

Selective accumulation of dissolved organic matter in the sea surface microlayer: Insights from CDOM and FDOM characterisation at a Mediterranean coastal site.

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Supplementary material

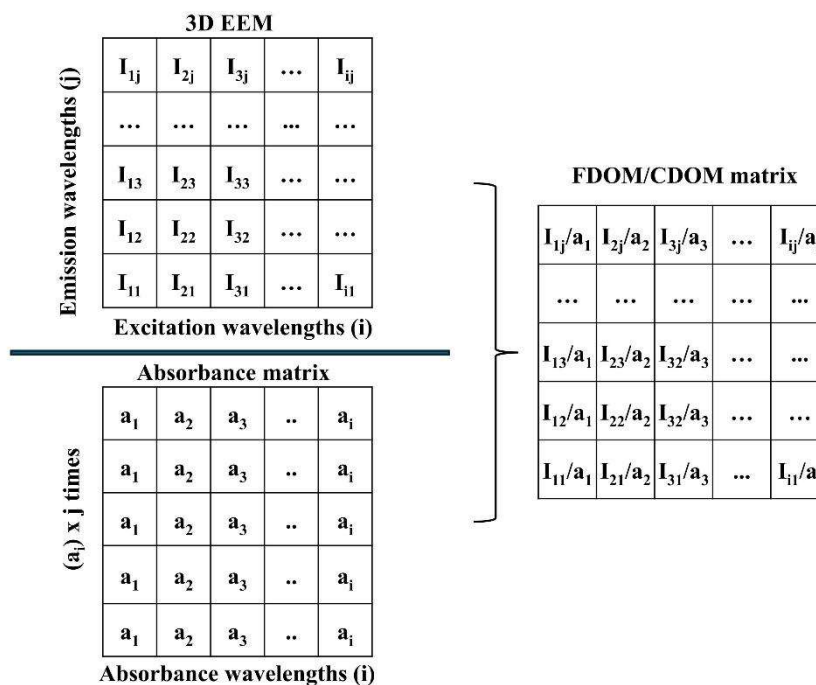


Fig. S1 The FDOM/CDOM index is calculated as follows: The fluorescence intensity (I_{ij}) at each excitation wavelength (Ex_i) of the EEM matrix is divided by the corresponding absorption coefficient (a_i) obtained from the absorption measurements. This is repeated for all emission wavelengths (Em_j) (a_i x j times), thus yielding the ratio I_{ij}/a_i i.e. the FDOM/CDOM (R.U.m) index, in the form of a 3-dimensional matrix where $Ex=250-450nm$ and $Em=260-550nm$

Table S1. Measured environmental and physicochemical variables during samplings.

Sampling date	SML thickness d_{SML}	Wind speed	Solar irradiance E	Seawater Temperature T	Seawater Salinity	DOC	
	μm	$m s^{-1}$	$W m^{-2}$	$^{\circ}C$	psu	$mg L^{-1}$	
				<i>At 1m depth</i>		<i>SML</i>	<i>ULW</i>
2/06/2016	45.99	0-0.8	600-750	17.2	38.5	3.039	0.964
16/06/2016	50.79	0.9-1.8	600-850	23.0	38.5	3.584	1.019
1/07/2016	52.60*	0.8-2.0	650-800	22.1	38.9	6.561	0.917
2/08/2016	41.05	0-0.8	650-900	25.8	38.9	3.208	0.916
18/08/2016	50.42	0-1.8	650-900	26.3	38.9	2.865	0.977
6/09/2016	45.22	0-0.9	500-650	26.0	38.9	-	0.996
21/09/2016	42.85*	0-1.4	500-650	26.5	38.9	3.876	0.924
7/10/2016	48.62*	0	300-450	25.7	38.8	1.585	1.263
21/10/2016	49.07*	0-1.9	250-350	24.4	38.8	3.008	0.871
3/11/2016	51.81*	0-1.5	200-320	23.0	38.6	1.462	0.913
18/11/2016	58.71*	0-1.5	200-320	21.8	38.7	3.714	0.864
2/12/2016	54.99*	0- 2.0	200-300	20.7	38.9	3.228	0.887
20/12/2016	51.59*	0.4-1.7	200-250	19.0	38.7	2.498	0.860
4/01/2016	57.02	0-1.5	200-350	17.2	38.6	1.830	0.815
28/01/2017	60.05*	0-2.2	130-200	15.6	38.6	2.321	0.777
9/02/2017	56.37	3.5	150-280	14.1	38.5	1.090	0.787
22/02/2017	48.83	0-0.7	400-500	14.2	39.0	1.215	0.832
7/03/2017	51.22*	0.5-2.1	200-450	14.3	39.0	1.990	0.891
3/04/2017	49.47	0-0.1	520-690	15.5	38.2	1.116	0.832
25/04/2017	44.29*	0-1.3	550-690	15.5	38.9	1.909	0.879
4/05/2017	47.09*	0-1.7	580-750	17.0	39.0	6.85	0.850
10/06/2017	56.79	0-0.7	600-820	19.1	38.3	3.575	0.938
Average				20.2	38.8	2.480	0.908
Standard Deviation				4.5	0.5	0.942	0.102
CV (%)				22.0	1.1	38.0	11.2

*Visible slicks

Table S2. Spectral position of the PARAFAC components deconvoluted by the 2 different models using the seawater (SML and UWL) EEMs and for the rainwater EEMs.

Seawater	Rainwater
C1 Ex/Em= 240,370/ 485 Peak A, C	R1 Ex/Em= 240,290/ 394 Peak A, M
C2 Ex/Em= 240,280/ 325 Peak T	R2 Ex/Em= 245,335/ 456 Peak A, C
C3 Ex/Em= 240,297/ 408 Peak A, M	R3 Ex/Em= 240,270/ 299 Peak B
C4 Ex/Em= 265/296 Peak B	

Table S3 Absorption coefficients $a_{(\lambda)}$ (m^{-1}) and spectral slope $S_{275-295}$ (nm^{-1}) for the SML and ULW samples

Sampling date	a_{265} (m^{-1})		a_{280} (m^{-1})		a_{300} (m^{-1})		a_{370} (m^{-1})		$S_{275-295}$ (nm^{-1})	
	<i>SML</i>	<i>ULW</i>	<i>SML</i>	<i>ULW</i>	<i>SML</i>	<i>ULW</i>	<i>SML</i>	<i>ULW</i>	<i>SML</i>	<i>ULW</i>
2/06/2016	-	2.546	-	1.810	-	0.979	-	0.198	-	0.031
16/06/2016	5.002	1.102	3.719	0.748	2.403	0.367	0.892	0.083	0.023	0.035
1/07/2016	12.29	1.372	9.429	0.921	6.362	0.483	2.896	0.122	0.020	0.033
2/08/2016	4.992	1.219	3.635	0.810	2.133	0.421	0.695	0.121	0.026	0.034
18/08/2016	4.073	0.910	3.282	0.599	1.991	0.282	0.686	0.090	0.023	0.037
6/09/2016	5.852	1.424	4.293	0.964	2.666	0.451	0.777	0.084	0.023	0.036
21/09/2016	5.761	0.953	4.180	0.635	2.452	0.306	0.766	0.062	0.027	0.037
7/10/2016	2.552	1.890	1.845	1.474	1.017	0.740	0.291	0.140	0.029	0.030
21/10/2016	4.898	1.406	3.633	0.927	2.216	0.434	0.693	0.092	0.024	0.037
3/11/2016	2.564	1.313	1.815	0.853	1.021	0.391	0.329	0.070	0.029	0.038
18/11/2016	7.402	1.109	5.757	0.724	3.741	0.327	1.466	0.073	0.021	0.039
2/12/2016	6.339	1.248	4.794	0.843	3.031	0.418	1.208	0.096	0.023	0.035
20/12/2016	5.923	1.506	4.419	1.035	2.538	0.560	0.829	0.157	0.028	0.031
4/01/2016	3.006	0.956	2.211	0.653	1.223	0.302	0.404	0.060	0.030	0.036
28/01/2017	4.948	1.161	3.925	0.803	2.286	0.404	0.740	0.099	0.025	0.034
9/02/2017	1.772	1.790	1.304	1.418	0.758	0.685	0.251	0.119	0.027	0.031
22/02/2017	2.119	1.254	1.531	0.897	0.852	0.528	0.270	0.184	0.030	0.027
7/03/2017	4.651	1.147	3.536	0.780	2.335	0.425	0.894	0.090	0.021	0.030
3/04/2017	1.591	0.905	1.119	0.621	0.569	0.338	0.138	0.103	0.034	0.031
25/04/2017	3.443	1.403	2.610	0.963	1.592	0.530	0.635	0.140	0.026	0.030
4/05/2017	12.91	1.116	12.73	1.084	9.347	0.638	5.877	0.202	0.015	0.027
10/06/2017	6.264	1.682	4.965	1.197	3.332	0.700	1.453	0.174	0.021	0.026
Average	4.376	1.337	3.293	0.944	2.008	0.487	0.706	0.116	0.025	0.033
Standard Deviation	1.725	0.381	1.349	0.303	0.908	0.173	0.381	0.044	0.004	0.004
CV (%)	39.4	28.5	41.0	32.1	45.2	35.5	54.0	37.5	16.7	11.6

Table S4. Enrichment Factors (EFs) of DOC, absorption coefficients (a_i) and fluorescence intensities (I_{1-4}) of the identified PARAFAC components (all EFs are significantly greater than unity, $p < 0.05$). Average values and ranges in parentheses.

	All (July 2016 and May 2017 excluded)	July 2016	May 2017
DOC	2.7 (1.3 - 4.3)	7.2	8.1
a_{265}	3.6 (1.5 - 4.8)	8.2	13.3
a_{280}	3.8 (1.6 - 5.4)	10.2	13.5
a_{300}	4.8 (1.8 - 7.0)	12.7	17.8
a_{370}	7.4 (2.3 - 13.0)	22.4	37.1
I1	4.2 (2.8 - 5.7)	10.9	24.3
I2	4.5 (2.1 - 6.7)	25.0	18.5
I3	3.4 (2.2 - 4.8)	110.9	33.7
I4	2.8 (1.1 - 5.9)	9.7	16.6

Table S5. Maximum fluorescence intensities (I_{1-4}) (R.U.) of the 4 components resolved by the PARAFAC seawater model.

Sampling date	I₁ (R.U.)		I₂ (R.U.)		I₃ (R.U.)		I₄ (R.U.)	
	<i>SML</i>	<i>ULW</i>	<i>SML</i>	<i>ULW</i>	<i>SML</i>	<i>ULW</i>	<i>SML</i>	<i>ULW</i>
2/06/2016	0.140	0.019	0.099	0.017	0.083	0.013	0.126	0.011
16/06/2016	0.056	0.022	0.051	0.019	0.050	0.016	0.024	0.037
1/07/2016	0.241	0.027	0.429	0.023	1.249	0.016	0.141	0.016
2/08/2016	0.083	0.018	0.073	0.017	0.064	0.009	0.051	0.009
18/08/2016	0.068	0.014	0.065	0.014	0.053	0.008	0.106	0.011
6/09/2016	0.080	0.017	0.060	0.015	0.056	0.007	0.058	0.017
21/09/2016	0.087	0.022	0.075	0.021	0.052	0.017	0.048	0.017
7/10/2016	0.051	0.036	0.046	0.035	0.039	0.036	0.022	0.046
21/10/2016	0.098	0.016	0.092	0.017	0.072	0.015	0.057	0.012
3/11/2016	0.045	0.026	0.047	0.024	0.030	0.021	0.032	0.013
18/11/2016	0.106	0.017	0.093	0.016	0.058	0.011	0.035	0.003
2/12/2016	0.112	0.027	0.106	0.022	0.075	0.022	0.041	0.009
20/12/2016	0.100	0.031	0.136	0.021	0.064	0.025	0.036	0.009
4/01/2016	0.086	0.016	0.110	0.021	0.048	0.018	0.027	0.022
28/01/2017	0.112	0.017	0.116	0.019	0.078	0.018	0.080	0.014
9/02/2017	0.038	0.023	0.038	0.020	0.039	0.021	0.020	0.009
22/02/2017	0.061	0.025	0.093	0.019	0.032	0.011	0.001	0.011
7/03/2017	0.095	0.015	0.077	0.010	0.044	0.013	0.012	0.007
3/04/2017	0.033	0.020	0.051	0.019	0.016	0.016	0.002	0.004
25/04/2017	0.067	0.021	0.085	0.015	0.040	0.015	0.021	0.004
4/05/2017	0.398	0.020	0.315	0.017	0.394	0.013	0.196	0.013
10/06/2017	0.101	0.017	0.117	0.014	0.057	0.010	0.048	0.004
Average	0.081	0.081	0.053	0.045	0.021	0.019	0.016	0.014
Standard Deviation	0.028	0.028	0.017	0.031	0.006	0.005	0.006	0.010
CV (%)	34.8	34.0	32.8	70.4	27.0	26.6	40.4	76.5

Table S6. Rainwater data of DOC (mg L⁻¹), absorbance coefficients a_i (m⁻¹) and maximum fluorescence intensities (I₁₋₃) (R.U.) of the 3 components resolved by the PARAFAC rainwater model.

Sampling date	DOC (mg L ⁻¹)	a_{265} (m ⁻¹)	a_{280} (m ⁻¹)	a_{300} (m ⁻¹)	a_{370} (m ⁻¹)	$S_{275-295}$ (nm ⁻¹)	I ₁ (R.U.)	I ₂ (R.U.)	I ₃ (R.U.)
15/12/2016	5.745	16.26	12.81	8.001	2.361	0.025	0.786	0.389	0.203
28-29/12/2016	2.494	5.128	4.123	2.424	0.734	0.026	0.374	0.126	0.223
09-10/01/2017	3.471	11.99	9.381	6.049	1.659	0.022	1.091	0.302	0.336
15/01/2017	1.238	4.645	3.580	2.396	0.683	0.021	0.375	0.134	0.101
24/01/2017	2.798	4.689	3.826	2.287	0.567	0.023	0.315	0.138	0.197
07/02/2017	1.257	7.115	6.258	3.567	0.741	0.023	0.453	0.295	0.381
08/02/2017	0.681	2.219	1.733	1.124	0.393	0.023	0.162	0.065	0.071
07/03/2017	6.266	16.50	12.82	8.070	2.331	0.023	0.741	0.376	0.457
08-09/03/2017	0.596	2.895	2.432	1.465	0.452	0.023	0.120	0.057	0.145
09/03/2017	1.186	3.381	2.869	1.707	0.537	0.023	0.192	0.072	0.186
11/03/2017	-	2.186	2.081	0.931	0.161	0.030	0.108	0.025	0.123
18/05/2017	3.463	10.09	7.871	4.658	1.368	0.025	0.297	0.187	0.223
21/05/2017	0.886	2.611	2.063	1.361	0.367	0.021	0.114	0.074	0.056
22/05/2017	2.281	7.947	5.965	3.486	0.871	0.026	0.156	0.090	0.082
Average	2.489	6.976	5.558	3.395	0.945	0.024	0.377	0.166	0.199
Standard Deviation	1.851	4.969	3.831	2.431	0.711	0.002	0.299	0.123	0.120
CV (%)	74.4	71.2	68.9	71.6	75.3	10.0	79.2	74.2	60.5