Biologically labile photoproducts from riverine non-labile dissolved organic carbon in the coastal waters

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Abstract

In order to assess the production of biologically labile photoproducts (BLPs) from non-labile riverine dissolved organic carbon (DOC), we collected water samples from ten major rivers, removed labile DOC and mixed the residual non-labile DOC with artificial seawater for microbial and photochemical experiments. Bacteria grew on non-labile DOC with a growth efficiency of 11.5 % (mean; range from 3.6 to 15.3 %). Simulated solar radiation transformed a part of non-labile DOC into BLPs, which stimulated bacterial respiration and production, but did not change bacterial growth efficiency (BGE) compared to the non-irradiated dark controls. In the irradiated water samples, the amount of BLPs stimulating bacterial production depended on the photochemical bleaching of chromophoric dissolved organic matter (CDOM). The apparent quantum yields for BLPs supporting bacterial production ranged from 9.5 to 76 (mean 39) (µmol C mol photons⁻¹) at 330 nm. The corresponding values for BLPs supporting bacterial respiration ranged from 57 to 1204 (mean 320) (µmol C mol photons⁻¹). According to the calculations based on spectral apparent quantum yields and local solar radiation, the annual production of BLPs ranged from 21 (St. Lawrence) to 584 (Yangtze) mmol C m⁻² yr⁻¹ in the plumes of the examined rivers. Complete photobleaching of riverine CDOM in the coastal ocean was estimated to produce 10.7 Mt C BLPs yr⁻¹ from the rivers examined in this study and globally 38 Mt yr⁻¹ (15 % of riverine DOC flux from all rivers), which support 4.1 Mt yr⁻¹ of bacterial production and 33.9 Mt yr⁻¹ bacterial respiration.

1 Introduction

Rivers transport 246 Mt C yr⁻¹ of dissolved organic carbon to the ocean Cai (2011). A part (19 ± 16 %) (Søndergaard and Middelboe, 1995) of this terrestrial DOC is biologically labile and quickly consumed by heterotrophic bacteria in the coastal waters (Lønborg et al., 2009; Lønborg and Álvarez Salgado, 2012). The remaining majority...
(81 ± 16 %) of terrestrial DOC (tDOC) is biologically non-labile (Sendergaard and Middelboe, 1995). In the coastal waters, the primary sinks for non-labile DOC are slow microbial metabolism or photochemical transformations (Bauer et al., 2013). Photochemical reactions can transform non-labile tDOC to dissolved inorganic carbon (DIC) or biologically labile photoproducts (BLPs), the latter being rapidly assimilated by microbes (Wetzel et al., 1995). The assimilation of non-labile tDOC (directly or after photochemical transformation) contributes to heterotrophy of coastal waters (Smith and Hollibaugh, 1993) and couples IDOC to marine food webs (Vähätalo and Järvinen, 2007; Vähätalo et al., 2011). The extent of this coupling depends also on the fraction of assimilated IDOC converted to bacterial biomass (i.e., bacterial growth efficiency, BGE) (del Giorgio and Cole, 1998; del Giorgio and Davis, 2003).

By operational definition, BLPs are compounds produced by photochemical reactions and transformed into a more labile form than the original compounds in DOC. The amount of BLPs is typically quantified experimentally as bacterial respiration, bacterial production or associated loss of DOC (= bacterial carbon demand) in irradiated DOC in excess of that found in non-irradiated dark control DOC (Wetzel et al., 1995; Smith and Benner, 2005). In order to translate the experimental findings to environmental processes, the amounts of BLPs have been related to the number of photons absorbed by chromophoric dissolved organic matter (CDOM) yielding to an apparent quantum yield (AQY) for production of BLPs (Miller et al., 2002; Vähätalo et al., 2011; Aarnos et al., 2012; Reader and Miller, 2014; Cory et al., 2014).

The production of BLPs is also linearly related to the photochemical loss of CDOM (photobleaching) (Kieber et al., 1990; Miller and Moran, 1997; Bertilsson and Tranvik, 2000; Obernosterer and Herndl, 2000; Brinkmann et al., 2003). Although, this quantitative relationship between the production of BLPs and photobleaching could be also used to estimate the photoproduction of BLPs in the surface waters, it has to our knowledge never been used for such a purpose. Bacterial production on BLPs can support both heterotrophic food webs and primary production in the coastal waters (Vähätalo and Järvinen, 2007; Vähätalo et al., 2011). The bacterial production on BLPs depends in part on BGE on BLPs. Irradiation of DOC can decrease (15 studies) or increase BGE (5 studies) compared to non-irradiated DOC (reviewed by Abboudi et al. (2008)). Despite of these comparisons, between irradiated and non-irradiated DOC, the BGE on BLPs has not been determined and our study provides the first BGE estimate on BLPs.

This study estimates the production of BLPs from non-labile tDOC in the coastal waters and determines BGE on BLPs. We collected water samples from ten large rivers that produce together 28 % of tDOC flux to the ocean and aged the samples with indigenous microbes for the removal of labile DOC. The remaining non-labile DOC was mixed (1 : 1) with artificial seawater to simulate chemical matrix of coastal ocean. The sterile filtered mixtures of non-labile DOC and seawater were irradiated with simulated solar radiation. The irradiated waters received indigenous bacteria and the amount of BLPs was measured separately as bacterial production (BP on BLPs) and respiration (BR on BLPs) in excess of that found in the non-irradiated dark control waters. The BP or BR on BLPs was related to the number of absorbed photons for the calculation of AQY and also to the photobleaching (BLPs vs. photobleaching approach). The annual production of BP on BLPs and BR on BLPs (mol C m⁻² yr⁻¹) in the river plumes was calculated from AQYs and the annual solar radiation in the coastal ocean in the front of each river. We calculated the annual production of BLPs from the annual CDOM fluxes for each river (Mt C yr⁻¹ per river) using the BLPs vs. photobleaching approach and assuming that photobleaching of tDOM in the coastal ocean equals the annual tDOM flux. As the rivers examined contribute 28 % of tDOM flux to the ocean, we dared to extrapolate our finding to global scale simply by assuming that the rivers examined here are representative for the remaining 72 % of tDOM flux by other rivers.
2 Material and methods

2.1 Material

The rivers selected for this study (Table 1) drain 25% of the land area, contribute 28% to the global tDOC flux, and 33% to the freshwater discharge to the ocean (Carlson, 2002; Cauwet, 2002; Coyne et al., 2005; Milliman and Farnsworth, 2011). For the collection of water samples, empty polyethylene containers (cleaned with detergent, rinsed with HCl and finally copiously rinsed with ion exchanged water; MQ) were shipped to the local collaborators at ten major rivers (see acknowledgments). The containers were filled in the center of the stream by direct immersion below the surface, except for the Mississippi and St. Lawrence Rivers where water about 3 m below the surface was collected with Niskin bottles. The samples collected for this study has been used earlier for the determination of dissolved black carbon (Jaffé et al., 2013), dissolved iron (Xiao et al., 2013) and the photochemical isotopic fractionation of DOC (Lalonde et al., 2014).

Artificial seawater was prepared according to Kester et al. (1967) by dissolving pro analysis grade of inorganic salts (VWR International) to MQ water. Prior to use, glassware and quartzware were washed in a dishwasher, rinsed out with 7% HCl and MQ water, and combusted for several hours (450°C).

2.2 Experimental

2.2.1 Sample preparation

In order to remove labile DOC, the collected water samples were not filtered or preserved, but kept in darkness and sent to our laboratory in Helsinki, Finland by air cargo. The median transport time between the sampling and the arrival to Helsinki was 33 days (Table 1). Upon arrival to the laboratory, the water samples were filtered through 1 µm filters (quick rinsed membrane cartridge, Nuclepore or double layer of track-etch polyester membrane filter cartridge, Graver Technologies) and stored in the dark at +4°C. We assume that the microbes present in the water samples consumed the labile DOC during the transportation, which allowed us to carry out the experimental work with non-labile DOC. The amount of labile DOC from the St. Lawrence river sample was 19 ± 1% (n = 3) in the St. Lawrence River sample (Lalonde et al., 2014), which is in agreement with the proportion of labile riverine DOC being 19 ± 16% (Søndergaard and Middelboe, 1995; Lenborg and Álvarez Salgado, 2012; Asmala et al., 2014).

Our salinity adjustment followed by filtration mimics a potential removal of iron via flocculation and related loss in photochemical reactivity and is expected to result a matrix characteristic for photochemical transformation of non-labile tDOC in the coastal waters 2.2.1. In order to assess BGEs and the production of BLPs from non-labile tDOC under conditions representing coastal waters, the 1 µm-filtered river water samples were mixed 1:1 with artificial seawater. In the mixtures, the ionic composition was similar to that of seawater but the salinity (16) was half of that found in the ocean. For abiotic photochemical experiments, the 1 µm-filtered river water samples mixed with artificial seawater were further aseptically filtered through 0.2 µm membrane filters (Pall Supor 200) into 170 mL glass or quartz flasks to be closed with ground-glass stoppers without headspace.

2.2.2 Irradiations

The quartz flasks were irradiated for 44 to 46 h with 765 Wm⁻² simulated solar radiation (Atlas Suntest CPS+ solar simulator) in a MQ-water bath regulated to 20°C with a Lauda RE-112 thermostat like in our earlier study (Aarnos et al., 2012). The glass flasks wrapped into aluminum foil were kept in the same water bath (dark controls) or at 4°C (initials).
2.2.3 Bioassays

For the bioassays, the irradiated and the dark control samples from each river received a 10 % (vol/vol) inoculum of bacterioplankton prepared from their corresponding river by passing the 1 µm-filtered river water through GF/F filters (nominal pore size of 0.7 µm, Whatman) for the removal of the grazers of bacterioplankton. The bioassay samples received NH$_4$Cl and KH$_2$PO$_4$ to the final concentrations of 1.2 mg N L$^{-1}$ and 0.13 mg P L$^{-1}$, respectively, and were divided into two aliquots for the determination of bacterial respiration (BR) or bacterial production (BP).

2.2.4 Bacterial respiration

BR was determined as a consumption of dissolved oxygen (O$_2$) measured with needle-type oxygen microsensor optodes (PreSens GmbH, Regenburg, NTH-PSt1-L5-TF-NS40) (Warkentin et al., 2007, 2011) at 15 min intervals from aliquots closed in biological oxygen demand bottles incubated in darkness in a water bath at 20 °C (Lauda RE-112 thermostat). An optode was inserted into the sample via a hole drilled through the ground-glass stopper and sealed with parafilm. The drift of instrument defining the detection limit for BR was measured in three blank experiments, where MQ water was incubated for 300 h under conditions identical to respiration measurements. During the blank experiments, the apparent decline of O$_2$ was 1.5 ± 0.5 µmol L$^{-1}$ 300 h$^{-1}$ (mean ± sd, n = 3). The decline in the concentration of O$_2$ was converted into an increase in the concentration of CO$_2$ assuming 1 : 1 molar ratio between the consumed O$_2$ and the produced CO$_2$ in BR. The selected respiratory quotient makes our study comparable to earlier studies, which have used values ranging from 0.82 to 1.2 (Søndergaard and Middelboe, 1995; del Giorgio et al., 1997; del Giorgio and Cole, 1998; Cory et al., 2014). The temporal trend of accumulated CO$_2$ was determined by a polynomial fitting to the measurements with the smooth spline function in R software (R Core Team, 2014).

2.2.5 Bacterial production

To determine bacterial production (BP), 10 mL samples were preserved with formaldehyde (final concentration 5 %) daily from aliquots incubated in dark conditions at room temperature (mean 22 °C, range from 20 to 24 °C) with an air-head space. The bacterial cells from the preserved samples were filtered on 0.2 µm polycarbonate filters (GE water & Process Technologies) and stained with acridine orange (Hobbie et al., 1977). Bacterial densities were estimated from cell counts from ≥ 20 fields with an epifluorescence microscope (Aristoplan). The cell volumes were determined by digital image analysis (Image Analysis & LabMicrobe software; Massana et al. 1997). The volumes of cells were converted to carbon using a conversion factor of 0.12 pg C (µm$^3$)$^{0.7}$ and the total carbon-biomass of bacterioplankton assemblage was calculated by multiplying the organic carbon content of cells with the density of cells (Norland, 1993).

2.2.6 Defining BLPs and BGEs

For the bacteria growing in the irradiated sample, the response to BLPs was considered to be largest in the end of logarithmic growth phase defined as the first day with maximum biomass during the 12 day-long bioassay (Stepanauskas et al., 2002). On that day (varying from 5 to 12 days), the difference in the accumulated BP or BR between the dark control and the irradiated samples represented the BP or BR on BLPs. The bacterial growth efficiency (BGE) was calculated as BP/(BP + BR).

2.3 Analytical measurements

The absorbance by CDOM was measured with a spectrophotometer (Shimadzu UV 2550) in triplicates against MQ water reference using a 0.05 m quartz cuvette. The absorbance by CDOM was converted into an absorption coefficient ($a_{CDOM,λ}$) accounting for the path length of the cuvette and transforming the 10-base logarithm to a Naperian-based logarithm (ln(10)).
2.4 The apparent quantum yields for the production of BLPs

Spectral apparent quantum yields (AQYSs) for the production of BLPs supporting bacterial production (BP) or bacterial respiration (BR) (AQY_{BP,λ} or AQY_{BR,λ}) were calculated as:
\[
\text{AQY}_{BP,λ} = \frac{\text{BP or BR}}{\text{photons absorbed by CDOM}(λ)} \quad (1)
\]
where BP or BR on BLPs are the bacterial production or respiration based on BLPs (molC) and photons absorbed represents the spectrally resolved absorption of photons by CDOM during the irradiation experiment (mol photons at the spectral range from 290 to 750 nm) and λ specific wavelength. The latter was calculated by accounting for the spectral dose of photons, the optical path length, and the absorption characteristics of samples as explained in our earlier study (Aarnos et al., 2012). AQY_{BP,λ} and AQY_{BR,λ} were assumed to depend on wavelength according to:
\[
\text{AQY}_λ = cd^{−dλ} \quad (2)
\]
where AQY_λ is AQY_{BP,λ} or AQY_{BR,λ}, c (molC mol photons^-1) and d (nm^-1) are positive constants, and λ is the wavelength (nm). The parameters c and d in Eq. (2) were iterated from Eq. (1) by unconstrained nonlinear optimization (the "fminsearch" function of the Matlab 7.9.0) as in our earlier publications (Vähätalo et al., 2011; Aarnos et al., 2012).

2.5 The production of BLPs based on AQYSs

The measured AQY_{BP,λ} or AQY_{BR,λ} was used to calculate the production rate of BLPs in the river plumes according to:
\[
\text{pr} = \int_{λ_{\text{min}}}^{λ_{\text{max}}} \text{AQY}_λ Q_λ(a_{\text{CDOM,λ}}a_{\text{tot,λ}})^{-1} dλ \quad (3)
\]
where pr is the production rate of BLPs supporting BP or BR over the entire water column (molC m^-2 yr^-1), AQY_λ is AQY_{BP,λ} or AQY_{BR,λ}, Q_λ represents the spectrum of solar radiation absorbed by the entire water column (mol photons m^-2 yr^-1 nm^-1), and the ratio a_{CDOM,λ}a_{tot,λ} (dimensionless) is the contribution of tDOC to the total absorption coefficient a_{tot,λ} (m^-1 nm^-1) (Aarnos et al., 2012). The integration was done from λ_{min} of 290 nm to λ_{max} of 750 nm. Q_λ was calculated as the product of a standard solar radiation spectrum (ASTM G173-03; Chu and Liu, 2009) normalized with global radiation and the annual mean global radiation determined for the area of each river plume examined. The latter was calculated from monthly values over the years 1984 to 2000 (Hatzianastassiou et al., 2005). Terrestrial CDOM was assumed to absorb all photolytic photons (a_{CDOM,λ}a_{tot,λ} = 1; Eq. 3). Therefore the calculated rates apply for those coastal regions, where tCDOM from rivers dominates the absorption of photolytic solar radiation (e.g. river plumes).

2.6 The production of BLPs based on photobleaching

The annual production of BLPs from tCDOM in the coastal ocean was estimated from the measured relationship between BLPs and photobleaching. The latter was assumed to be the only sink for tCDOM discharged by rivers to coastal ocean (Nelson and Siegel, 2013). In this case, the amount of photobleached tCDOM equals the CDOM flux by the rivers. The annual CDOM fluxes for Lena, Mississippi and St. Lawrence rivers were taken from the literature (Stedmon et al., 2011; Spencer et al., 2013) and converted to a_{CDOM,300} flux with spectral slope coefficients (Stedmon et al. (2011); 17.6 and 16.3 μm^-1) measured for Mississippi and St. Lawrence CDOM, respectively. In the absence of published fluxes for the remaining rivers, the annual CDOM fluxes were estimated by multiplying the measured a_{CDOM,300} with the annual water discharge (Cauwet, 2002; Coynel et al., 2005). The production of BLPs supporting BP by each river (mol C yr^-1) was calculated by multiplying the CDOM flux of each river (m^2 yr^-1) with the relationship (mol C m^-3) between the BP on BLPs and photobleaching of...
CDOM at 300 nm. The BR on BLPs was calculated from the mean BGE on BLPs (BR = BP/BGE – BP). Finally, the total production of BLPs (molC yr⁻¹) was obtained as a sum of BR and BP on BLPs.

2.7 Statistical analysis

Statistical differences between the samples were tested with two-tailed paired t tests (heteroscedastic) by comparing observed response between the irradiated and the dark control samples. All statistical analyses were carried out by using R language and a significance level of 0.05 (R Core Team, 2014). We used linear regression to evaluate the dependency between photobleaching and and BP or BLPs.

3 Results

3.1 Photobleaching of riverine CDOM in a seawater matrix

When 0.2 µm filtered river waters without labile DOC (Table 1) were mixed with artificial seawater and irradiated, the simulated solar radiation photobleached CDOM at 300 nm (ΔaCDOM,300) by 50.4 ± 2.6 % (mean ± sd here and elsewhere in the results; Table 2). The amount of photobleaching expressed as absorption coefficient ranged from 0.48 ± 0.06 m⁻¹ (Ganges–Brahmaputra) to 12.42 ± 0.06 m⁻¹ (Congo) when calculated as the difference in ΔaCDOM,300 between the dark control and the irradiated samples (ΔaCDOM,300, Table 2).

3.2 Bacterial production

In order to assess bacterial production (BP) on the irradiated and the dark control non-labile DOC, we introduced an inoculum of riverine bacterioplankton to the irradiated and the dark control samples resulting in the bacterial cell densities from 0.006 to 0.240 × 10⁹ cellsL⁻¹ (t = 0 in Table 3). The bacteria increased their densities by one to two orders of magnitude in five to 12 days (Table 3). The bacterial cell densities were converted to biomasses by accounting for the bacterial cell volumes, which were not different between the dark control and the irradiated samples (paired t test, df = 9, p > 0.05). In the dark controls, the accumulated BP ranged from 0.5 ± 0.1 (Lena) to 3.9 ± 0.2 (Congo) µmolCL⁻¹ (Fig. 1). BP was higher in the irradiated than in the dark control samples (paired t test, df = 9, p = 0.003) and ranged from 1.2 ± 0.1 (Lena) to 8.7 ± 0.6 (Congo) µmolCL⁻¹ (Fig. 1). BP on BLPs, calculated as the difference between the irradiated and the dark control samples, ranged from 0.6 ± 0.3 (Ganges–Brahmaputra) to 4.8 ± 0.8 (Congo) µmolCL⁻¹ (Fig. 1). The BP on BLPs was significantly related to the photobleaching by a linear regression coefficient of 0.336 mmolCLm⁻² (Fig. 2).

3.3 Bacterial respiration

In the dark controls, bacterial respiration (BR) accumulated usually linearly with time indicating relatively constant rates of respiration throughout the bioassay (Fig. 3). In the irradiated samples, the kinetics of BR was different and rates typically higher than in the dark control samples (Fig. 3). The BR on BLPs (Fig. 4) was calculated from the difference in respiration between the irradiated and dark control samples (Fig. 3). After a lag-phase, BR on BLPs typically accumulated rapidly, but leveled off at the late phase of bioassay (Fig. 4). The BR on BLPs accumulated by the time of maximum biomass was undetectable (−1.4 ± 1.39 µmolCL⁻¹) with Ganges–Brahmaputra BLPs and highest (27.8 ± 1.33 µmolCL⁻¹) with Yangtze BLPs (Fig. 4).

3.4 Bacterial growth efficiency

When BGE was calculated from the biomass (Fig. 1) and the respiration gained by the time of maximum biomass (Figs. 3 and 4), it was lowest 3.0 % and highest 27.7 % in the irradiated DOC from Yangtze and Ganges–Brahmaputra, respectively, while in the
dark controls BGE ranged from 3.6 % (Yangtze) to 15.3 % (Amazon) (Table 4). BGE on BLPs ranged from 2.8 % (Yangtze) to 21.5 % (Amazon) (Table 4). The mean BGEs were not different among the irradiated DOC, the dark control DOC or BLPs (paired t test, df = 7, p > 0.05) (Table 4).

3.5 Apparent quantum yields and production rates of BLPs

When the BP on BLPs (Fig. 1) was divided by the spectrum of photons absorbed during the irradiation, the spectral AQY for the production of BLPs supporting BP (AQYBP,λ; Eq. 2) was defined by the parameters c and d shown in Table 5. Based on these parameters, the calculated AQYBP ranged from 9.5 to 76 with median of µmol C mol photons−1 at 330 nm, a wavelength of solar radiation responsible for highest production of BLPs (Table 5) (Miller et al., 2002; Vähätalo et al., 2011; Aarnos et al., 2012). The corresponding values for the production of BLPs supporting BR (AQYBR,330) ranged from 57 to 1203 with median of 186 µmol C mol photons−1 (Table 5).

In the river plumes, the annual production of BLPs supporting BP ranged from 1.0 (Lena) to 33 mmol C m−2 yr−1 (Ganges–Brahmaputra) (Table 6) when calculated (Eq. 3) with AQYBP,λ (Table 5) and the local annual mean solar irradiance in the coastal ocean at the front of each river. The corresponding production of BLPs supporting BR ranged from 19 (St. Lawrence) to 574 mmol C m−2 yr−1 (Yangtze) (Table 6). The total production of BLPs ranged from 21 (St. Lawrence) to 584 mmol C m−2 yr−1 (Yangtze) when calculated as the sum of BLPs supporting BP and BR (Table 6).

3.5.1 An estimate for the global production of BLPs

The relationship between BP on BLPs and ∆µCDOM,300 (Fig. 2) was multiplied with the annual CDOM fluxes (Table 7) to estimate the photobleaching of CDOM and related production of BLPs from non-labile tDOC of each river in the coastal ocean. The photobleaching of CDOM fluxes was calculated to promote altogether 1.1 ± 0.3 Mt C yr−1 BP on BLPs (mean ± 95 % confidence interval; Table 7). The corresponding amount of 15.9 Mt C yr−1 when accounting for the 12.0 % BGE on BLPs (Table 7). The sum of BP and BR on BLPs was 10.7 ± 4.5 Mt C yr−1 representing the total production of BLPs (Table 7). This total production of BLPs corresponds to 15 ± 6.8 % of the total DOC flux (69 Mt C yr−1) of examined rivers (Table 7). Assuming that the rivers examined responsible for 28 % of global DOC flux are representative for the remaining 72 % DOC flux to ocean, the estimate for the global coastal production of BLPs from tDOC is 38.0 ± 15.9 Mt C yr−1 supporting 4.1 ± 1.1 Mt C yr−1 BP and 33.9 ± 16.9 Mt C yr−1 BR.

4 Discussion

4.1 Global fluxes of BLPs from terrestrial DOC

Our study provides the first estimate for the production of BLPs from tDOC in the coastal waters in the front of ten major rivers across five continents. The BLPs from tDOC (38.0 ± 15.9 Mt C yr−1; this study) contribute little to the production of BLPs in global coastal water estimated earlier (206 Mt C yr−1) (Miller et al., 2002). That estimate is nearly as large as global riverine DOC flux to the ocean (246 Mt C yr−1) (Cai, 2011). There much of the earlier estimate must be based on the autochthonous production in marine waters and tells little about the coupling of tDOC to marine waters through the microbial loop.

The annual production of BLPs from tDOC in coastal waters (38.0 ± 15.9 Mt C yr−1) estimated in this study is larger than the global photochemical production of dissolved inorganic carbon (DIC) in inland waters (Koehler et al., 2014). This comparison indicates that although solar radiation transforms a remarkable amount of DOC in lakes and rivers, the majority of photochemical processing of terrestrial and freshwater DOC takes place in coastal waters.

According to the present study, the BGE on BLPs is 12 % and thus the majority of assimilated BLPs will be quickly respired to DIC totaling 33.9 ± 16.9 Mt C yr−1 in the global
coastal waters. This amount provides an additional source of DIC to coastal ocean in addition to the riverine flux of DIC (407 MtC yr\(^{-1}\); Cai, 2011). This study estimates that BLPs from tDOC support 4.1 ± 1.1 MtC yr\(^{-1}\) of BP in the global coastal waters. This BP is not alone a source of carbon to food webs, but is associated with N and P bound in bacterial biomass (Smith and Benner, 2005; Vähätalo et al., 2011). Assuming stoichiometric amounts of N and P associated to bacterial biomass (mass C : N : P ratio of 17 : 4 : 1) (Goldman et al., 1987), the assimilation of BLPs from terrestrial tDOC transfers 4.5 MtC yr\(^{-1}\), 1.06 MtN yr\(^{-1}\) and 0.26 MtP yr\(^{-1}\) to the coastal food webs through the grazers of bacterioplankton.

### 4.1.1 BLPs, photobleaching and CDOM fluxes

In this study, the production of BLPs is related to the photobleaching of CDOM with a \( R^2 \) 0.88 (Fig. 2). Similar relationships has been found also in earlier studies (Miller and Moran, 1997; Obernosterer and Herndl, 2000; Brinkmann et al., 2003). For example, \( \Delta f_{\text{CDOM},365} \) explains extremely well \( (R^2 > 96 \%) \) of the photoproduction of three individual BLP-compounds: formaldehyde, acetaldehyde and glyoxylate (Kieber et al., 1990). The corresponding \( R^2 \) is lower (0.67) for the relationship between a group of BPLs (carboxylic acids) and \( \Delta f_{\text{CDOM},365} \) determined for 38 Swedish lakes (Bertilsson and Tranvik, 2000). Our \( R^2 \)-value (Fig. 2) is higher than the corresponding one for 38 lake water samples (Bertilsson and Tranvik, 2000). This is at first glance surprising since our DOC was collected from ten global rivers covering a wide climatic range and land use not limited for a small region (Sweden) as in an earlier study (Bertilsson and Tranvik, 2000). The relatively high \( R^2 \)-values in this study may be explained in part by the same chemical matrix (artificial coastal water) used in our experiments. Additionally, the rivers examined here integrate the variability of DOM across their large catchments. For example, one third of 7838 different chemical compounds assigned by ultrahigh-resolution mass spectral analysis to the water samples examined in this study were shared among all river samples (Wagner et al., 2015). A conclusion from this and many other studies (Kieber et al., 1990; Miller and Moran, 1997; Bertilsson and Tranvik, 2000; Obernosterer and Herndl, 2000; Brinkmann et al., 2003) is that the production of BLPs is quantitatively linked the photobleaching of CDOM, which makes it as a useful proxy for the production of BLPs.

Our estimate for the global production of BLPs from terrestrial DOM bases on an assumption that the riverine CDOM flux will be photobleached completely in the coastal ocean. We used published CDOM fluxes for Mississippi, St. Lawrence and Lena Rivers (Stedmon et al., 2011; Spencer et al., 2013), but for the remaining rivers the CDOM flux was estimated simply by multiplying the measured CDOM with the published water discharge (Table 7). This method provides only rough estimates for CDOM fluxes and causes uncertainty also for our global estimates of BLPs. Therefore an additional data on riverine CDOM fluxes in the future will improve our estimate for CDOM fluxes and related production of BLPs. The majority of global riverine CDOM flux enters to the mixing layer of coastal waters, where solar radiation photobleaches CDOM efficiently and leaves not traces of terrestrial CDOM to be found in the surface of open ocean (review by Nelson and Siegel (2013) and references therein). Our assumption for complete photobleaching may not hold entirely for the rivers (such as Lena in this study) discharging to Arctic Ocean, which transfers 78 200 Gm\(^{-2}\) yr\(^{-1}\) of riverine CDOM to North Atlantic (calculated for 300 nm from the slope and flux estimated by Granskog et al., 2012). A part of this CDOM flux is directed to the deep ocean without photobleaching as a part of deep water formation in the North Atlantic (Nelson and Siegel, 2013). Thus our assumption for complete photobleaching is relatively well but not entirely supported by our current estimate for photobleaching being the major sink for riverine CDOM in the coastal ocean.

### 4.1.2 AQYs for BLPs

Our \( AQY_{\text{BP,330}} \)s (9.5–76 µmol C mol photons\(^{-1}\)) (Table 5) overlap the range of \( AQY_{\text{BP,330}} \) in the Baltic Sea (23 to 111 µmol C mol photons\(^{-1}\)) (Aarnos et al., 2012). Our
AQY_{BR,330} (57 to 1204 (µmolC mol photons\(^{-1}\)) are generally lower than the previously
reported 1391 (µmolC mol photons\(^{-1}\)) for river water and 1090 (µmolC mol photons\(^{-1}\))
for water draining a salt marsh (Miller et al., 2002), but similar to those for rivers and
lakes in Alaska (Cory et al., 2014). In the earlier studies, the AQY_{BP} reported by
Aarnos et al. (2012) are lower than AQY_{BR} reported by Miller et al. (2002) and Cory
et al. (2014). To the best of our knowledge, our study presents the first simultaneous
determinations of AQY_{BP} and AQY_{BR} and shows that AQYs for bacterial respiration are
larger than for bacterial production.

In this study, BLPs were consumed by riverine bacteria, which survived at the coastal
salinities, increased their biomass by one to two orders of magnitude and reached a de-
tectable peak in biomass within < 12 days. The bacterial inoculum used by Miller et al.
(2002) was thousand-times larger and the time of bioassay longer than in the present
study. The bacteria used by Miller et al. (2002) were able to assimilate more BPLs re-
sulting in higher AQYs than in our study. Although our bioassays for the determination
of BPLs lasted up to 12 days, the initial cell densities of inoculum were low and reached
typical densities found in surface water not until the end of bioassay (Table 3). The BLPs
determined in this study likely represent the most bioavailable fraction of BLPs (Kieber
and Mopper, 1987). The number of known chemically distinct BLP-compounds was 14
in an early review (Moran and Zepp, 1997), but had increased to 44 in a later review
(Vähätalo, 2009). A more recent study using a high resolution of mass spectrometry
identified 1835 chemical formulae that were produced by solar radiation-induced photo-
chemical reactions (Rossel et al., 2013). From these formulae 44 % were not observed
in a treatment with high microbial activity indicating that the number of BLP-compounds
was 807 and that BLPs represent a diverse group of compounds (Rossel et al., 2013).
Although, by a definition BLPs are biologically more labile than the original DOC, the
biodegradability of individual BLP-compounds likely varies and may form a continuum
like with the bulk DOM (Moran and Zepp, 1997; Vähätalo, 2009; Vähätalo et al., 2010;
Rossel et al., 2013). Thus, as the present study refers to the most bioavailable fraction
of BLPs, the entire pool of BLPs is likely larger than what was measured in this study.

4.1.3 BGEs on BLPs and non-labile DOC

Our BGE on BLPs (12.0 ± 7.2 %; Table 4) provides the first direct estimate for the BGE
of microbial communities on a group of compounds classified as BLPs. Our values
can be compared to BGEs reported for single compounds such as acetic and formic
acids (Bertilsson and Tranvik, 1998). BGEs on formic and acetic acids has been 2 and
41 %, in one study (Bertilsson and Tranvik, 1998), but 20–27 and 73–80 %, respectively,
in another study (Remington et al., 2011). The earlier studies demonstrate that BGE
on a single BLP compound can vary and thus it is a challenge to determine BGE
separately for each BLP compound and compile them together for an overall BGE on
all BLPs. Such a simple overall BGE (12.0 ± 7.2 %) can now be applied on BLPs based
on the results of the present study.

Our BGE on DOM in the dark controls (11.5 ± 3.9 %, Table 4) represents an estimate
for BGE on non-labile tDOC in coastal waters. This estimate falls to the lower range
of hundreds BGE determinations done with freshly collected water representing BGEs
primarily on labile DOC (Kroer, 1993; del Giorgio and Cole, 1998; Wikner et al., 1999).
Our BGE on non-labile DOC is similar to BGE (mean 11 %) on riverine DOC aged for
100 to 450 days (Asmala et al., 2014). An extensive aging of humic lake water by 6
years resulted in BGEs of 5–6 % (Kragh et al., 2008). The results of this (Figs. 1 and 3;
Tables 3 and 4) and earlier studies (Kragh et al., 2008; Berggren et al., 2009; Vähätalo
et al., 2010; Asmala et al., 2014) emphasize that bacteria can assimilate non-labile
tDOC, but a relatively low BGE.

5 Conclusions

Our study shows that the mineralization and transformation of tDOC will continue in
the coastal ocean after the quick consumption of labile tDOC at estuaries (Figs. 1–
3, Tables 3 and 4). As the tDOC is transported towards open ocean, the microbes
will continue to assimilate non-labile DOC with BGEs around 11.5 % (Table 4; Asmala
These reactions transform tDOC directly into CO$_2$, the turbidity maximum, advection and mixing into optically transparent marine waters. The photochemical production of BLPs in coastal waters can be estimated with two approaches. The AQYs can estimate the production of BLPs locally in the rivers plumes at any specified time with known solar irradiance (Tables 5 and 6). Similar estimates can be made by multiplying photobleaching of CDOM (Whitehead et al., 2000; Osburn et al., 2001; Vähätalo and Wetzel, 2004) with 0.335 mmol C m$^{-2}$ (Fig. 2). Photobleaching also provides a robust estimate for the annual production of BLPs by each river or all rivers (Table 7). Although this estimate does not specify where and when the photochemical transformations take place, it improves integrative synthesis on the fate of tDOC in the coastal ocean and its linkages to marine food webs (Bauer et al., 2013).

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Table 1. Locations and dates for sampling. City refers to a location close to the site of sampling given by coordinates. Transport time expresses the days elapsed between the sampling and the arrival of the sample to laboratory.

| River       | Country | City    | Latitude | Longitude | Date     | Sampling | Transport time |
|-------------|---------|---------|----------|-----------|----------|----------|----------------|
| Rio Negro   | Brazil  | Manaus  | 03°07’59’’S | 59°54’09’’W | 3 Jun 2010 | 82       |
| Rio Solimões a | Brazil | Manaus  | 03°07’58’’S | 59°54’04’’W | 3 Jun 2010 | 82       |
| Congo       | Congo   | Kinshasa | 04°18’18’’S | 15°28’32’’E | 1 May 2009 | 25       |
| Danube      | Romania | Tulcea  | 45°13’38’’N | 28°44’50’’E | 19 Apr 2010 | 21       |
| Ganges–Brah b | Bangladesh | Dhaka | 23°34’12’’N | 90°10’53’’E | 1 Oct 2009 | 68       |
| Lena        | Russia  | Tiski   | 71°54’14’’N | 12°15’16’’E | 16 Aug 2009 | 155      |
| Mekong      | Cambodia | Phnom Penh | 11°33’29’’N | 104°56’53’’E | 21 Aug 2009 | 34       |
| Mississippi | USA     | New Orleans | 29°02’20’’N | 89°19’20’’W | 22 Apr 2009 | 34       |
| Paraná      | Argentina | Buenos Aires | 34°18’07’’S | 58°32’47’’W | 29 Mar 2009 | 18       |
| St. Lawrence | Canada  | Quebec  | 46°54’45’’N | 70°52’32’’W | 12 Jun 2009 | 33       |
| Yangtze     | China   | Shanghai | 31°45’49’’N | 121°2’22’’E | 7 Sep 2009 | 17       |

a Amazon River sample was prepared by mixing samples from Rio Negro (25%) and Rio Solimões (75%).
b Ganges–Brahmaputra.
Table 2. Absorption coefficients of chromophoric dissolved organic matter at wavelength 300 nm ($a_{\text{CDOM},300}$ m$^{-1}$) in the initial, the dark and the irradiated samples (mean ± sd of three determinations), the amount of photobleaching (Dark–Irradiated) given as absorption coefficient ($\Delta a_{\text{CDOM},300}$ m$^{-1}$) as well as the relative difference (%) between the irradiated and to dark controls (Dark–Irradiated/Dark).

| River           | $a_{\text{CDOM},300}$ Initial | Dark  | Irradiated | Photobleaching $\Delta a_{\text{CDOM},300}$ (Dark–Irradiated)/Dark (%) |
|-----------------|-------------------------------|-------|------------|-------------------------------------------------|
| Amazon          | 13.06 ± 0.03                  | 12.92 ± 0.02 | 5.97 ± 0.02 | 6.95 ± 0.04 | 54 ± 0.1 |
| Congo           | 21.61 ± 0.03                  | 21.54 ± 0.03 | 9.12 ± 0.03 | 12.42 ± 0.06 | 58 ± 0.1 |
| Danube          | 4.08 ± 0.03                   | 3.79 ± 0.01 | 1.73 ± 0.02 | 2.06 ± 0.03 | 54 ± 0.4 |
| Ganges–Brah.*   | 1.08 ± 0.03                   | 1.12 ± 0.03 | 0.64 ± 0.03 | 0.48 ± 0.06 | 43 ± 1.1 |
| Lena            | 10.92 ± 0.04                  | 10.86 ± 0.02 | 5.22 ± 0.03 | 5.64 ± 0.05 | 52 ± 0.2 |
| Mekong          | 2.41 ± 0.02                   | 2.41 ± 0.01 | 1.21 ± 0.03 | 1.20 ± 0.04 | 50 ± 1.0 |
| Mississippi     | 5.90 ± 0.05                   | 6.01 ± 0.05 | 2.79 ± 0.04 | 3.22 ± 0.09 | 54 ± 0.3 |
| Paraná          | 4.49 ± 0.08                   | 4.48 ± 0.01 | 2.70 ± 0.01 | 1.78 ± 0.02 | 40 ± 0.1 |
| St. Lawrence    | 6.39 ± 0.17                   | 6.29 ± 0.07 | 3.12 ± 0.16 | 3.17 ± 0.23 | 50 ± 2.0 |
| Yangtze         | 2.57 ± 0.05                   | 2.63 ± 0.08 | 1.26 ± 0.03 | 1.37 ± 0.15 | 52 ± 0.3 |

* Ganges–Brahmaputra.

Table 3. Bacterial cell densities (10$^9$ cells L$^{-1}$, mean ± sd of two replicates) in the beginning of bioassay ($t = 0$) and at the time of maximum cell density in the irradiated (Irradiated) samples and in the dark control samples (Dark), the time of maximal density (in days) and the relative increase in the density based on BLPs: (Irradiated–Dark)/Dark (%).

| River      | Cell density at $t = 0$ | Dark  | Irradiated | Time of max density (d) | (Irradiated–Dark)/Dark (%) |
|------------|-------------------------|-------|------------|-------------------------|---------------------------|
| Amazon     | 0.01                    | 0.67 ± 0.02 | 1.54 ± 0.04 | 8                        | 130 ± 01                  |
| Congo      | 0.03                    | 1.89 ± 0.04 | 4.01 ± 0.12 | 5                        | 112 ± 02                  |
| Danube     | 0.02                    | 0.59 ± 0.02 | 1.04 ± 0.02 | 8                        | 108 ± 04                  |
| Ganges–Brah.* | 0.02                | 0.48 ± 0.03 | 0.73 ± 0.07 | 5                        | 52 ± 05                   |
| Lena       | 0.03                    | 0.36 ± 0.07 | 0.48 ± 0.04 | 6                        | 33 ± 15                   |
| Mekong     | 0.02                    | 0.64 ± 0.06 | 1.00 ± 0.04 | 12                       | 56 ± 08                   |
| Mississippi| 0.02                    | 1.58 ± 0.03 | 2.53 ± 0.15 | 10                       | 60 ± 06                   |
| Paraná     | 0.24                    | 0.80 ± 0.03 | 1.09 ± 0.03 | 9                        | 36 ± 01                   |
| St. Lawrence| 0.03                 | 0.59 ± 0.01 | 0.87 ± 0.00 | 12                       | 47 ± 01                   |
| Yangtze    | 0.03                    | 0.64 ± 0.06 | 1.08 ± 0.02 | 9                        | 69 ± 13                   |

* Ganges–Brahmaputra.
Table 4. Bacterial growth efficiency (%) (mean ± sd) on the irradiated DOC, the dark control DOC and on BLPs. BGE was calculated from BP (Fig. 1) and BR (Figs. 3 and 4). NA = not available.

| River           | Irradiated | Dark | BLPs |
|-----------------|------------|------|------|
| River           | BGE (%)    |      |      |
| Amazon          | 18.8 ± 0.7 | 15.3 ± 1.0 | 21.5 ± 2.0 |
| Danube          | 12.8 ± 0.7 | 11.2 ± 0.1 | 15.5 ± 1.3 |
| Ganges–Brah.*   | 27.7 ± 2.5 | 13.4 ± 1.7 | NA |
| Lena            | 5.8 ± 0.1  | 9.9 ± 0.4  | 4.5 ± 0.9 |
| Mekong          | 14.0 ± 0.2 | 12.5 ± 3.5 | 15.8 ± 4.5 |
| St. Lawrence    | 13.2 ± 1.7 | 14.5 ± 2.1 | 12.0 ± 4.5 |
| Yangtze         | 3.0 ± 0.2  | 3.6 ± 1.0  | 2.8 ± 1.1 |
| Average         | 13.6 ± 8.1 | 11.5 ± 3.9 | 12.0 ± 7.2 |

* Ganges–Brahmaputra.

Table 5. The apparent quantum yields for the production of BLPs supporting bacterial production and respiration at 330 nm (molC/mol absorbed photons$^{-1}$), as well as the parameters $c$ and $d$ (nm$^{-1}$) for the calculation of spectral AQYs (Eq. 2).

| River           | BP,330 | c     | d     | BR,330 | c     | d     |
|-----------------|--------|-------|-------|--------|-------|-------|
| Amazon          | 18.6   | 0.44  | 0.0305| 56.5   | 0.57  | 0.0279|
| Congo           | 42.0   | 0.52  | 0.0286| –      | –     | –     |
| Danube          | 35.9   | 0.49  | 0.0289| 147.8  | 0.66  | 0.0255|
| Ganges–Brah.*   | 75.7   | 0.59  | 0.0271| –      | –     | –     |
| Lena            | 9.9    | 0.37  | 0.0319| 186.2  | 0.73  | 0.0251|
| Mekong          | 60.8   | 0.57  | 0.0277| 269.6  | 0.78  | 0.0241|
| Mississippi     | 56.1   | 0.57  | 0.0280| –      | –     | –     |
| Paraná          | 20.1   | 0.41  | 0.0301| –      | –     | –     |
| St. Lawrence    | 9.5    | 0.37  | 0.0320| 71.5   | 0.59  | 0.0273|
| Yangtze         | 36.2   | 0.49  | 0.0289| 1203.6 | 1.03  | 0.0205|

* Ganges–Brahmaputra.
Table 6. Calculated annual production of biologically labile photoproducts (mmolC m$^{-2}$ yr$^{-1}$) supporting bacterial production (BP on BLPs) and respiration (BR on BLPs) separately as well as their sum (BPLs). For these calculations, Eq. (3) received AQY$^{BP}$, $\lambda$ or AQY$^{BR}$, $\lambda$ from Table 5 and the spectral annual global radiation in the front of rivers examined.

| River          | BP on BLPs | BR on BLPs | BLPs  |
|---------------|------------|------------|-------|
| Amazon        | 8.1        | 27.8       | 35.9  |
| Congo         | 20.0       | –          | –     |
| Danube        | 9.4        | 46.7       | 56.1  |
| Ganges–Brahmaputra | 32.6     | –          | –     |
| Lena*         | 1.0        | 25.8       | 26.8  |
| Mekong        | 24.2       | 132.1      | 156.3 |
| Mississippi   | 22.1       | –          | –     |
| Paraná        | 6.4        | –          | –     |
| St. Lawrence  | 2.0        | 18.9       | 20.9  |
| Yangtze       | 10.2       | 573.8      | 584.0 |

“–” = Not determined.
* The attenuation of solar radiation by sea ice ignored.

Table 7. The absorption coefficient of CDOM at 300 nm, water discharge, CDOM and DOC fluxes, bacterial production (BP) and respiration (BR) based on BLPs, the total amount of BLPs and the fraction of BLPs from the DOC flux.

| River            | $a_{\text{CDOM,300}}$ (m$^{-1}$) | discharge (km$^{3}$ yr$^{-1}$) | CDOM flux (Gm$^{2}$ yr$^{-1}$) | DOC flux (MtC yr$^{-1}$) | BP based on BLPs (MtC yr$^{-1}$) | BR based on BLPs (MtC yr$^{-1}$) | BLPs (BP + BR) (MtC yr$^{-1}$) | fraction |
|------------------|---------------------------------|--------------------------------|-------------------------------|-------------------------|---------------------------------|---------------------------------|---------------------------------|----------|
| Amazon           | 26.4                            | 6300                           | 166 320                       | 37.5                    | 0.67                            | 5.58                            | 6.25                            | 0.17     |
| Congo            | 49.4                            | 1300                           | 64 220                        | 10.15                   | 0.26                            | 2.16                            | 2.41                            | 0.24     |
| Danube           | 7.6                             | 210                            | 1596                          | 0.59                    | 0.01                            | 0.05                            | 0.06                            | 0.10     |
| Ganges–Brah.     | 2.1                             | 1120                           | 2352                         | 3.6                     | 0.01                            | 0.08                            | 0.09                            | 0.02     |
| Lena             | 21.2                            | 520                            | 27 818                        | 3.6                     | 0.11                            | 0.93                            | 1.05                            | 0.29     |
| Mekong           | 5.1                             | 550                            | 2805                         | 0.87                    | 0.01                            | 0.09                            | 0.11                            | 0.12     |
| Mississippi      | 11.6                            | 490                            | 8800                         | 3.5                     | 0.04                            | 0.30                            | 0.34                            | 0.09     |
| Paraná           | 8.4                             | 530                            | 4452                         | 5.9                     | 0.02                            | 0.15                            | 0.17                            | 0.03     |
| St. Lawrence     | 12.1                            | 340                            | 612                          | 1.55                    | 0.01                            | 0.02                            | 0.03                            | 0.01     |
| Yangtze          | 5.5                             | 900                            | 4500                         | 1.8                     | 0.02                            | 0.15                            | 0.17                            | 0.09     |
| Total            | 12 260                          | 283 475                        | 69.06                         | 1.4                     | 9.5                             | 10.6                            | –                              | 0.16     |

* $a_{\text{CDOM,300}}$ refers to the measured values from the water samples upon their arrival (Table 1), water discharge from Milliman and Farnsworth (2011). CDOM fluxes are calculated as the product of $a_{\text{CDOM,300}}$ and water discharges, but for Mississippi, St. Lawrence and Lena published CDOM fluxes were used (Stedmon et al., 2011; Spencer et al., 2013). DOC flux is from Cauwet (2002) but updated for Amazon (Coynel et al., 2005) and calculated for Mekong as the product of water discharge and DOC measured (1.58 mgL$^{-1}$) upon arrival of the Mekong sample. BP on BLPs is calculated from CDOM flux using the slope 0.333 mmolC m$^{-2}$ (Fig. 2), BR is calculated using BGE of 12.0% on BLPs.
* Ganges–Brahmaputra.
Figure 1. Bacterial production (µmol C L⁻¹; mean ± sd, n = 2) on the irradiated DOC (Irradiated), on the dark control DOC (Dark) and on BLPs, the latter calculated as the difference between the treatments (BLPs = Irradiated–Dark) by the end of logarithmic growth phase specified in Table 3.

Figure 2. The relationship between the bacterial production based on biologically labile photoproducts (BP on BLPs) and the photobleached CDOM at 300 nm. ∆a_{DOM,300} shows individual samples, the solid line linear fit to the individual samples (BP on BLPs = 0.336 ∆a_{DOM,300}; \( R^2 = 0.871, F_{1,9} = 68.77, df = 1,9, p < 0.001 \)) and the dotted lines shows the 95% confidence intervals of linear regression.
Figure 3. Cumulative bacterial respiration during the bioassay in the irradiated (gray line; Irradiated), and dark control samples (black line; Dark). Red line shows apparent respiration in the MQ-blank experiment (MQ-blank) and black arrows point out the end of log-phase in the irradiated samples (Table 3).

Figure 4. Cumulative bacterial respiration based on BLPs (BR on BLPs) calculated from Fig. 3 as the difference between irradiated and dark. Further details found in Fig. 3.