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Supporting Information for

The biogeochemistry of electroactive humic substances and its connection to iron chemistry in the North East Atlantic and the Western Mediterranean Sea

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Introduction

This supporting information contains three figures (S1 to S3) and two tables (Table S1 and S2). Figure S1 presents a comparison humic like substance concentrations for 24 samples at station 11 in the Mediterranean sector determined by a SEC-LC-OCD device and by cathodic stripping voltammetry on a mercury drop electrode. Figure S2 shows the average precipitation rate during the cruise and the decrease of salinity induced at station 11 by an intense rain event. Figure S4 shows the presence of a strong anti-cyclonic eddy at station 11 during the cruise. Table S1 presents the locations and depths of samples used for the intercomparison presented figure 2 in the main text. Table S2 is presenting the electroactive humic-like substances measured along the section and discussed in this study.

Figure S1. Comparison between Humic like substances (HS) concentrations normalized in Swannee River Fulvic Acid (SRFA) measured at station 11 in the Mediterranean sector by a size exclusion column liquid chromatography with organic carbon detector (SEC-LC-OCD HS, open circles) and electroactive humic like substances (eHS) by cathodic stripping voltammetry on a mercury drop electrode (filled circles). Note the different scales.

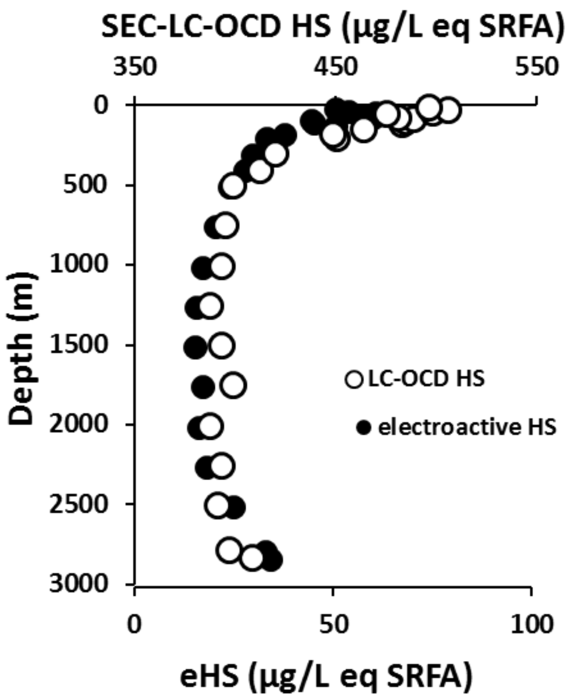

Figure S2. (a) Average precipitation rate (mm d-1) during the cruise (15^{th} – 22th May, data generated using TRMM model), sampling stations are indicated. **(b)** Absolute salinity (S_A) distribution in the upper 300 meters at station 9, 11 and 14. **(c)** Backward air mass trajectory for the day of sampling at station 11 (22th May, generated using Hysplit ensemble model, http://ready.arl.noaa.gov).

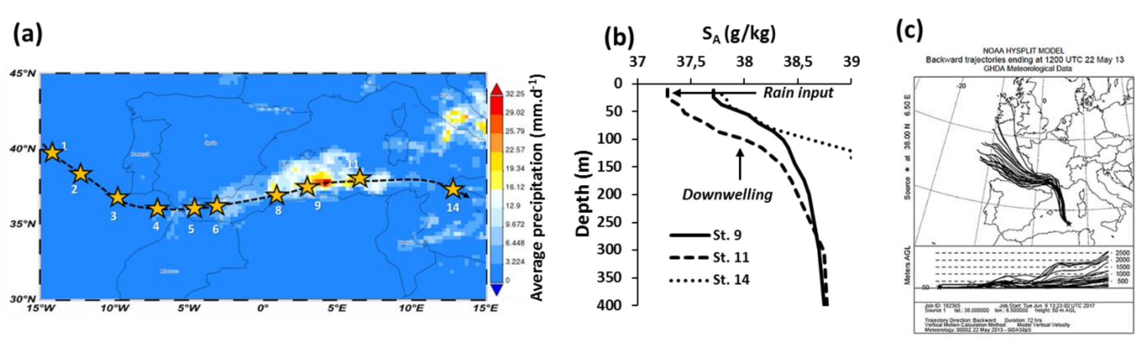

Figure S3. (a) Map of absolute dynamic topography on the 20th May 2013. Anti-cyclonic eddy is located at station 11. Map generated using AVISO data (https://www.aviso.altimetry.fr/). (b) Zonal section of potential density between 0.7°E and 11°E during the expedition. Downwelling of density isocline is observed at station 11.

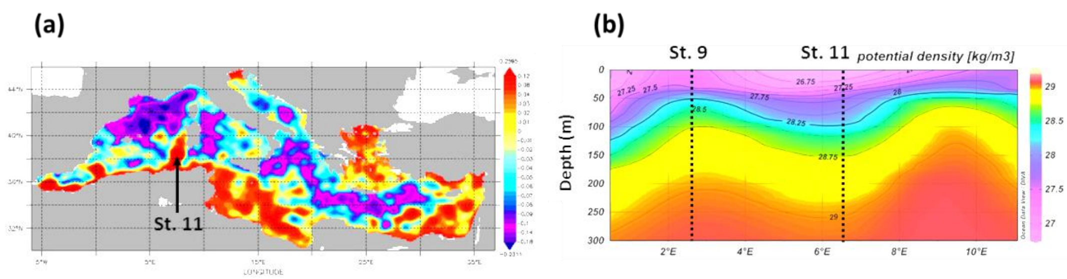

Table S1. Station locations and depth associated of the seawater samples used for the intercomparison between the Laglera et al. (2007) and Pernet-Coudrier et al. (2013) methods for the determination of electro-active humic-like substances. All these samples (except the coastal seawater from the bay of Brest) were originally acidified with HCl. Prior analysis with the Fe-HS method HCl was neutralized using suprapure® NaOH (Merck) to reach a pH of 8 ± 0.02.

Sample	**Location**	**Depth (m)**
Bay of Brest	Bay of Brest, France	1
GA04	40°N; 6°E, North Western Mediterranean Sea	40
		2815
GS	BATS, North Atlantic	2
GD	BATS, North Atlantic	2000
S1	SAFe station, North Pacific	2
D1	SAFe station, North Pacific	1000
DSR	Strait of Florida, North Atlantic	700

Table S2. Station locations and depth associated to electroactive humic like substances (eHS) concentrations in µg L^{-1} of equivalent Suwannee River Fulvic acid (µg eqSRFA L^{-1}) measured during the cruise. Standard deviations (SD eHS) on measurements are in µg eqSRFA L^{-1}.

Station	Latitude	Longitude	Depth (m)	eHS (µg eqSRFA L^{-1})	SD eHS (µg eqSRFA L^{-1})
1	39°44’N	14°10’W	5348	35.5	3.3
1	39°44’N	14°10’W	5000	27.2	0.4
1	39°44’N	14°10’W	3997	26.0	0..7
1	39°44’N	14°10’W	2999	27.9	1.3
1	39°44’N	14°10’W	1999	31.5	0.4
1	39°44’N	14°10’W	1499	26.6	0.2
1	39°44’N	14°10’W	1251	22.9	0.1
1	39°44’N	14°10’W	1001	24.7	1.1
1	39°44’N	14°10’W	501	33.3	0.7
1	39°44’N	14°10’W	300	33.6	1.1
1	39°44’N	14°10’W	199	34.2	2.5
1	39°44’N	14°10’W	101	43.4	0.3
1	39°44’N	14°10’W	75	43.9	0.5
1	39°44’N	14°10’W	48	50.9	1.0
1	39°44’N	14°10’W	23	81.2	4.2
1	39°44’N	14°10’W	9	66.9	0.5
2	38°8.48’N	12°12.44’W	4996	29.4	0.9
2	38°8.48’N	12°12.44’W	4949	24.1	1.4
2	38°8.48’N	12°12.44’W	3999	24.2	0.5
2	38°8.48’N	12°12.44’W	3002	19.5	1.0
2	38°8.48’N	12°12.44’W	1999	18.7	0.7
2	38°8.48’N	12°12.44’W	1499	14.2	0.5
2	38°8.48’N	12°12.44’W	1246	17.8	0.3
2	38°8.48’N	12°12.44’W	999	23.0	0.7
2	38°8.48’N	12°12.44’W	500	30.4	1.5
2	38°8.48’N	12°12.44’W	300	31.3	1.6
2	38°8.48’N	12°12.44’W	200	30.7	1.8
2	38°8.48’N	12°12.44’W	101	40.0	1.6
2	38°8.48’N	12°12.44’W	74	45.8	1.4
2	38°8.48’N	12°12.44’W	51	47.3	2.8
2	38°8.48’N	12°12.44’W	24	48.1	0.5
2	38°8.48’N	12°12.44’W	9	49.7	3.0
3	36° 34' N	9° 51.96' W	3875	25.9	0.3
3	36° 34' N	9° 51.96' W	3823	21.2	1.1
3	36° 34' N	9° 51.96' W	3251	16.8	0.2
3	36° 34' N	9° 51.96' W	2751	24.3	0.2

3	36° 34' N	9° 51.96' W	2000	19.7	0.2
3	36° 34' N	9° 51.96' W	1499	20.1	0.6
3	36° 34' N	9° 51.96' W	1001	20.8	0.8
3	36° 34' N	9° 51.96' W	752	21.9	1.1
3	36° 34' N	9° 51.96' W	503	27.4	0.3
3	36° 34' N	9° 51.96' W	300	25.3	1.0
3	36° 34' N	9° 51.96' W	151	33.2	0.3
3	36° 34' N	9° 51.96' W	100	33.8	1.4
3	36° 34' N	9° 51.96' W	75	32.9	1.7
3	36° 34' N	9° 51.96' W	50	30.6	1.9
3	36° 34' N	9° 51.96' W	24	32.0	1.3
3	36° 34' N	9° 51.96' W	8	34.3	0.7
4	35° 50.39' N	7° 15.26' W	1043	37.9	1.3
4	35° 50.39' N	7° 15.26' W	1000	24.9	0.1
4	35° 50.39' N	7° 15.26' W	801	29.7	0.5
4	35° 50.39' N	7° 15.26' W	701	23.9	2.7
4	35° 50.39' N	7° 15.26' W	601	31.4	0.5
4	35° 50.39' N	7° 15.26' W	499	29.4	0.4
4	35° 50.39' N	7° 15.26' W	398	28.5	0.1
4	35° 50.39' N	7° 15.26' W	250	37.9	0.4
4	35° 50.39' N	7° 15.26' W	174	37.1	0.0
4	35° 50.39' N	7° 15.26' W	144	37.1	0.0
4	35° 50.39' N	7° 15.26' W	115	33.3	1.1
4	35° 50.39' N	7° 15.26' W	100	37.5	0.6
4	35° 50.39' N	7° 15.26' W	68	39.4	0.5
4	35° 50.39' N	7° 15.26' W	59	47.5	0.2
4	35° 50.39' N	7° 15.26' W	25	45.7	0.6
4	35° 50.39' N	7° 15.26' W	10	60.9	1.4
5	36° 3.52' N	4° 49.38' W	934	15.5	0.1
5	36° 3.52' N	4° 49.38' W	899	12.1	0.8
5	36° 3.52' N	4° 49.38' W	800	16.8	0.5
5	36° 3.52' N	4° 49.38' W	700	20.5	1.3
5	36° 3.52' N	4° 49.38' W	499	18.4	0.2
5	36° 3.52' N	4° 49.38' W	400	22.8	0.5
5	36° 3.52' N	4° 49.38' W	249	29.2	3.7
5	36° 3.52' N	4° 49.38' W	144	40.0	0.1
5	36° 3.52' N	4° 49.38' W	113	33.1	1.3
5	36° 3.52' N	4° 49.38' W	98	45.4	1.6
5	36° 3.52' N	4° 49.38' W	69	39.8	0.6

5	36° 3.52' N	4° 49.38' W	54	57.6	0.0
5	36° 3.52' N	4° 49.38' W	39	58.8	1.5
5	36° 3.52' N	4° 49.38' W	27	67.0	0.9
5	36° 3.52' N	4° 49.38' W	9	64.0	2.0
6	36° 2.37' N	3° 12.97' W	1578	15.7	0.3
6	36° 2.37' N	3° 12.97' W	1528	14.4	0.8
6	36° 2.37' N	3° 12.97' W	1250	14.2	0.1
6	36° 2.37' N	3° 12.97' W	1000	14.9	0.3
6	36° 2.37' N	3° 12.97' W	400	18.1	0.7
6	36° 2.37' N	3° 12.97' W	300	20.3	0.4
6	36° 2.37' N	3° 12.97' W	205	32.4	1.6
6	36° 2.37' N	3° 12.97' W	175	30.6	1.9
6	36° 2.37' N	3° 12.97' W	145	39.3	2.0
6	36° 2.37' N	3° 12.97' W	100	49.2	1.4
6	36° 2.37' N	3° 12.97' W	100	50.6	1.0
6	36° 2.37' N	3° 12.97' W	79	51.8	2.1
6	36° 2.37' N	3° 12.97' W	56	54.7	0.6
6	36° 2.37' N	3° 12.97' W	40	51.4	2.6
6	36° 2.37' N	3° 12.97' W	24	63.3	3.2
6	36° 2.37' N	3° 12.97' W	10	66.8	1.3
8	37° 0.71' N	0° 43.42' E	2710	16.6	0.7
8	37° 0.71' N	0° 43.42' E	2660	15.3	0.9
8	37° 0.71' N	0° 43.42' E	2250	16.1	0.2
8	37° 0.71' N	0° 43.42' E	2001	11.9	0.7
8	37° 0.71' N	0° 43.42' E	1503	14.0	0.7
8	37° 0.71' N	0° 43.42' E	1250	13.7	0.8
8	37° 0.71' N	0° 43.42' E	750	21.8	0.2
8	37° 0.71' N	0° 43.42' E	451	21.4	0.6
8	37° 0.71' N	0° 43.42' E	301	31.3	0.9
8	37° 0.71' N	0° 43.42' E	145	40.7	2.5
8	37° 0.71' N	0° 43.42' E	98	44.6	2.3
8	37° 0.71' N	0° 43.42' E	71	46.3	2.8
8	37° 0.71' N	0° 43.42' E	53	46.9	2.8
8	37° 0.71' N	0° 43.42' E	42	55.4	3.3
8	37° 0.71' N	0° 43.42' E	27	53.9	0.5
8	37° 0.71' N	0° 43.42' E	10	54.9	1.7
9	37° 20.89' N	2° 44.99' E	2772	13.1	0.8
9	37° 20.89' N	2° 44.99' E	2721	13.4	0.7
9	37° 20.89' N	2° 44.99' E	2499	19.9	0.6

9	37° 20.89' N	2° 44.99' E	1997	12.2	0.6
9	37° 20.89' N	2° 44.99' E	1499	11.9	0.7
9	37° 20.89' N	2° 44.99' E	1000	13.0	0.3
9	37° 20.89' N	2° 44.99' E	500	16.4	0.6
9	37° 20.89' N	2° 44.99' E	301	20.8	1.1
9	37° 20.89' N	2° 44.99' E	174	28.3	0.8
9	37° 20.89' N	2° 44.99' E	115	35.2	0.4
9	37° 20.89' N	2° 44.99' E	101	37.8	1.5
9	37° 20.89' N	2° 44.99' E	71	39.9	1.6
9	37° 20.89' N	2° 44.99' E	55	59.2	2.4
9	37° 20.89' N	2° 44.99' E	37	60.7	2.4
9	37° 20.89' N	2° 44.99' E	25	44.2	1.3
9	37° 20.89' N	2° 44.99' E	11	44.0	2.2
11	37° 46.32' N	6° 39.69' E	2830	33.2	1.8
11	37° 46.32' N	6° 39.69' E	2781	24.4	0.7
11	37° 46.32' N	6° 39.69' E	2502	25.1	0.5
11	37° 46.32' N	6° 39.69' E	2250	18.4	0.7
11	37° 46.32' N	6° 39.69' E	2002	16.3	2.2
11	37° 46.32' N	6° 39.69' E	1751	17.3	1.2
11	37° 46.32' N	6° 39.69' E	1500	15.3	0.6
11	37° 46.32' N	6° 39.69' E	1252	15.7	0.2
11	37° 46.32' N	6° 39.69' E	1001	17.4	0.6
11	37° 46.32' N	6° 39.69' E	751	20.5	1.4
11	37° 46.32' N	6° 39.69' E	500	17.5	0.7
11	37° 46.32' N	6° 39.69' E	400	27.8	0.1
11	37° 46.32' N	6° 39.69' E	303	23.0	0.6
11	37° 46.32' N	6° 39.69' E	200	33.3	0.3
11	37° 46.32' N	6° 39.69' E	176	37.8	1.1
11	37° 46.32' N	6° 39.69' E	146	49.5	2.5
11	37° 46.32' N	6° 39.69' E	115	50.9	0.1
11	37° 46.32' N	6° 39.69' E	100	45.4	1.0
11	37° 46.32' N	6° 39.69' E	86	44.8	0.5
11	37° 46.32' N	6° 39.69' E	71	60.0	0.6
11	37° 46.32' N	6° 39.69' E	53	56.9	0.3
11	37° 46.32' N	6° 39.69' E	40	60.9	1.1
11	37° 46.32' N	6° 39.69' E	26	54.0	0.1
11	37° 46.32' N	6° 39.69' E	10	50.8	0.5
14	37° 12.88' N	12° 28.02' E	133	24.8	1.0
14	37° 12.88' N	12° 28.02' E	120	25.2	0.8

14	37° 12.88' N	12° 28.02' E	100	37.1	3.0
14	37° 12.88' N	12° 28.02' E	91	37.4	1.5
14	37° 12.88' N	12° 28.02' E	80	44.2	4.4
14	37° 12.88' N	12° 28.02' E	70	35.8	1.4
14	37° 12.88' N	12° 28.02' E	60	37.2	2.6
14	37° 12.88' N	12° 28.02' E	50	44.4	4.4
14	37° 12.88' N	12° 28.02' E	40	37.8	3.8
14	37° 12.88' N	12° 28.02' E	30	42.8	3.0
14	37° 12.88' N	12° 28.02' E	20	36.2	2.5
14	37° 12.88' N	12° 28.02' E	10	39.3	3.5

Conclusions: Electroactive humic-like substances were quantified along a part of the GEOTRACES A04N section. The intercomparison exercise shows an excellent agreement between Laglera et al. (2007) and Pernet-Coudrier et al. (2013) methods. Full depth profiles shown surface enrichment and low concentrations in the deep sea. This distribution was related to the biological mediated production of humics in the euphotic layer and bacterial degradation in the mesopelagic layer. Humic biogeochemistry is thought to impact dissolved iron distribution through an iron humic shuttle.

References:

Laglera, L. M., Battaglia, G., & van den Berg, C. M.G. (2007). Determination of humic substances in natural waters by cathodic stripping voltammetry of their complexes with iron. *Analytica chimica acta*, *599*(1), 58-66.

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