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# Characteristics of chromophoric and fluorescent dissolved organic matter in the Nordic Seas

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**Supplementary information**

The water identification was based on Rudels at al. (2005) with the modifications noted in Table S1. In general we assumed that water characterized by density, potential temperature and salinity found south of 74N parallel could not be regard as PSW or PSWw due strong influence of high temperature on density.

Table S1. Water masses definition by Rudels et al. (2005) with modifications and remarks.

| | Rudels at al. (2005) | | | Modifications | | | |
|---|---|---|---|---|---|---|---|
| Water Masses | Symbol | Θ [°C] | $\sigma_\theta$ [kg*m$^{-3}$] | S | Lat [N] | D [m] | Remarks |
| Atlantic Water | AW | >2 | $27.7<\sigma_\theta\leq27.97$ | | | | |
| | AW | >0 | $27.97<\sigma_\theta$, $\sigma_{0.5}\leq30.44$ | | | | |
| | AW | >0 | ≤27.7 | >34.9 | | | This part was separated from PSWw on the basis of high salinity >34.9. It covers the Atlantic domain where low density is caused by high temperatures |
| Polar Surface Water | PSW | ≤0 | ≤27.7 | | >74 | | Assumption that PSW does not occur south of 74 N |
| Polar Surface Water warm | PSWw | >0 | ≤27.7 | ≤34.9 | >74 | ≤50 | Assumption that PSW does not occur south of 74 N, and surface water occur in first 50 m |
| Arctic Atlantic Water | AAW | 0 < x≤2 | $27.7<\sigma_\theta\leq27.97$ | | | | |
| Deep water | DW(AIW) | ≤0 | $27.97<\sigma_\theta$, $\sigma_{0.5}\leq30.44$ | | | | All waters classified as AIW in AREX cruises occur close to the bottom. |

Table S1: The results of T test with variables grouped by year and water masses. Table results of t-test that measure significance in differences in mean value. The difference between variable averages in selected layer are significant if significance level $p<0.05$. NS - not significant, S – significant differences (bold text).

| Variable | Year | Water masses | t-value | df | p | Significance |
|---|---|---|---|---|---|---|
| $a_{CDOM}(350)$ | 2013 | AW vs. PSW | 0.077730 | 44 | 0.938395 | NS |
| | | AW vs. PSWw | -1.55385 | 74 | 0.124487 | NS |
| | | PSW vs. PSWw | -0.484689 | 34 | 0.631005 | NS |
| | 2014 | AW vs. PSW | 1.057659 | 176 | 0.291660 | NS |
| | | AW vs. PSWw | -0.057183 | 200 | 0.954456 | NS |
| | | AW vs. AAW | -0.084527 | 176 | 0.932733 | NS |
| | | AW vs. IW/DW | -1.31413 | 183 | 0.190446 | NS |
| | | PSW vs. PSWw | -1.20685 | 30 | 0.236920 | NS |
| | | PSW vs. AAW | -1.16764 | 6 | 0.287250 | NS |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | PSW vs. IW/DW | -1.31478 | 13 | 0.211308 | NS |
| | | PSWw vs. AAW | -0.068131 | 30 | 0.946133 | NS |
| | | PSWw vs. IW/DW | -1.11398 | 37 | 0.272473 | NS |
| | | AAW vs. IW/DW | -0.511292 | 13 | 0.617720 | NS |
| | 2015 | AW vs. PSW | **-4.44626** | **160** | **0.000016** | S |
| | | AW vs. PSWw | **-4.06548** | **227** | **0.000066** | S |
| | | AW vs. AAW | **-4.78185** | **163** | **0.000004** | S |
| | | AW vs. IW/DW | **3.248989** | **173** | **0.001392** | S |
| | | PSW vs. PSWw | **2.620125** | **77** | **0.010584** | S |
| | | PSW vs. AAW | 0.295868 | 13 | 0.772004 | NS |
| | | PSW vs. IW/DW | **4.306062** | **23** | **0.000263** | S |
| | | PSWw vs. AAW | **-2.64463** | **80** | **0.009840** | S |
| | | PSWw vs. IW/DW | **4.851875** | **90** | **0.000005** | S |
| | | AAW vs. IW/DW | **5.090324** | **26** | **0.000026** | S |
| $S_{300-600}$ | 2013 | AW vs. PSW | 0.524860 | 44 | 0.602315 | NS |
| | | AW vs. PSWw | 1.118054 | 74 | 0.267160 | NS |
| | | PSW vs. PSWw | 0.064696 | 34 | 0.948795 | NS |
| | 2014 | AW vs. PSW | -0.405673 | 176 | 0.685476 | NS |
| | | AW vs. PSWw | 0.874175 | 200 | 0.383071 | NS |
| | | AW vs. AAW | 0.240337 | 176 | 0.810348 | NS |
| | | AW vs. IW/DW | 1.881482 | 183 | 0.061494 | NS/close |
| | | PSW vs. PSWw | 0.811732 | 30 | 0.423340 | NS |
| | | PSW vs. AAW | 0.713604 | 6 | 0.502273 | NS |
| | | PSW vs. IW/DW | 1.561149 | 13 | 0.142494 | NS |
| | | PSWw vs. AAW | -0.123383 | 30 | 0.902627 | NS |
| | | PSWw vs. IW/DW | 1.316258 | 37 | 0.196184 | NS |
| | | AAW vs. IW/DW | 1.058590 | 13 | 0.309061 | NS |
| | 2015 | AW vs. PSW | 0.455974 | 160 | 0.649027 | NS |
| | | AW vs. PSWw | 1.928425 | 227 | 0.055050 | NS/close |
| | | AW vs. AAW | **2.012286** | **163** | **0.045837** | S |
| | | AW vs. IW/DW | **-2.89410** | **173** | **0.004292** | S |
| | | PSW vs. PSWw | 0.193909 | 77 | 0.846757 | NS |
| | | PSW vs. AAW | 0.752780 | 13 | 0.464996 | NS |
| | | PSW vs. IW/DW | -1.49834 | 23 | 0.147646 | NS |
| | | PSWw vs. AAW | 0.900161 | 80 | 0.370736 | NS |
| | | PSWw vs. IW/DW | **-3.14968** | **90** | **0.002219** | S |
| | | AAW vs. IW/DW | **-2.86486** | **26** | **0.008150** | S |

Table S3: The results of T test with variables grouped by water masses and year. Table list results of t-test that measure significance in differences in mean value. The difference between variable averages in selected layer are significant if significance level $p<0.05$. NS - not significant, S – signify cant differences (bold text).

| Variable | Water mass | Year | t-value | df | p | Significance |
|---|---|---|---|---|---|---|
| $a_{CDOM}(350)$ | AW | 2013 vs. 2014 | **13.20111** | **215** | **0.000000** | S |
| | | 2013 vs. 2015 | **11.62407** | **197** | **0.000000** | S |
| | | 2014 vs. 2015 | **-5.97262** | **328** | **0.000000** | S |
| | PSW | 2013 vs. 2014 | **6.162425** | **5** | **0.001638** | S |
| | | 2013 vs. 2015 | 0.254644 | 7 | 0.806317 | NS |
| | | 2014 vs. 2015 | **-3.16292** | **8** | **0.013336** | S |
| | PSWw | 2013 vs. 2014 | **5.540343** | **59** | **0.000001** | S |
| | | 2013 vs. 2015 | **5.685240** | **104** | **0.000000** | S |
| | | 2014 vs. 2015 | **-5.42899** | **99** | **0.000000** | S |

| | | | | | | |
|---|---|---|---|---|---|---|
| | AAW | 2014 vs. 2015 | **-3.05781** | **11** | **0.010894** | S |
| | IW/DW | 2014 vs. 2015 | 1.086729 | 28 | 0.286424 | NS |
| $S_{300\text{-}600}$ | AW | 2013 vs. 2014 | **-5.34852** | **215** | **0.000000** | S |
| | | 2013 vs. 2015 | **-4.23678** | **197** | **0.000035** | S |
| | | 2014 vs. 2015 | **6.410876** | **328** | **0.000000** | S |
| | PSW | 2013 vs. 2014 | -1.99294 | 5 | 0.102863 | NS |
| | | 2013 vs. 2015 | -0.817157 | 7 | 0.440760 | NS |
| | | 2014 vs. 2015 | 1.788011 | 8 | 0.111578 | NS |
| | PSWw | 2013 vs. 2014 | **-3.98031** | **59** | **0.000191** | S |
| | | 2013 vs. 2015 | **-2.50249** | **104** | **0.013890** | S |
| | | 2014 vs. 2015 | **3.544709** | **99** | **0.000602** | S |
| | AAW | 2014 vs. 2015 | **3.045325** | **11** | **0.011140** | S |
| | IW/DW | 2014 vs. 2015 | -1.30430 | 28 | 0.202751 | NS |

Significant difference between averaged $a_{CDOM}(350)$ values in classified water masses were observed only in 2015 except of PSW vs. AAW with a low number of samples. Similarly, significantly different average slope values were observed in 2015 for four sets of water masses pairs. The interannual differences in averages values of $a_{CDOM}(350)$ were insignificant (p>0.05) in PSW for 2013 and 2015 and in IW/DW in 2014 and 2015. All other pairs of interannual differences for distinct water masses were significant. In case of S300-600 average values interannual differences were significant in all AW, PSWw and AAW. In the other hand PSW and IW/DW average values with a low number of samples were insignificant interannually.

The example of excitation–emission matrix (EEM) from AREX expedition with marked ex/em region for three channels of Wet Star Wet Lab CDOM fluorometer is presented (Figure S1). Coble (1996) specific peak areas: the humic–like ‘A’ region at 260 nm excitation (ex) and 380–460 nm emission (em); terrestrial fulvic ‘C’ region ex: at 350 nm and em: in range 420–480 nm; marine humic–like ‘M’ region ex: at 312 nm and em: in range 380–420 nm; and the tryptophan–like or protein–like ‘T’ region ex: at 275 nm and em: in range 340 nm were marked on Figure S1. This allowed for association of channels with different excitation/emission characteristics with specific peak areas as given in Coble (1996): Channel 1 (CH1), ex./em. 310/450 nm, represents marine ultraviolet humic–like peak C and marine humic–like peak M; Channel 2 (CH2), ex./em. 280/450 nm, represents UVC terrestrial humic–like peak A; and Channel 3 (CH3), ex./em. 280/350 nm, represents the protein–like tryptophane peak T (Figure S1).

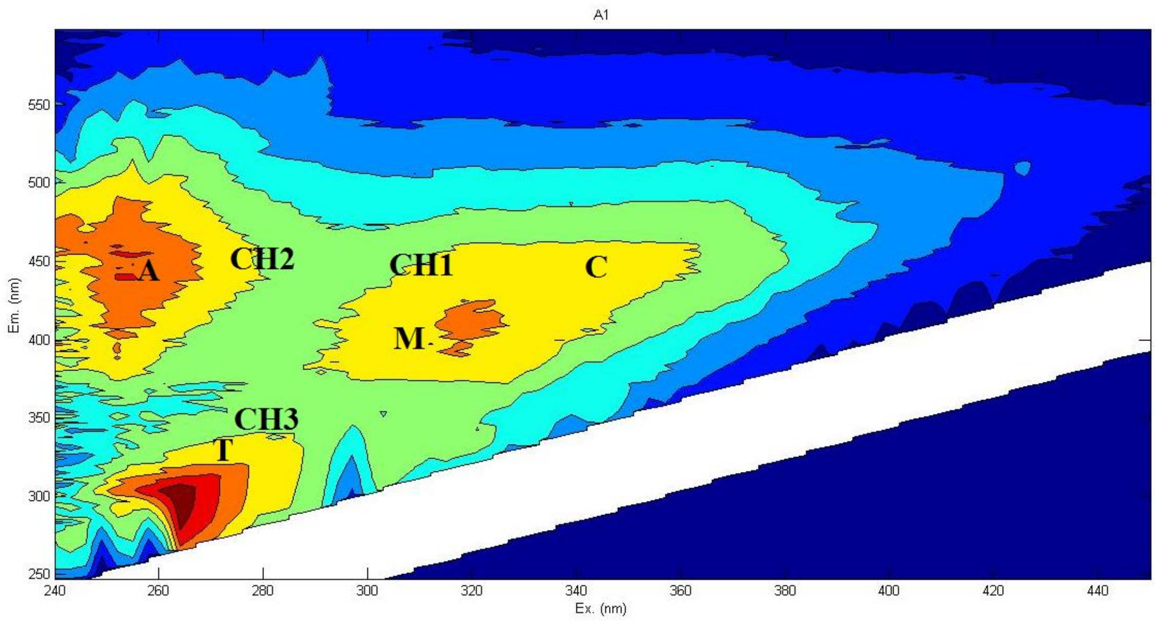
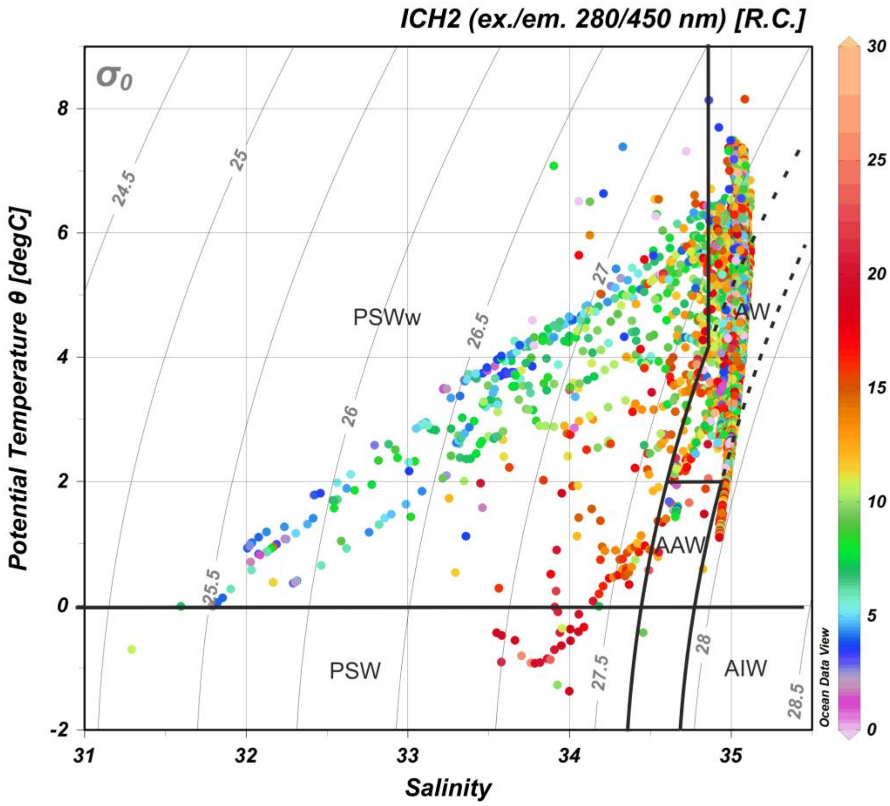



Figure S1: Typical example of excitation–emission matrix (EEM) from AREX expedition with marked ex/em region for three channels of Wet Star Wet Lab CDOM fluorometer (Channel 1 (CH1), ex./em. 310/450 nm, Channel 2 (CH2), ex./em. 280/450 nm,; Channel 3 (CH3), ex./em. 280/350 nm) together with Coble's specific EEM regions which characterize different sources of FDOM (the humic–like 'A' region at 260 nm excitation (ex) and 380–460 nm emission (em); terrestrial fulvic 'C' region at 350 nm ex and 420–480 nm em; marine humic–like 'M' region at 312 nm ex and 380–420 nm em; and the tryptophan–like or protein–like 'T' region at 275 nm ex and 340 nm em.

The distribution of fluorescence intensity of the terrestrial humic–like FDOM ($I_{CH2}$), and $SUVA_{254}$ (ratio $a_{CDOM}254$ and DOC) in the TS diagram was shown in Figure S2. The highest terrestrial humic-like FDOM values were observed in PSW and part of PSWw in depth range 15-50 m. The lowest $I_{CH2}$ values were found in surface layer of PSWw and there was a large variability in AW (Figure S2a). There was a large variability and no consistent trends in distribution of $SUVA_{254}$ values in different water masses in the study area, as shown in the TS diagram (Figure S2c).

a)


ICH2 (ex./em. 280/450 nm) [R.C.]
σ0
Potential Temperature θ [degC]
Salinity
PSWw
PSW
AW
AAW
AIW
24.5
25
25.5
26
26.5
27
27.5
28
28.5
Ocean Data View
30
25
20
15
10
5
0

b)

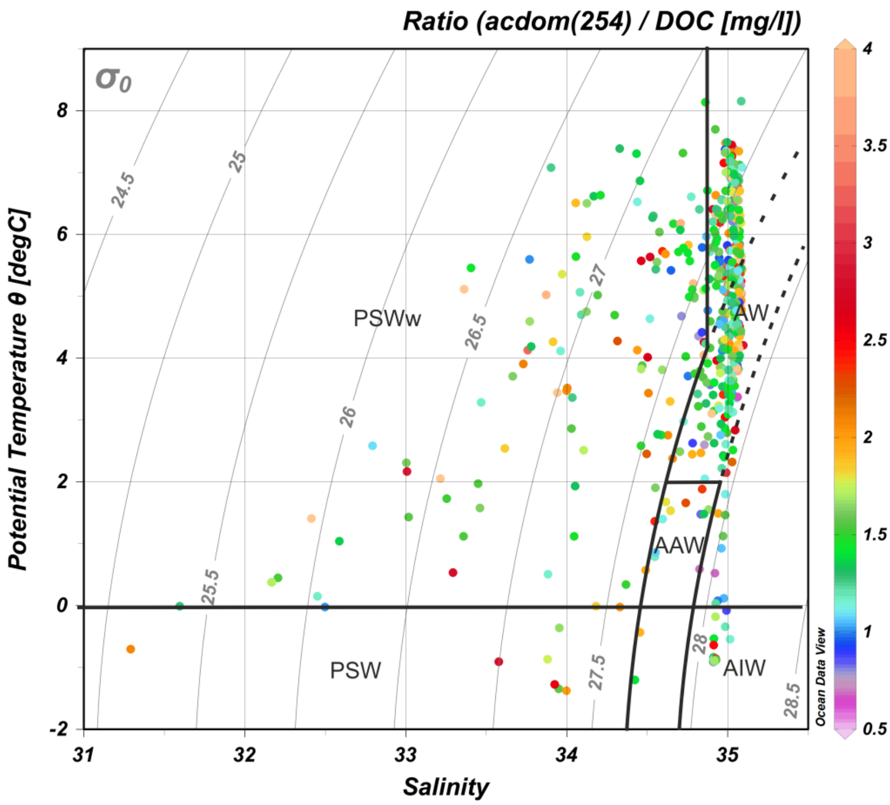

Ratio (acdom(254) / DOC [mg/l])
σ0
Potential Temperature θ [degC]
Salinity
PSWw
PSW
AW
AAW
AIW
24.5
25
25.5
26
26.5
27
27.5
28
28.5
Ocean Data View
4
3.5
3
2.5
2
1.5
1
0.5

Figure S2: TS diagram of water mass distribution on the study 2013–2015. A) color represents terrestrial humic–like fraction fluorescence intensity $I_{CH2}$, ( ex./em. 280/450 nm, [RC]). B) color bar represents values of carbon specific CDOM absorption coefficient at 254 nm, $SUVA_{254}$ [$m^2$ $gC^{-1}$]. The lower number of points in B) resulted from fewer number of discrete water samples for determination of CDOM. Water masses: AW (Atlantic Water), AAW (Arctic Atlantic Water), AIW (Arctic Intermediate Water), PSW (Polar Surface Water), PSWw (Polar Surface Water warm). Three areas noted as AW follow the three sets of conditions that define AW (see Table S1).

We presented the relationship between absorption coefficient at 676 and stimulated chlorophyll a fluorescence in 2014 and 2015 in the selected water masses to prove that measurements were not biased by instrument offset . The stability of chlorophyll *a* intensity output was assessed by regressing the measured fluorescence intensity values against calibrated values of total absorption coefficient non–water at 676 nm, $a_{tot-w}(676)$ in selected water masses. Value of the $a_{tot-w}(676)$ is a good proxy of the chlorophyll *a* concentration (Roesler and Barnard, 2013). There was very good linear relationship between $I_{FChla}$ and $a_{tot-w}(676)$ in selected water masses in 2014 and 2015 with no visible offset in $I_{FChla}$, values in both years ensuring negligible time drift in MicroFlu–Chl output (Figure S3). The difference in the in the $I_{FChla}$, and $a_{tot-w}(676)$ vertical distribution near the ocean surface in AW, shown on Figure 4, could in part be explained by a decrease in the fluorescence quantum yield by phytoplankton photoinhibition resulting from the stronger irradiance near the surface (Cullen, 1982).

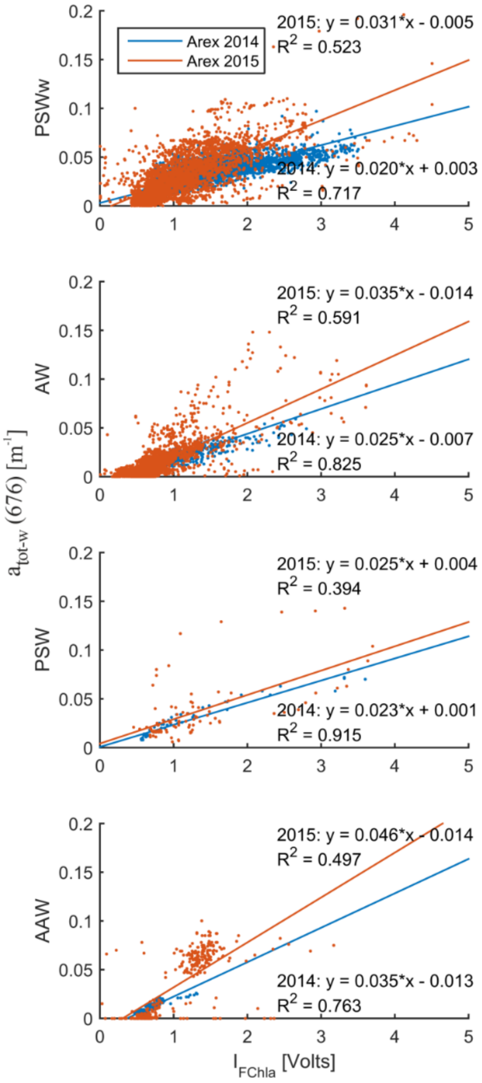



Figure S3: Relationship between total absorption coefficient non–water at 676 nm ($a_{tot-w}$(676) and stimulated chlorophyll a fluorescence ($I_{FChla}$) in different water masses in 2014 and 2015.

According to Roesler and Barnard (2013) chlorophyll a concentration can be very well approximated by $a_{tot-w}$(676). The very good correlation between $I_{FChla}$ and $a_{tot-w}$(676) in selected water masses shown on Figure S3, as well together with very good correlation between $I_{CH3}$ and $I_{FChla}$ suggested a direct dependence between $I_{CH3}$ and $a_{tot-w}$(676). There was a significant correlation between $I_{CH3}$ and $a_{tot-w}$(676) as summarized on the Figure S4. This was another evidence confirming strong contribution of phytoplankton dynamics to spatial and temporal variability of FDOM protein–like fraction in Nordic Seas.

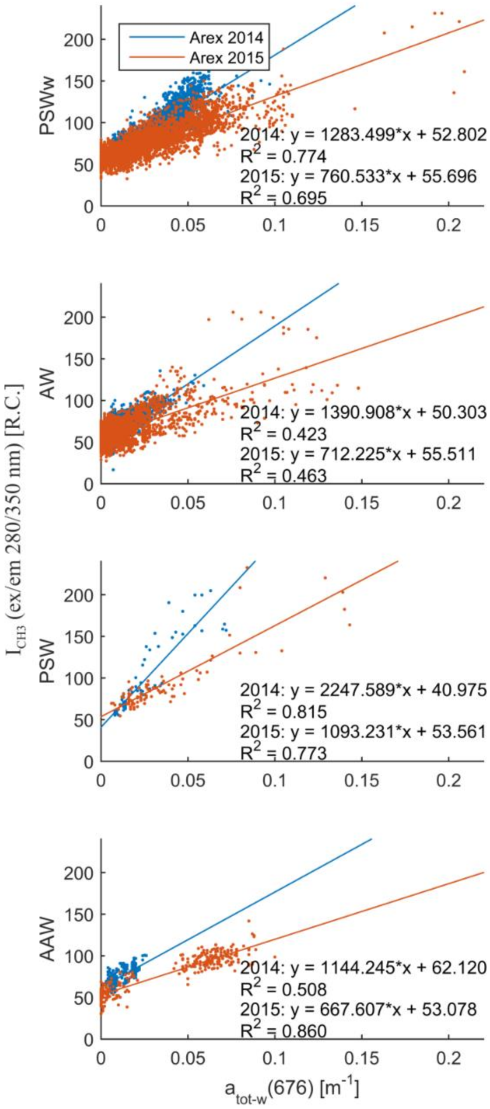



Figure S4: Relationship between fluorescence intensity of the protein–like component ($I_{CH3}$) and particulate absorption coefficient at 676 ($a_{tot-w}(676)$ ) in different water masses in 2014 and 2015.

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