Supplementary Material to:

Seasonal phototransformation of dissolved organic matter to ammonium, dissolved inorganic carbon, and labile substrates supporting bacterial biomass across the Baltic Sea

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Calculation of the apparent quantum yield spectrum (ϕ_λ)

To determine the apparent quantum yield spectrum (ϕ_λ) for phototransformation of DOM, two parameters are needed. First, the number of photons absorbed by the sample ($Q_{abs,\lambda}$; Eqs. S1 and S2), which is the product of the scalar photon flux density spectrum at depth z ($Q_{s,z,\lambda}$; mol photons m^{-2} d^{-1} nm^{-1}) and the absorption coefficient spectrum of CDOM ($a_{CDOM,\lambda}$; m^{-1} nm^{-1}), and secondly, the amount of a photoproduct (NH_4^+, DIC, or photostimulated bacterial biomass (bact-C)). Thus, the ϕ_λ describes the amount of photoproduct in moles per mole of photons absorbed in the sample [*Hu et al.*, 2002].

The number of photons absorbed in the sample ($Q_{abs,\lambda}$). The number of photons absorbed by CDOM ($Q_{abs,d,\lambda}$ for downwelling and $Q_{abs,u,\lambda}$ for upwelling irradiance; mol photons m^{-2} exposure $time^{-1}$ nm^{-1}) was calculated as:

$$Q_{abs,d,\lambda} = Q_{v,d,\lambda}\left[1 - e^{(-a_{CDOM,\lambda} L \mu_d)}\right] \quad \text{(S1)},$$

where $Q_{v,d,\lambda}$ is a vector photon flux density spectrum for downwelling irradiance ($Q_{v,u,\lambda}$ for upwelling irradiance; mol photons m^{-2} exposure $time^{-1}$ nm^{-1}), and L is the mean optical path length inside the sample bottle ($L = 0.5\ \pi r$, where r is the inner radius of sample tube) [*Vähätalo and Zepp*, 2005]. The parameter μ_d refers to the mean cosine of downwelling photons (i.e., a cosine of mean angle for downwelling photons). In Eq. S1, $a_{CDOM,\lambda}$ specifically refers to the mean value of $a_{CDOM,\lambda}$ during the irradiation.

The total number of absorbed photons ($Q_{abs,\lambda}$) in the sample is a sum of the absorbed downwelling ($Q_{abs,d,\lambda}$) and upwelling ($Q_{abs,u,\lambda}$) vector photon flux densities (mol photons m^{-2} exposure $time^{-1}$ nm^{-1}; Eq. S2).

$$Q_{abs,\lambda} = Q_{abs,d,\lambda} + Q_{abs,u,\lambda} \quad \text{(S2)}$$

We measured vector photon flux densities $Q_{v,d,\lambda}$ and $Q_{v,u,\lambda}$ incident to the surface of the sample bottles under 3 cm of cooling water in the exposure chamber (Atlas Suntest CPS+) with a spectroradiometer (Macam SR991) for wavelengths 240-800 nm, accounting for an immersion correction factor of 1.34. In order to determine μ_d and μ_u , scalar photon flux densities for downwelling ($Q_{s,d,\lambda}$) and upwelling irradiance ($Q_{s,u,\lambda}$) at the range from 400 nm to 700 nm were measured in the same site with a spherical scalar irradiance sensor (QSL 2101, Biospherical Instruments, San Diego, CA, USA) by blanketing the lower or upper hemisphere, respectively. For downwelling irradiance, the vector and the scalar photon flux density spectra at the range from 400 nm to 700 nm were nearly equal, resulting in a mean cosine ($\mu_d = Q_{v,d}\, Q_{s,d}^{-1}$) of 0.988. For the upwelling irradiance, the mean cosine (μ_u) was 0.172.

Determination of apparent quantum yield with Matlab

Our method uses the 'fminsearch'-algorithm of Matlab for the determination of *c* and *d* based on the relationship between the magnitude of photochemistry (mol of product m^{-2}) and the magnitude of photons absorbed into 461 spectral bands (mol of photons nm^{-1} m^{-2}). The method assumes that ϕ_λ has exponential spectral dependence defined by *c* and *d* of Eq. 3 as has been found out in several studies using monochromatic or narrow spectral bands over the spectrum of photolytic radiation [reviewed by *Vähätalo*, 2009]. The determination of *c* and *d* is based on iteration. A Matlab script, "fitBaltic.m", gives the initial values of *c* and *d* for the iteration process. In our script, we have selected initial values of 1 and 0.03 for *c* and *d*, respectively, because such values are theoretically feasible and similar values have been obtained in earlier studies [*White et al.*, 2010]. The

“fitBaltic”-script calls another script, “funBaltic.m” which calculates the photoreaction rate on the basis of absorbed photons during the irradiation and ϕ_λ defined by *c* and *d* (according to Eq. 1). The calculated photoreaction rate is compared to the measured rate (the amount of a photoproduct during experimental irradiation). The "funBaltic"-script calculates a relative error between the measured and the calculated photoreaction rates (*ress*). The value of *ress* is returned back to “fitBaltic.m”, which examines if a change in *c* and/or *d* will improve the fit between the calculated and the measured photoreaction rates by searching a minimum value for *ress*. The 'fminsearch' uses a Nelder-Mead simplex direct search for the minimization of *ress*. The 'fminsearch' eventually reports those values of *c* and *d*, which minimize *ress*.

As a further Supplementary Material, we provide the Matlab-files used for the determination of ϕ_λ for the photochemical production of DIC during the irradiation experiment in Sep 2006. The “absorbed_photons_and_photomineralization_in_September.mat”-file includes the input parameters: the magnitude of photochemically produced DIC (*photoproduct*; mol of product m^{-2}) and the magnitude of photons absorbed by CDOM during the irradiation experiment (*absQ*; mol of photons nm^{-1} m^{-2}). This input data is also given in Tables S1 and S2. The Supplementary Material includes also the Matlab-scripts, “fitBaltic.m” and “funBaltic.m”. The content of these files is also given below as a part of this word-file. For those who wishes to run the scripts in their own computer, need to modify the path (line 19 of funBaltic.m) showing the location of the “absorbed_photons_and_photomineralization_in_September.mat”
-file. The iteration is started by giving the name of script, "fitBaltic", in the command window of Matlab.

It should be noticed that the values of *c* and *d* of Eq. 3 are not independent. Additionally, the iteration does not produce a mathematically unique solution for *c* and *d*. A change in *c* can

compensate modified *d* and result in an identical photoreaction rate [*Vähätalo et al.*, 2000]. Therefore, the user of our scripts should not be surprised if the values of *c* and *d* are not identical to the values presented in this study. Although the actual values of *c* and *d* may differ, the value of ϕ_λ remains nearly the same. The error of iteration is negligible at least when compared to the experimental error involved in the irradiation experiments (reported as CV% in Table 4).

funBaltic.m

```
function [ress,pmzest] = funBaltic(cd);

% where pmzest is the estimated photochemical mineralisation at depth z
% (mol product m-2 d-1), ress sums the squared difference between estimated %
(pmzest) and measured photomineralisation (pmzmes). funBaltic(cd) refers % to
the function of optimizing the values of c and d so, that ress is as
% small as possible and represents the best estimate for apparent quantum
% efficiency.

l = 290:1:750;
c = cd(1);
d = cd(2);
fiil = c*exp(-d*l);

% where l is the range of wavelengths between 290 nm and 750 nm with 1-nm  %
steps, c and d are the optimized coefficients given by cd, fiil is the
% theoretical equation for apparent quantum yield spectrum in 290-750 nm.

load C:\My Documents\Balticsea2006\MATLAB\absorbed_photons_and_photomineralizati
on_in_September

% This command loads a file containing a matrix of the number of photons
% absorbed by the samples (Qabs; Table S1) and the amount of DIC produced
% during the irradiation (Table S2). The unit for the number of absorbed
% photons (Qabs) is mol m-2 nm-1 exposure-1.  The unit for the amount of
% photoproduct is mol m-2 exposure-1. This value is calculated from the
% measured photoproduction of DOC (Table 3, mol m-3 exposure-1) by
% multiplying it with L , the mean optical path length inside the sample
% bottle (0.0424 m).

pmzestl = absQ(:,5).*fiil';
pmzest = sum(pmzestl);

% The first command calculates the estimate for photochemical
% mineralisation at depth z for each wavelength in a sample collected from % the
station 5 (Arkona Sea) based on the suggested apparent quantum yield
% (fiil) and the number of photons absorbed by the sample (Qabs, Table S1).
% pmzest sums the estimated values over the wavelengths 290-750 nm.

pmzmes = photoproduct(5,:);
```

```
% The measured amount of photoproduct (Table S2) is expressed as pmzmes for %
each sampling station. Here, the station 5 (Arkona Sea) is selected.

diff = pmzmes - pmzest;
relative_diff = diff./pmzmes;
ress = (relative_diff).^2;

% The difference (diff) between the pmzmes and pmzest is first calculated
% and then the relative difference is squared and expressed as residual
% (ress). The ress value is minimized with a 'fminsearch' command in the
% following script ("fitBaltic").
```

FitBaltic.m

```
% This m-file executes iteration of best variables, c and d, for the
% apparent quantum yield efficiency.

global l pmzmes mpzest
cd0 = [1;0.03];

% cd0 sets the starting values for iteration.

[cd_opt,fval,exitflag,output] = fminsearch('funBaltic', cd0)

% This command calls a function 'funBaltic' and minimizes the ress of the
% function, which leads to the optimization of c and d variables of
% apparent quantum efficiency (Eg. 3). The starting values for iteration
% are given by cd0.

[ress,pmzest] = funBaltic(cd_opt)

% This command computes the estimated photomineralization (pmzest) with the
% optimized apparent quantum yield. The residual (i.e., error between
% pmzest and pmzmes) is also reported.

pmzmes          % For comparison pmzmes is reported.
cd_opt          % the optimized c and d.
```

Table S1. The number of photons absorbed in the sample ($Q_{abs,\lambda}$; mol photons m^{-2} exposure $time^{-1}$ nm^{-1}; Eq. S2) in the experiment for photoproduction of DIC in Sep 2006. The data forms a 461×5 matrix, as the spectra range from 290 nm to 750 nm (i.e., 461 one-nm bands) determined for the five sampling stations (from left: Neva Bay, Helsinki, Gulf of Finland, Gotland Basin, Arkona Sea). Note that only the 20 first and last values are presented here

0.004302	0.002965	0.002630	0.001943	0.001741
0.004955	0.003395	0.003006	0.002214	0.001983
0.005590	0.003807	0.003366	0.002470	0.002212
0.006506	0.004405	0.003889	0.002844	0.002547
0.007365	0.004958	0.004371	0.003187	0.002852

0.008341	0.005585	0.004916	0.003570	0.003196
0.009436	0.006284	0.005521	0.003996	0.003575
0.010652	0.007051	0.006188	0.004463	0.003991
0.011918	0.007848	0.006876	0.004942	0.004421
0.013204	0.008646	0.007563	0.005419	0.004846
0.014710	0.009579	0.008368	0.005980	0.005345
0.016373	0.010608	0.009251	0.006591	0.005890
0.018170	0.011707	0.010193	0.007237	0.006469
0.020102	0.012880	0.011201	0.007924	0.007087
0.022314	0.014220	0.012354	0.008716	0.007788
0.023887	0.015145	0.013139	0.009250	0.008257
0.026075	0.016450	0.014247	0.010011	0.008939
0.028680	0.018011	0.015577	0.010920	0.009757
0.030970	0.019361	0.016735	0.011701	0.010466
0.033055	0.020572	0.017763	0.012400	0.011090
…	…	…	…	…
0.000395	0.000180	0.000201	0.000327	0.001043
0.000431	0.000196	0.000219	0.000357	0.001143
0.000406	0.000185	0.000207	0.000337	0.001084
0.000290	0.000132	0.000147	0.000241	0.000777
0.000242	0.000110	0.000123	0.000202	0.000654
0.000202	0.000092	0.000103	0.000169	0.000548
0.000229	0.000104	0.000117	0.000192	0.000626
0.000397	0.000180	0.000202	0.000333	0.001089
0.000565	0.000256	0.000287	0.000475	0.001559
0.000576	0.000261	0.000293	0.000485	0.001600
0.000409	0.000185	0.000208	0.000345	0.001143
0.000215	0.000097	0.000110	0.000182	0.000605
0.000164	0.000074	0.000083	0.000139	0.000462
0.000157	0.000071	0.000080	0.000133	0.000446
0.000147	0.000066	0.000075	0.000125	0.000420
0.000162	0.000073	0.000083	0.000138	0.000467
0.000199	0.000090	0.000102	0.000171	0.000577
0.000222	0.000100	0.000113	0.000190	0.000646
0.000220	0.000099	0.000112	0.000189	0.000643
0.000172	0.000077	0.000087	0.000148	0.000505

Table S2. The amount of photoproduct (mol DIC m^{-2} exposure $time^{-1}$) in the experiment for photoproduction of DIC in Sep 2006. Each experiment produced one value of the photoproduct per each sampling station (from top: Neva Bay, Helsinki, Gulf of Finland, Gotland Basin, Arkona Sea), thus, the data is a vector of five rows

0.002733
0.000987
0.000859
0.000519
0.000342