Normalized distribution of elemental oxygen-to-carbon (O/C) ratios of the surface and pore water samples, respectively, from site Wendewiesen. Compound classes are sorted as in Table 2 and Fig. 1.

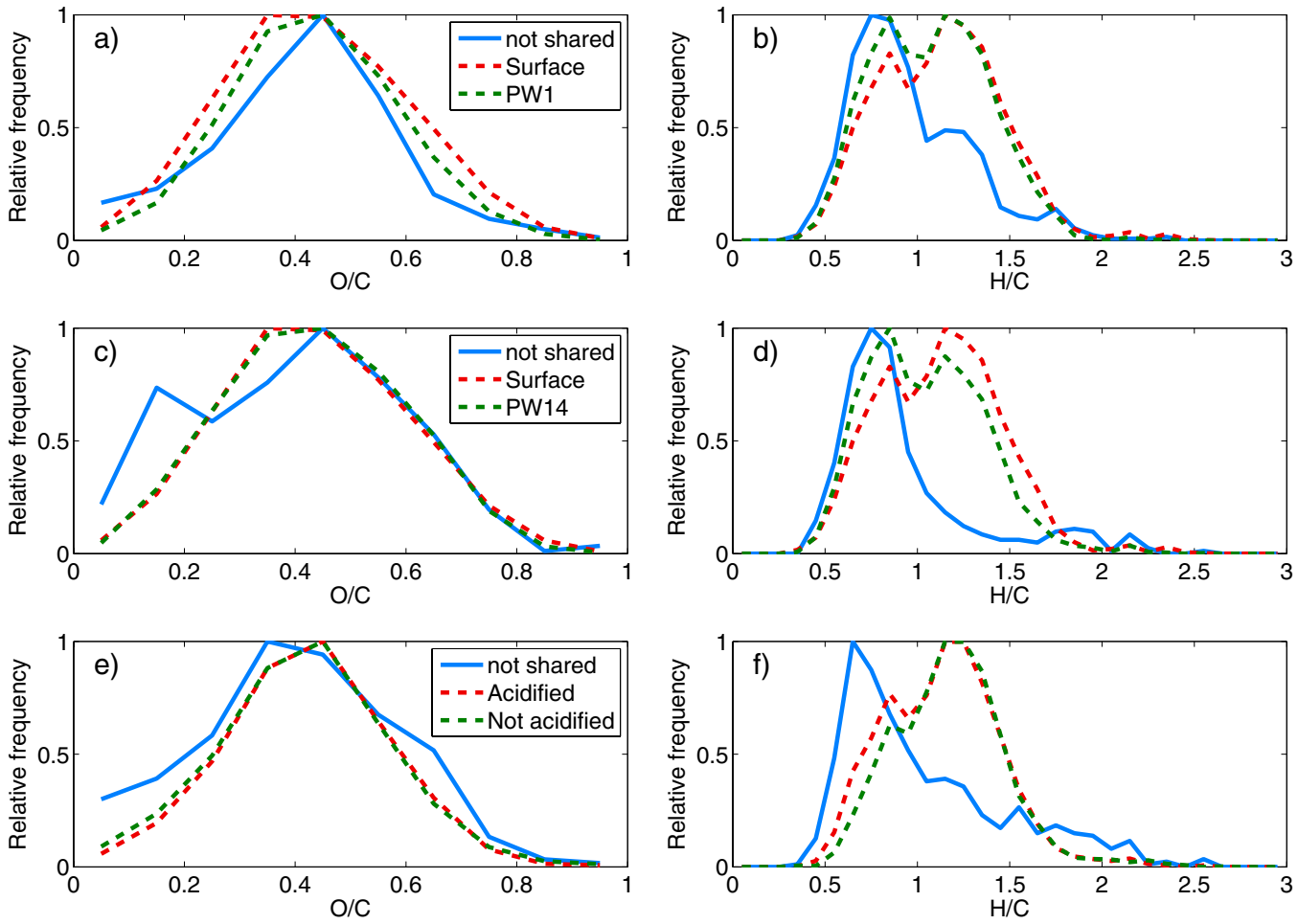

Fig. S3. Normalized distribution of elemental ratios for all formulas (CHON0-2S0-1P0-1) found per sample and all formulas not shared between two samples. (*A* and *B*) Comparison of surface (red) and pore water (PW; green) samples taken at 5–10 cm at Wendewiesen. (*C* and *D*) Comparison of surface (red) and PW (green) samples taken at 55–60 cm at Wendewiesen. (*E* and *F*) Comparison of pore water sample from the "Zarnekow" site with (not acidified, green) and without Fe(III) precipitation (acidified, red). Elemental ratios of formulas not shared are shown in blue.

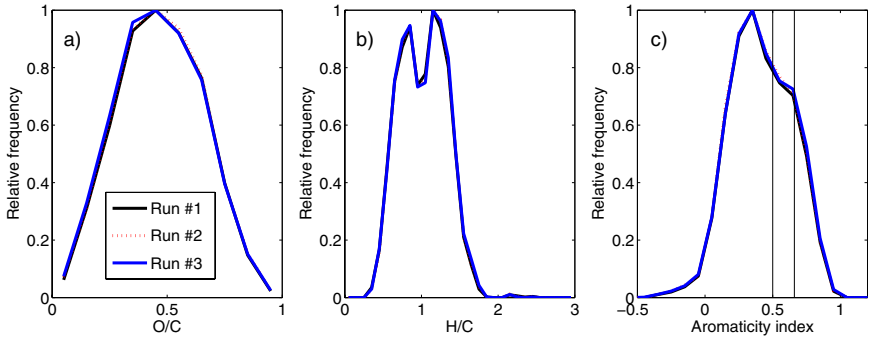

Fig. S4. Example of triplicate analysis of a sample to illustrate the precision of the ESI-FT-ICR-MS analysis. (*A*) Oxygen-to-carbon ratio; (*B*) Hydrogen-to-carbon ratio; (*C*) AI. The sample shown is a river water sample from another study extracted and measured using the same procedures used in this study. Number-averaged ratios (±SD) are as follows: O/C ratio: 0.468 ± 0.002, H/C ratio: 1.029 ± 0.002, percentage of formulas with aromaticity index > 0.5: 34.8 ± 0.4, and percentage of formulas with aromaticity index >0.66: 14.3 ± 0.4.

Table S1. Concentrations of dissolved iron and organic carbon before and after aeration of pore water samples from both sites and from different sampling campaigns

	Before aeration		After aeration				
Site/date	Fe, μM	DOC, μM	Fe, μM	DOC, μM	Initial DOC/Fe	Fe removed, %	DOC removed, %
Wendewiesen							
April 2004	411	6,667	23	4,583	16	94	31
April 2004	536	6,500	20	4,417	12	96	32
April 2004	304	5,500	23	3,750	18	92	32
June 2004	839	9,167	5	5,333	11	99	42
June 2004	857	9,583	5	5,333	11	99	44
June 2004	482	7,500	7	5,000	16	99	33
September 2004	1,000	9,583	11	6,500	10	99	32
September 2004	1,000	9,167	16	5,750	9	98	37
September 2004	857	8,333	18	5,417	10	98	35
November 2004	1,339	13,417	7	8,667	10	99	35
November 2004	857	10,333	7	6,667	12	99	35
November 2004	625	6,417	7	4,417	10	99	31
June 2008	261	5,167	4	3,750	20	98	27
June 2008	305	6,500	5	4,750	21	98	27
June 2008	250	8,250	7	6,833	33	97	17
July 2011	393	6,917	30	5,667	18	92	18
July 2011	411	9,333	30	7,167	23	93	23
July 2011	464	8,833	34	6,917	19	93	22
July 2012	261	5,417	20	4,083	21	92	25
July 2012	321	6,250	8	4,583	19	98	27
July 2012	286	6,330	18	4,333	22	94	32
Zarnekow							
May 2005	1,661	17,333	21	12,417	10	99	28
May 2005	1,679	18,500	23	13,583	11	99	27
May 2005	1,696	20,667	39	15,917	12	98	23
June 2005	1,625	16,667	25	12,500	10	98	25
June 2005	1,607	18,333	29	12,500	11	98	32
June 2005	1,607	20,000	45	15,000	12	97	25
July 2005	1,304	19,000	29	14,083	15	98	26
July 2005	1,321	21,500	38	15,083	16	97	30
July 2005	1,321	20,333	41	16,500	15	97	19
May 2011	459	11,833	7	10,250	26	98	13
May 2011	1,446	16,500	6	12,583	11	100	24
May 2011	929	14,083	5	11,750	15	99	17
July 2011	661	13,583	12	12,167	21	98	10
July 2011	1,821	19,833	9	14,500	11	100	27
July 2011	875	17,083	12	14,250	20	99	17
November 2011	275	8,583	7	5,917	31	98	31
November 2011	375	5,917	3	4,667	16	99	21
November 2011	338	6,917	5	5,333	20	99	23
July 2012	320	8,917	6	7,083	28	98	21
July 2012	446	6,667	4	4,833	15	99	28
July 2012	393	10,667	12	8,083	27	97	24

DOC, dissolved organic carbon.