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# A worldwide view of organic carbon export from catchments

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**Abstract** Growing interest in the effects of global change on the metabolism, stoichiometry and cycling of carbon in aquatic ecosystems has motivated research on the export of organic carbon (OCE) from catchments. In this article, quantitative and functional features of the annual export rates of total, particulate and dissolved organic carbon (TOC, POC and DOC) were reviewed, and the stoichiometry of export (OC:N, OC:P and N:P) from 550 catchments worldwide was reported. TOC export ranged 2.1–92,474 kg C $km^{-2}$ $year^{-1}$, POC export ranged 0.4–73,979 kg C $km^{-2}$ $year^{-1}$ and DOC export ranged 1.2–56,946 kg C $km^{-2}$ $year^{-1}$. Exports of TOC and DOC were strongly linked, but POC export was unrelated to DOC. The DOC fraction comprised on average 73 ± 21% of TOC export. The export rates of organic carbon were poorly related to those of total nitrogen and total phosphorus. Discrete and continuous environmental variables failed to predict TOC export, but DOC export was influenced by discharge and catchment area worldwide. Models of OCE in different catchment types were controlled by different environmental variables; hydrological variables were generally better predictors of OCE than anthropogenic and soil variables. Elemental ratios of carbon export in most catchments were above the Redfield ratio, suggesting that phosphorus may become the limiting nutrient for downstream plant growth. These ratios were marginally related to environmental data. More detailed hydrological data, consideration of in-stream processes and the use of quasi-empirical dynamical models are advocated to improve our knowledge of OCE rates and those of other nutrients.

**Keywords** Controlling factors · Climatic regions · Biomes · In-stream processes · Stoichiometry · Nitrogen · Phosphorus

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## Introduction

Organic carbon export (OCE) from watersheds establishes the functional relationships between terrestrial and aquatic environments (Schlesinger 2001), and it affects ecosystem processes in freshwater (Cole et al. 2007) and coastal marine environments (Caffrey 2004). Organic carbon, often of allochthonous (terrestrial) origin, subsidizes heterotrophic microbial production that promotes heterotrophic conditions of aquatic ecosystems (Duarte and Prairie 2005). C transport and transformations in the Biosphere have received growing research interest because of their mediation in global warming (IPCC 2001). Despite the increasing recognition of the role of organic C in ecological processes, knowledge on the export rates from catchments is limited and restricted mainly to local scale studies (Table 1 in Electronic supplementary material). While the seminal articles by Schlesinger and Melack (1981), Meybeck (1982) and Mulholland and Watts (1982) have sparked much interest in OCE, only few efforts have been made to synthesize an increasing body of empirical research. Attempts have been made to review OCE for cold temperate catchments (Hope et al. 1994, 1997; Mulholland 2003); however, a global focus is still lacking. In this study, the authors aim to fill this knowledge gap by reviewing OCEs and their controlling environmental factors from different climatic areas and biomes around the world.

Many studies have identified controlling mechanisms of OCE to gain a better understanding of increased human pressures or natural constraints on global C cycles (Hope et al. 1994; Mulholland 2003; Lerman et al. 2004; Cole et al. 2007). Relevant environmental factors are rainfall (Clair et al. 1994), runoff (Brinson 1976), land use characteristics (Schlesinger and Melack 1981; Tipping et al. 1997), slope conditions and soil texture (Dosskey and Bertsch 1994; Clark et al. 2004), C:N ratios in catchment soils (Aitkenhead and McDowell 2000), pH (Brooks et al. 1999), the chemical composition of soil horizons (Hope et al. 1997), and the occurrence of lake and wetland systems in the catchments (Koprivnjak and Moore 1992). The influence of these variables depends on environmental settings at local scales, and it is not surprising that the relationships of these environmental features with OCE vary between individual catchments.

Recent worldwide N export studies (Caraco and Cole 2001; Alvarez-Cobelas et al. 2008) have demonstrated the qualitative effect of runoff, which is mediated through climate-dependent hydrological conditions in catchments. The authors are therefore particularly interested in how global OCE relates to hydrological variables because current climatic change scenarios predict either decreasing or increasing rainfall in many areas of the world (IPCC 2001). These changes will likely result in altered net heterotrophic conditions and consequently altered ecosystem function in freshwaters and coastal marine environments. Rainfall increase usually results in greater runoff and, hence greater OCE, whereas rainfall decrease may promote the opposite effect. Thus, the strength of relationship between OCE and hydrological variables in different geographic areas might help us assess how OCE is affected by climatic conditions, and may provide insight into how OCE could change with global warming. In addition, the revealing of the strength of correlation between OCE and surrogates of anthropogenic stress (e.g. land use practices, human population in catchments) could provide a better understanding of global change imprints on global OCE.

Most OCE studies focused almost only on dissolved organic carbon (DOC). Export and transformations of particulate (POC) forms have been dealt with less frequently (e.g. Brinson 1976; Stutter et al. 2008). This limits a process-based understanding of organic C export because riverine transformations of C fractions through microbial activity could play an important role (Raymond and Bauer 2001). Because POC inputs to streams appear to be important everywhere (Ivarsson and Jansson 1994; Kao and Liu 1997; Hilton et al. 2008), the POC:DOC ratio in streams could serve as a simple indicator of in-stream transformation efficiency; that is, the lower the ratio the stronger the in-stream transformation of POC.

Cycles of C, N and P in running waters can be coupled at local scales (Dillon and Molot 1997; Goodale et al. 2005). Assuming constant ratios of C, N and P in organic matter, it is likely that the stoichiometry of nutrients during export is also constant provided that processes affecting outgassing ($CO_2$, $CH_4$ and $N_2$ volatilization) and sediment immobilization are of lower importance. C:N ratios in streams explained up to 41% of variability in N-specific uptake rates of USA streams (Dodds et al. 2004); this enables to link C with N-cycling models across these streams. Data from recent reviews on global N and P export (Alvarez-Cobelas et al. 2008, 2009) hold potential to determine the relationship between the export rates of these nutrients on a worldwide scale.

In this article, easy-to-use environmental variables that have been found to predict OCE well at local scales explain OCE at the scales of biomes, climatic regions and the entire world will be tested. This is timely in view of the recent reports of steady OCE increase in some Northern Hemisphere catchments (Worrall and Burt 2008). The authors make use of available data (e.g. catchment area, soil C and N and their ratio, population density, rainfall, runoff, altitude and percentage of land use types (crops, forests, heathlands, peatlands, grasslands, rangelands, urban areas), soil types, river order, and the abundance of lake and wetland systems in catchments) to predict global export rates of organic C. To prove if man-made constraints are involved in organic C export, discharge-weighted DOC concentrations in the analyses have also been used to discard hydrological effects and hence to assess the importance of anthropogenic sources on OCE. In addition, models are tested in different biomes and climatic regions to assess how general the predictions are from the qualitative (variables explaining export) and quantitative (strength of statistical relationships) side. The authors focus on the relative proportion of POC and DOC fractions at these spatial scales and relate fluxes of organic C, total N and total phosphorus with each other to assess the importance of coupled biogeochemical cycles and stoichiometry in nutrient export.

## Materials and methods

### Data sets

This article is based on data collected from the literature and web sources that were available until December 2008 (Table 1 in Electronic supplementary material). The authors also included our own data from Spain to increase the sample size for semi-arid areas in the analyses (Alvarez-Cobelas et al. 2010). The authors compiled data on DOC, POC and total organic carbon (TOC) export which have been reported in the original studies. In these studies, most estimates of POC have been obtained by calculating the difference between TOC and DOC, which is a rather crude measure that will increase uncertainty of POC export. As this compilation will show, the data base is to a large extent biased towards cold temperate catchments; thus more data from other geographic areas will be needed to obtain a more accurate picture of worldwide OCE.

When available, annual export rates of TOC, POC and DOC were included in the data set. Up to 550 systems were considered, but the available information on the export of organic C fractions was variable among catchments. When the original studies lasted more than one year, data were averaged for the whole study period or for each year of study. Although these two formats of data were not strictly comparable, the authors used both types of data in order to have more degrees of freedom in our statistical analyses. Multi-year averaging of data was often carried out in the original studies to reduce the effects of interannual climatic variation. The authors also computed coefficients of variation (CVs) of OCE by using studies where yearly OCE data were available for several years, resulting in the range of 7–44%. These interannual variabilities were not high, suggesting that interannual means of OCE can be used with certain confidence for analysis. When several years of OCE data were available, the authors chose the year with most data on OCE and environmental variables for analysis; the authors did not use all the yearly data to avoid autocorrelation bias. The authors used the original data from studies without additional statistical averaging. The years selected for these analyses were shown in Table 1 (Electronic supplementary material).

From the various data sets and qualitative information reported in the reviewed articles, the authors compiled information on annual discharge, rainfall, runoff, catchment area, altitude, river order, climatic region, biome, percentages of crops, forests, urban areas, rangelands, pastures, peatlands and heathlands in the catchment, soil type, population number and density (Table 2 in Electronic supplementary material). Selected variables lacked sometimes data, thus preventing us from testing some hypotheses (e.g. the relationship between soil type and the POC:DOC export ratio or the relationship between export nutrient ratios and land use). Quantitative data were used to seek for relationships between environmental factors and OCE. Information on discrete variables was considered to compare catchment OCE between different climatic areas [xeric (runoff $<0.1$ m year$^{-1}$) versus mesic catchments], river order, soil types (following the FAO (2003), classification in wide groups, such as arenosols, cambisols, histosols, leptosols, luvisols and podsols), land use types (dominance of a specific land use >80% of overall catchment area), the occurrence of point sources of nutrient contamination, upland versus lowland location of catchments, ascertained from data in each single study and the presence/absence of lentic waterbodies in the catchment. For land use typologies, the authors assembled data provided by each author to distinguish among croplands, forests, urban areas, heathlands, peatlands, grasslands and rangelands. Wherever possible, the authors followed CORINE recommendations (http://www.eea.europa.eu/publications/COR0-landcover) for land use assessment. Climatic regions were ascertained from FAO (http://www.fao.org/sd/eidirect/climate/eisp0002.htm) that followed the Köppen classification. Data from arid areas were lumped with those from warm temperate areas for analysis because of few available data; tropical and subtropical catchments were also pooled together.

Biomes were those reported by Ricklefs and Miller (1999). Recent analyses (DeFries et al. 2004) have demonstrated that more than three quarters of Earth's land surface has been reshaped by human activity. More than 80% of all people live in areas that are densely populated and which cover approximately 8% of global ice-free land. Human-manipulated ecosystems (including agricultural areas) now cover 37% of the land surface of the world. Although not generally regarded as a biome, the authors cannot ignore the important effect of these areas on regional and global biogeochemical processes. Therefore, the authors have considered agriculturally dominated catchments as belonging to a specific biome.

Because C and N in world soils and their elemental ratios partly explain OCE variability (Aitkenhead and McDowell 2000), the authors also used data compiled by Zinke (http://www.daac.ornl.gov/data/global_soil/Zinkesoil/data) to test for these relationships worldwide. The authors also split the data set into large (>100 km$^2$) and small catchments and catchments of different river order size to analyse the confounding effects of catchment size and the landscape position of catchments on OCE. Also upland and lowland position catchments were considered, using data gathered from each article.

## Methodological concerns

One issue that deserves comment is the methodologies used for measuring both water discharge values and C assessment which are jointly required to estimate OCE. For the former, many world catchments are still ungauged, and hence it has often been impossible to measure discharge continuously for a proper characterization of peak flows that are crucial to provide accurate estimations of C flux. A series of methods for measuring discharge in ungauged channels are currently available (Gordon et al. 2004), but they are not always used. Concerning C assessment, sampling designs have rarely engaged in appropriate sampling resolutions to account for the entire spatio-temporal environmental variability; thus, only raw estimations of TOC variability are often available. It is also important to discriminate between POC and DOC fractions in export. The boundary between both components has arbitrarily been set at 0.45 microns (Thurman 1985). The POC fraction is usually measured in elemental analysers (Lewis and Saunders 1989), and 'dissolved' C has been determined in either TOC analysers (Richey et al. 1990) or spectrophotometrically at different visible wavelengths (Cuthbert and del Giorgio 1992). While in the early literature TOC was colorimetrically measured after wet oxidation (Maciolek 1962), more recent determinations used a combustion method followed by nondispersive infrared analysis of carbon dioxide (Menzel and Vaccaro 1964), or even detection of $CO_2$ with a flame ionization detector (Grieve 1994). Sometimes TOC has been assumed to be an estimate of DOC, taking into account the low proportion of POC (Ivarsson and Jansson 1994). Consequently, propagation of measurement errors on water discharge, organic C fractions, along with the consideration of variable sampling frequencies, will result in uncertainty of TOC flux.

## Statistical treatments

Most data sets showed non-Gaussian distribution, as judged by the Kolmogorov–Smirnov test. Given these skewed data distributions (see the "Results" section), the authors used non-parametric tests (Siegel and Castellan 1988) to assess global trends in OCE. To determine the environmental control of OCE from the world's catchments, Spearman rank correlation analyses were carried out to relate the export rates of organic C fractions to quantitative environmental variables. When necessary, the determination coefficients ($R^2$) were calculated to infer the explanatory power of the significant relationships. In order to stabilize variances and due to the fact that non-linear processes were implicitly considered to act upon OCE, the authors also tried log–log, multivariate relationships using stepwise multiple regression analyses to model OCE. Regression models were tested on a world-wide basis, but also separately for broad climatic areas (cold temperate, warm temperate and arid, tropical and subtropical), for areas of distinct dominant runoff (mesic versus xeric, see above), biomes, soil types and land use types. Multivariate models were chosen by using the stepwise approach of forward variable selection which enabled selection only for the more meaningful, statistically independent variables. Best models were initially identified on the basis of model fit (adjusted $R^2$; Neter et al. 1996). However, stepwise regression has recently been criticized because of (1) biased parameter estimation, (2) inconsistencies among model selection algorithms, (3) problems in multiple hypothesis testing, and (4) inaccurate focuses on a single best model (Whittingham et al. 2006). In fact, using adjusted $R^2$ will allow for overfitted models, and hence information theoretic analysis has been suggested to represent a better approach to compare models (Burnham and Anderson 2002). Because previously reported models of organic C flux use adjusted $R^2$ as a means of goodness of fit (Dillon and Molot 1997; Aitkenhead-Peterson et al. 2005), the authors also present the values of adjusted $R^2$ when comparing predictive models. For our own model building, the Akaike Information Criterion (AIC hereafter) was estimated, which allowed us to select the best among competing models (Burnham and Anderson 2002). The AIC is considered a heuristic approach that provides a straightforward and meaningful way of ranking models based on their goodness of fit, simply by choosing those with the lowest AIC values that would reflect the precision and complexity of the model, and therefore it is a better tool for model selection (Burnham and Anderson 2002). Models were estimated only if at least 15 catchments of a given category had the required environmental predictor variables, and they will be selected on the basis of the lower AIC within the same group of variable and data sets.

Many models were built for different dependent variables and data sets, but only one (that of the lower AIC) was included for a given set of dependent variables and data. The number of models tested for each set varied between 3 and 15, depending on the degrees of freedom involved in each model and the authors used the second-order information criterion that accounts for small sample sizes (Burnham and Anderson 2002). Problems related to multicollinearity in the models were overcome by removing variables from analysis which were correlated with each other (Legendre and Legendre 1998). Statistical analyses were performed with STATISTICA 6.1.

Another way to discard the strong effect that hydrological features have on OCE (Mulholland 2003) is to deal with organic C concentrations instead of export. The authors have done this by estimating discharge-weighted organic C concentration from OCE, catchment area and discharge (or runoff) data (Tables 1, 2 in Electronic supplementary material). However, this has not always been possible in all the instances because many articles have not reported data on these variables.

Other recently collected global data sets (Alvarez-Cobelas et al. 2008, 2009) enabled us to search for links between organic C, total N and P export and concentration in world-wide catchments. Relationships were also tested using concentrations because some studies had reported a negative correlation between DOC and nitrate concentration in some areas (Goodale et al. 2005; Konohira and Yoshioka 2005). Stoichiometric ratios of organic C to total N, organic C to organic N, organic C to total P and total N to P (OC:N, OC:ON, OC:P and N:P) were calculated from these data. These ratios were related to environmental variables using compiled data sets (Tables 1, 2 in Electronic supplementary material of this study and those in Alvarez-Cobelas et al. 2008, 2009).

## Results

### Global organic carbon export

Annual OCE rates were assessed between 65°N and 42°S; its continental distribution was Africa-6 catchments, America-334 (296-North America and 38-Central and South America), Asia-21, Australia-43 and Europe-146 (Fig. 1). 550 catchments were considered (Table 1 in Electronic supplementary material), of which 485 and 397 catchments belonged to the Northern Hemisphere and Western longitudes, respectively. Concerning climatic areas, six

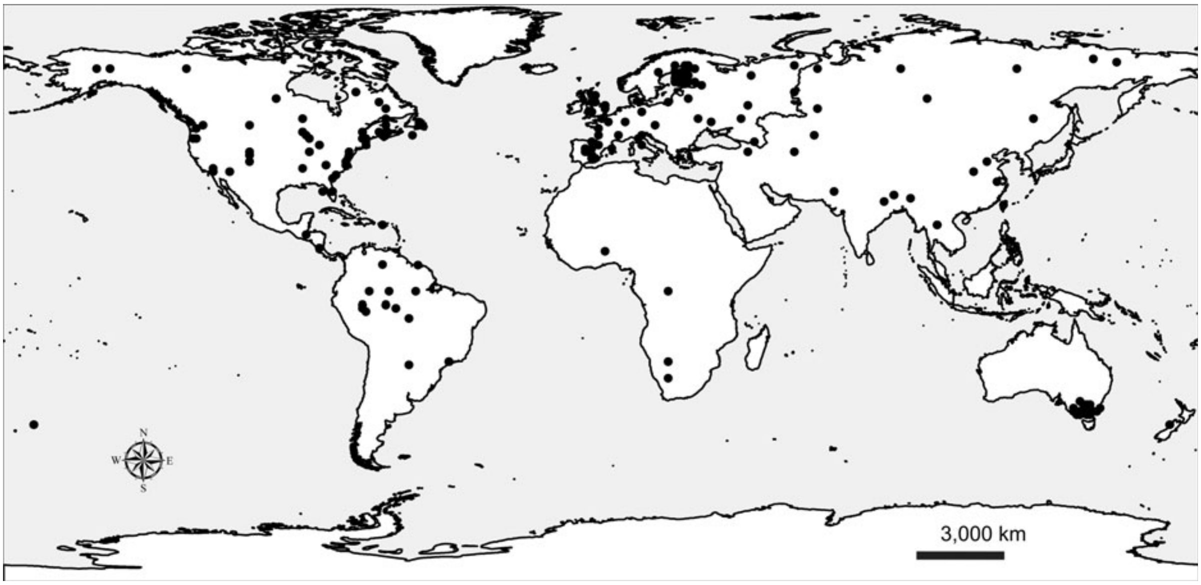


**Fig. 1** Sites whose carbon export data of catchments have been used in this study (see also Table 1 in Electronic supplementary material)

catchments (1%) were located in Arctic and Subarctic areas, 353 (64%) were found in cold temperate regions, 130 (24%) belonged to warm temperate and arid regions, whereas 61 (11%) occurred in tropical and subtropical areas. Concerning biomes, catchments of deserts, mountains, savanna and tundra each comprised some 2% of the whole data set, agricultural basins attained 14%, taiga and tropical forests each reached 6% of the data set, whereas temperate forests and shrublands comprised 45 and 20% of the whole data set, respectively. Total organic C export ranged 2.1–92,474 kg C $km^{-2}$ $year^{-1}$, POC export was between 0.4 and 73,979 kg C $km^{-2}$ $year^{-1}$ and DOC export ranged between 1.2 and 56,946 kg C $km^{-2}$ $year^{-1}$. All distributions were right-skewed (Fig. 2). CVs were 159, 367 and 152% for export of TOC, POC and DOC, respectively.

## Organic carbon export in different types of catchments

With regard to DOC export, xeric catchments had lower fluxes than mesic catchments; OCE was also more variable in the latter ($P < 0.05$; Mann–Whitney test; Fig. 3a). Lowlands and uplands did not differ in their DOC export rates ($P > 0.05$; Kruskal–Wallis test). Dissolved organic C export depended on soil types (Kruskal–Wallis test, $P < 0.05$; Fig. 3b, Table 3 in Electronic supplementary material); histosol, leptosol and podsol-dominating catchments had more variability in DOC export than the remaining soil types. Histosols exported more DOC than cambisols, inceptisols and luvisols; podsols had higher DOC export rates than cambisols, inceptisols and luvisols, and cambisols exported less DOC than arenosols and histosols (multiple comparisons based on a Kruskal–Wallis test; $P < 0.05$; Table 3 in Electronic supplementary material).

With regard to land use, forest and heathland-dominated catchments showed higher variability in DOC export than agricultural areas (affected by crops and livestock grazing in grasslands). Differences in DOC export among land use types were statistically significant (Kruskal–Wallis test, $P < 0.05$; Fig. 3c). Heathlands exported more organic C than croplands and forests. The occurrence of lentic waterbodies in catchments did not reduce DOC export on the global and biome scale ($P > 0.05$; TOC could not be analysed because of insufficient data). Point sources of pollution increased DOC export compared with either catchments without these contamination sources or catchments receiving diffuse sources of organic C (Mann–Whitney test, $P < 0.05$; Fig. 3d). Upstream catchments (i.e. those of river orders 1 and 2) showed higher variability of DOC export than higher order streams, but no significant differences

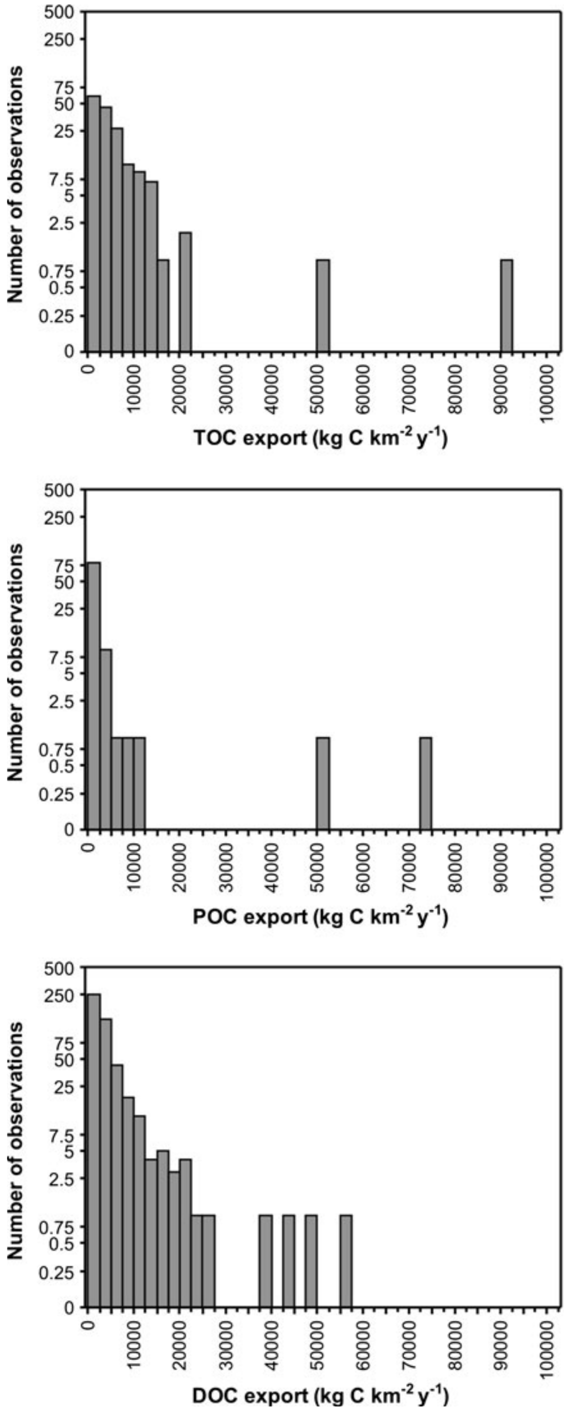


**Fig. 2** Histograms of catchment export of organic carbon compounds around the world on a logarithmic scale. *TOC* total organic carbon, *POC* particulate organic carbon, *DOC* dissolved organic carbon

were found among river orders (Kruskal–Wallis test, $P > 0.05$, Fig. 3e).

## Patterns in fractions of organic carbon export

Export of TOC and DOC was strongly correlated if an outlier of a southern Pennines catchment (UK; Pawson et al. 2008) was removed ($R^2 = 0.95, P < 0.05$; Fig. 4). If this outlier was included, then the explanatory power of the relationship decreased markedly ($R^2 = 0.56$, $P < 0.05$; Fig. 4). POC export was weakly related to DOC ($R^2 = 0.06$, $P < 0.05$; Table 4 in Electronic supplementary material), but POC export explained much variability of TOC export ($R^2 = 0.71, P < 0.05$; Table 4 in Electronic supplementary material).

On average, DOC export comprised 73 ± 21% of TOC export. DOC export as a fraction of TOC did not differ among climatic regions (Kruskal–Wallis test, $P > 0.05$). However, a significant difference was found in the biomes comparison (Kruskal–Wallis test, $P < 0.05$; see Table 5 in Electronic supplementary material). Climatic regions are larger than biomes and hence may encompass areas that cancelling out the environmental variability of OCE. In Arctic and Subarctic catchments, DOC export comprised 79 ± 16% of TOC. In cold temperate catchments, warm temperate catchments and arid, tropical and subtropical catchments, this fraction reached 76 ± 19, 61 ± 30 and 70 ± 19%, respectively. Concerning biomes, the lowest fraction of DOC was found in agricultural areas and deserts (21 ± 27 and 20 ± 26%, respectively), and the highest was observed in temperate shrublands and savannas (83 ± 12 and 87 ± 5%, respectively); crop-dominated catchments and deserts showed the highest variability of DOC as a fraction of TOC export, while savannas and taigas experienced the lowest variability (measured as CV). None of the environmental variables tested (including river order) were related with the POC:DOC ratio ($P > 0.05$).

## Environmental controls of organic carbon export and concentration

While DOC export showed a weak, inverse relationship with latitude, the other C fractions did not show

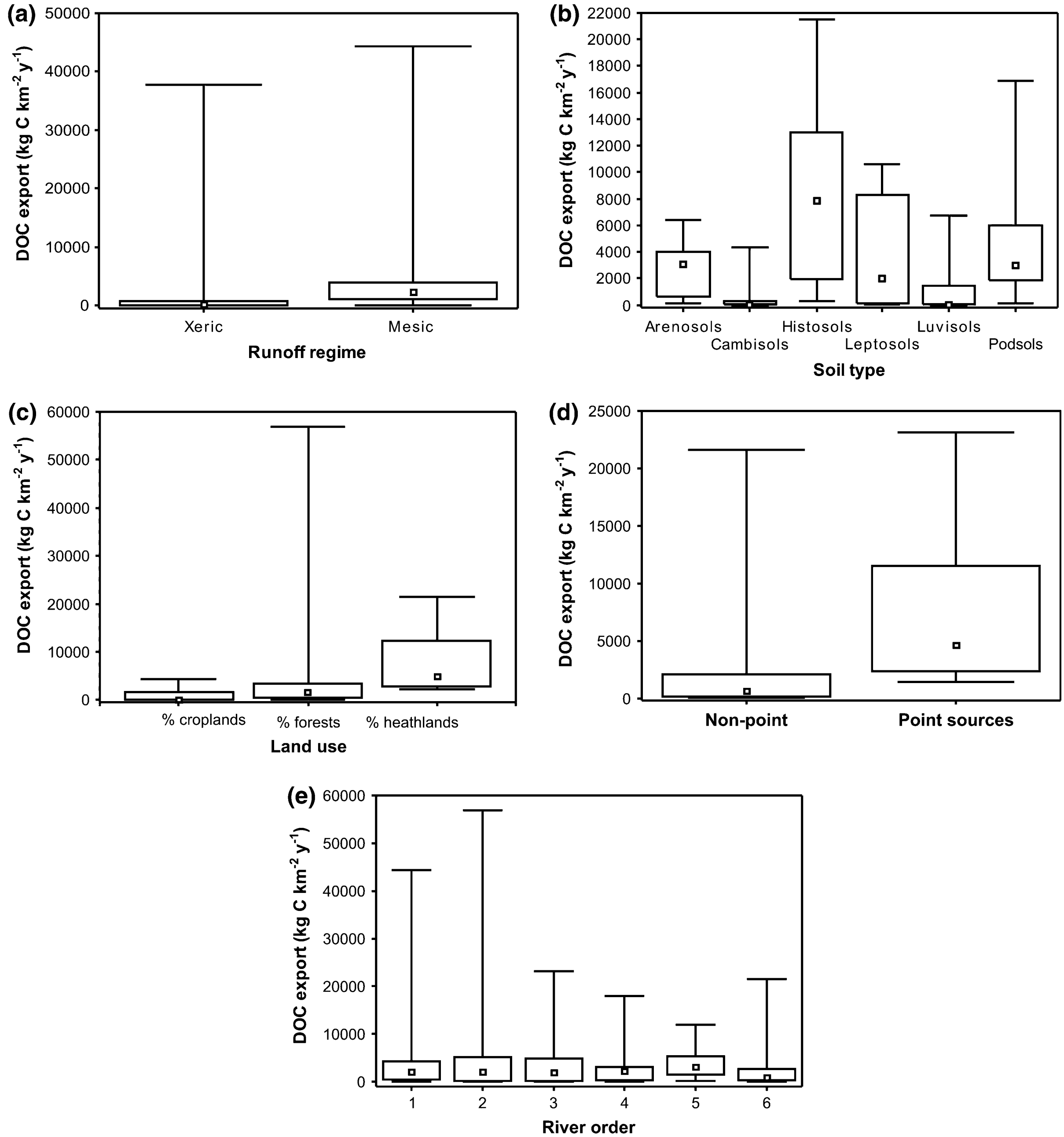


**Fig. 3** Box-whisker plots of DOC export related to different levels of environmental factors. The inner small quadrat is the median, the box is the 25–75% quartile, whereas the whisker is the range. Since DOC is strongly related to TOC (Table 3 in Electronic supplementary material), these plots are already applicable to TOC, **a** Runoff; xeric (runoff $< 0.1$ m year$^{-1}$) versus mesic catchments are compared, **b** Dominant soil type in the catchment, **c** Land use; only catchments having more than 80% of a given land use have been chosen, **d** Occurrence (Y) of point sources in the catchment, **e** River order

any significant relationship with either latitude or longitude (Table 5 in Electronic supplementary material, $P > 0.05$). Total organic C export was related to population density and to the percentage of croplands, forests and heaths in catchments ($P < 0.05$), but the explanatory power of these relationships was less than 50% (Table 5 in Electronic supplementary material). Particulate organic C

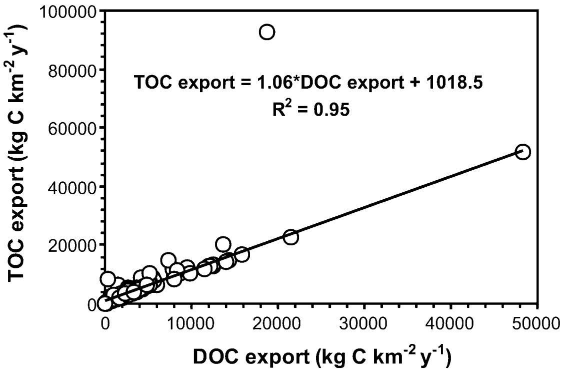


**Fig. 4** Dissolved organic versus total organic carbon export in world catchments. The outlier by Pawson et al. (2008), recorded in an eroding Pennines catchment (UK) with a very high contribution of particulate organic carbon, was included. The equation was estimated without the outlier ($N = 96$)

export was weakly related with rainfall but strongly related with percentage of heathlands and population density, albeit with a comparatively low number of degrees of freedom ($N = 9$–$19$, $P < 0.05$; Table 5 in Electronic supplementary material). Dissolved organic C export showed significant relationships with rainfall, runoff, population density and the fractions of crops, urban areas, pastures, peatlands and heathlands in the catchments (coefficients of correlation ranging from $-0.39$ to 0.64; Table 5 in Electronic supplementary material). Population density explained the highest variance (38%). Averaged C or N contents in catchment soils were unrelated with OCE ($P > 0.05$); however, there was a weak inverse relationship between the soil C:N ratio and DOC export (Fig. 5; Table 5 in Electronic supplementary material).

Catchment size and the percentage of wetland ecosystems had no effect on OCE variability (Table 5 in Electronic supplementary material). If catchments were split into small (below 100 $km^2$) and large (above 100 $km^2$) watersheds, then more OCE relationships were explained by environmental variables in larger catchments (8 vs. 14 significant relationships, Table 6 in Electronic supplementary material). Also the variability of OCE explained by these variables was higher in larger catchments (Table 6 in Electronic supplementary material). POC export showed a stronger relationship with TOC in smaller than in larger catchments ($R^2 = 70$ vs. 34%, respectively, $P < 0.05$). The soil C:N ratio was weakly, albeit inversely, related with DOC yield in small catchments (Table 6 in Electronic supplementary material).

TOC and DOC export were strongly related (Fig. 4). Multiple regression models of DOC export suggested that catchment area and discharge were significant controlling variables of annual OCE worldwide, in cold temperate catchments and the main biomes for which there were enough data to estimate these models (Table 7 in Electronic supplementary material). Smaller catchments showed higher OCE rates because there was a negative relationship between catchment area and OCE (Table 7 in Electronic supplementary material). The explained variability of OCE in warm temperate, arid and agricultural catchments was higher ($R^2 = 89$–90%, $P < 0.05$) than in the remaining climatic regions (i.e. cold temperate and tropical) and in the worldwide model ($R^2 = 54\%$, $P < 0.05$, Table 7 in Electronic supplementary material). The model for OCE in the temperate forest was less robust than that for agricultural catchments (Table 7 in Electronic supplementary material). Interestingly, independent explanatory variables changed among these models, population density being important in warm temperate and arid areas, and forest cover being important in tropical and subtropical areas. TOC and POC flux variability was higher in cold temperate areas than in the remaining climatic areas. There was an increase in variability of DOC yields downstream, with warm temperate and arid and tropical and subtropical areas exhibiting higher CVs of export (Table 8 in Electronic supplementary material). The tundra and the tropical forest showed the lowest and the highest variability of TOC export (CVs 33–120, Table 8 in Electronic supplementary material), but deserts and temperate forests had the highest variability range of POC export (CVs 7–79, Table 8 in Electronic supplementary material). Taiga and deserts had the lowest and highest variability of DOC export (CVs 42–198, Table 8 in Electronic supplementary material).

When hydrological effects were discarded using yearly averaged concentrations of DOC as the dependent variable, the explained variability was much lower than that of OCE (Table 9 in Electronic supplementary material), ranging from 6 to 36%. The explanatory variables also changed, and inhabitant density appeared to be important worldwide and in cold temperate areas. In agricultural areas and

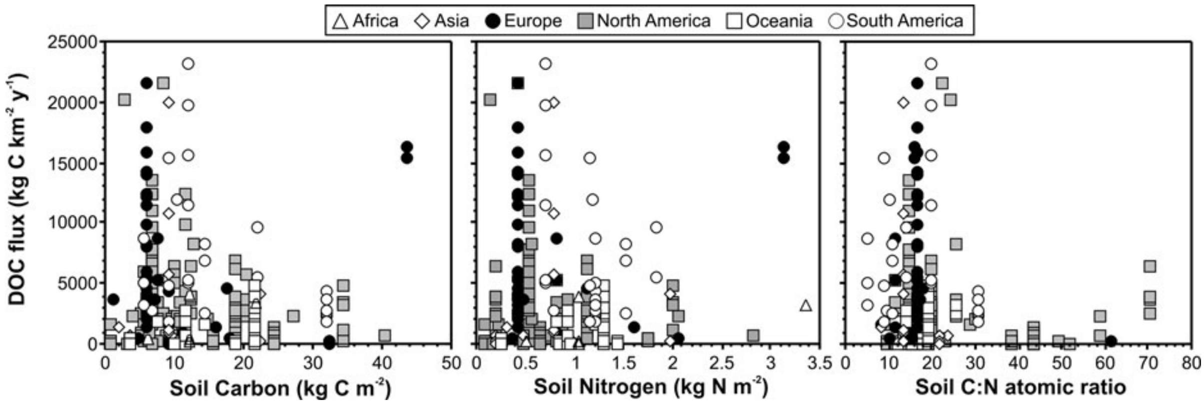


**Fig. 5** Bivariate plots of soil carbon, soil nitrogen and the soil C:N atomic ratio on DOC export worldwide. Soil data were gathered from Zinke (http://www.daac.ornl.gov/data/global_soil/Zinkesoil/data)

temperate forests. catchment size and discharge were influential to explain DOC concentration (Table 9 in Electronic supplementary material).

## Environmental controls of organic carbon export and concentration in different types of catchments

Environmental conditions had a strong effect on the explained variability in multivariate models (Table 10 in Electronic supplementary material), ranging from 2% (forest dominance) to 94% (crop dominance). The model of xeric climatic areas had the highest explained variability (Table 10 in Electronic supplementary material). Most models of OCE were controlled by different sets of environmental conditions. Runoff was the most frequently selected variable in the different models tested. Overall, variables related to natural environmental variability (rainfall, catchment area, runoff, etc.) rather than those related to anthropogenic stress (land use, population density, etc.) seemed to be more important to explain export rates, but population density also explained OCE variability in most models (Table 10 in Electronic supplementary material).

When hydrological and catchment area effects were discarded using organic C concentrations alone, the explained variability diminished markedly (Table 11 in Electronic supplementary material) relative to the OCE models, but these variables and population density were still important predictors in these models.

## Stoichiometry of nutrient export from catchments

THE TOC and DOC export were weakly related to total N and total P export in world catchments ($R^2 = 4$–$7\%$, $P < 0.05$; Table 12 in Electronic supplementary material). DOC yield was strongly related to dissolved organic N export, but did not show a significant correlation with nitrate export ($P < 0.05$; Table 12 in Electronic supplementary material). DOC and nitrate concentrations showed a positive relationship, but the explained variability was low ($R^2 = 4\%$, $P < 0.05$; Table 12 in Electronic supplementary material).

A high variability of elemental ratios was found in nutrient export from catchments in the worldwide analysis (Table 13 in Electronic supplementary material). Left-skewed distributions were found for all the ratios tested (Fig. 6) and stoichiometry of nutrient export in most catchments was well above Redfield ratios (1958; 106:16:1 for C:N:P; Sterner and Elser 2002). The highest variability of elemental ratios was found in warm temperate and arid catchments (Table 13 in Electronic supplementary material). Large rivers (i.e. those with a river order of 6) showed the lowest variability of elemental ratios (Table 13 in Electronic supplementary material). Agricultural areas showed the highest variability of stoichiometry in the inter-biome comparison (Table 13 in Electronic supplementary material). OC:N and N:P ratios were negatively related with the fraction of forest in catchments ($R^2 = 4\%$ and 16%, respectively, $P < 0.05$). OC:N, OC:ON, OC:P and N:P ratios were not related with river order ($P > 0.05$). OC:N, OC:ON, OC:P ratios were related with each other ($R^2 = 38–52\%$, $P < 0.05$).

## Discussion

### Global organic carbon export

The compiled data cover five orders of magnitude (Table 1 in Electronic supplementary material), thus increasing by two orders the range of previously reported values (Mulholland 2003). Tundra and polar regions are underrepresented in our data set because only six catchments have been studied so far. This is regrettable in view of the large area covered by these climatic regions (Ramsar Convention, www.ramsar.org) and because they are particularly sensitive to global warming (IPCC 2001).

The distribution of OCE is right-skewed (Fig. 2), suggesting that relatively low values of OCE dominate in world catchments. As a fraction of TOC in streams, anthropogenically derived organic C is, therefore, not high despite the pollution experienced by many catchments with high human settlement throughout the world, and the recognition that urban areas also increase DOC export (Fig. 3c; González and Pozo 1995; Tipping et al. 1997). It is true that discharge masks concentration effects, thus affecting the interpretation of patterns involved when discharge and catchment area are excluded and only concentrations are used; however, these models are weaker (Table 9 in Electronic supplementary material) compared with those built on flux, but the inclusion of the variable inhabitant density in all the models points to some anthropogenic influence on global OCE. Increases of anthropogenically derived organic C can increase the heterotrophic metabolism in streams and coastal marine environments that receive these human-derived organic loads (Cole et al. 2007). These inputs, however, could be partly counterbalanced by strong $CO_2$ degassing resulting from in-stream C metabolism (Cole and Caraco 2001; Mayorga et al. 2005). This could reduce OCE downstream and decrease the load of organic C to coastal areas.

### Organic carbon export in different types of catchments

On a broad basis, soil types appear to influence OCEs (Fig. 3b; Table 3 in Electronic supplementary

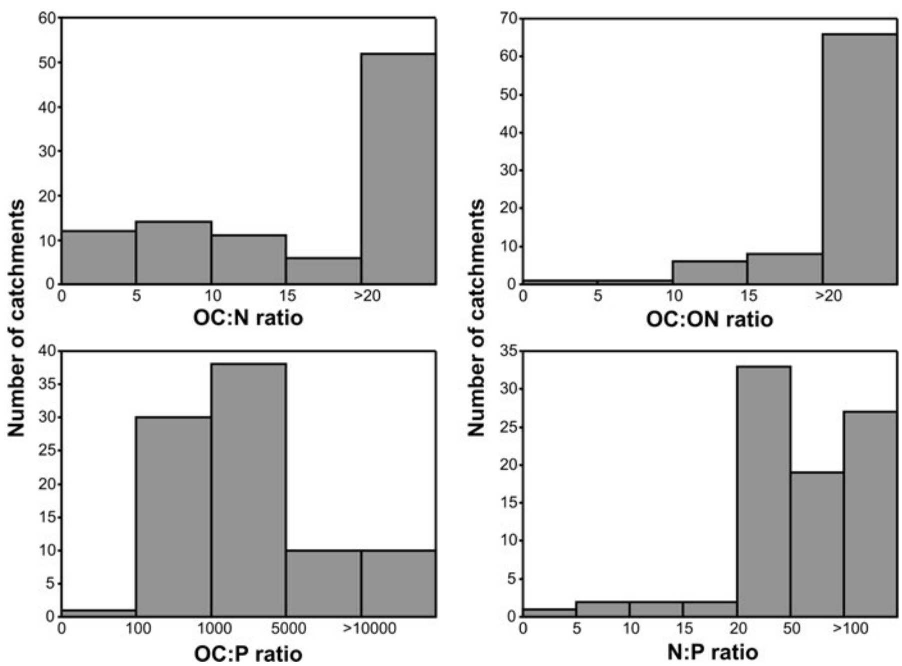


**Fig. 6** Histograms of elemental ratios of nutrient export in world catchments. Data to estimate these ratios were published in Alvarez-Cobelas et al. (2008, 2009; Tables 1, 2 in Electronic supplementary material) and in this study (Tables 1, 2 in Electronic supplementary material). *N* nitrogen, *OC* organic carbon, *ON* organic nitrogen, *P* phosphorus

material). This might result from the fact that organic C is exported to streams from the uppermost soil horizons and that their C contents vary depending upon the type of soil (Moore 2003). Differences in OCEs are also due to the different proportions of hydrophobic and hydrophilic organic layers of soils (Möller et al. 2005), which also differ between soil types. In particular, the variable potential of releasing DOC by the different types of soils is not only related with the different hydrophobicity of the water-soluble soil fractions (i.e. its variable amphyphilic character) but also to qualitative characteristics of the different humus types in soils. These characteristics are especially relevant at the molecular level where they mediate in the formation of pseudo-soluble organo-mineral adducts and in the intensity of soil matrix interactions. These processes are known to influence humification stages and, in turn, the linkages of soil organic matter with mineral fractions (Aiken et al. 1985). No strong relationship, however, has been found between soil C and N or soil C:N ratio with OCE worldwide (Fig. 5; Table 4 in Electronic supplementary material). This contrasts with the finding that the C:N soil ratio predicts OCE at local scales (Aitkenhead and McDowell 2000; Aitkenhead-Peterson et al. 2007).

It is also likely that different soil types could qualitatively affect OCE because a variety of hydrological mechanisms and the composition of the soil solution could change across soil order (Hope et al. 1994; van de Genachte et al. 1996). For instance, histosols are probably the thickest layered and the C content richest among the soil types and have long water retention times. Podsols are also C-rich but have shorter flowthrough times because they are typically found in comparatively young and shallow soils. These soil types are known for their potential to release pseudo-soluble organo-mineral complexes. Both histosols and podsols showed the highest variability of OCE (Fig. 3b). By contrast, arenosols are poorly developed soils, and they usually show rapid transmittance of water from surface soils to the stream, which could conceivably increase the OCE (FAO 2003).

Catchment size matters for OCE because the variability of export rates in larger catchments is better explained by environmental predictors than in smaller catchments (Table 6 in Electronic supplementary material). Our analysis, however, has not revealed a landscape position effect on OCE because upland rivers have not shown different OCE rates than lowland rivers. What is remarkable is the higher variability of OCE in upland rivers that have usually smaller basins (Fig. 3e). This suggests that catchment size mediates control of OCE and that these effects depend on landscape position. In larger catchments, DOC export is more strongly explained by environmental factors than in small basins (Table 6 in Electronic supplementary material). Smaller catchments are more variable from each other (Smith et al. 2005); this may influence the predictability of nutrient export. Within-environmental variability in small basins is certainly lower than that in large basins, but among-variability environmental features in small basins may be high enough to decrease the goodness of fit in statistical models. Smith et al. (2005) have found that inorganic N and P exports are explained by catchment size rather than environmental characteristics in basins. Within-catchment spatial heterogeneity might pose stronger constraints on OCE in smaller than in larger catchments. This interpretation seems encouraging given that OCE in large basins can be modelled more cost-effectively using available environmental variables.

Another factor that has been considered important for OCE control is the fraction of lakes and wetlands in the basin (Koprivnjak and Moore 1992; Dosskey and Bertsch 1994; Mattson et al. 2005; Williams et al. 2005). However, the abundance of lentic waterbodies in catchments did not influence DOC export either globally or in different climates or biomes (Table 4 in Electronic supplementary material). Complex interactions of processes can regulate the balance between autochthonous DOC production by bacteria and $CO_2$ outgassing in the stagnant ecosystems of the catchment; in addition, allochthonous, lateral inputs of DOC downstream of stagnant ecosystems may increase OCE from a catchment containing lentic areas upstream. All this will partly depend on water retention of each lentic ecosystems involved. If water retention is low, as usually occurs in many cold temperate catchments that comprise the core of our data set, then this might explain why there was no relationship in worldwide and biome models. It is possible that rapid flow from lentic waterbodies removes DOC too quickly to allow for efficient microbial mineralization of organic C to $CO_2$ (Dalzell et al. 2007). This highlights the need for a more careful consideration of retention times of waters in catchments as a potentially important predictor variable in OCE studies. Also hydrological storage and retention zones in streams widely vary (Battin et al. 2008), thus adding further complexity to transportation and transformations of organic C.

## Patterns in fractions of organic carbon export

Dissolved organic C roughly comprises three fourths of TOC but the dissolved fraction was poorly related to POC export (Table 4 in Electronic supplementary material). The DOC fraction of total organic C export was unrelated with river order, climatic region or biome. Also the POC:DOC ratio showed no relationship with environmental variables and river order. This lack of relationships suggests a different nature and origin of exported C fractions. The fact that POC export is less predictable than either DOC or TOC export could be explained with (i) the uncertainties arising from POC calculation (differencing DOC from TOC), which in turn depends on uncertainties in TOC and DOC fluxes, and (ii) the high complexity related to the fate of POC in streams. In contrast to readily metabolized DOC fractions (Williams and Pirbazari 2007), POC compounds can contain recalcitrant C fractions, such as humin (i.e. alkali-insoluble organic matter, frequently consisting of stable organic-mineral aggregates), which might also include soil-sequestered black C (Masiello and Druffel 2001). Transformations of POC in streams may depend on still poorly known processes, mediated by different sources, transformations and transport mechanisms of C (Raymond and Bauer 2001; Mayorga et al. 2005). More research is needed to understand the POC export mechanistically.

Dissolved and particulate organic C transformations vary between catchments (Raymond and Bauer 2001), and this is another reason why global OCE can be related weakly to environmental variables. Changing in situ transformations may also diminish the strength of environment-OCE relationships. In-stream processes support the view of ‘compounded pipe and reactor nature of rivers’ (Del Giorgio and Pace 2008). This view is based on the notion that river heterogeneity enables simultaneous transformation of organic C by bacteria and undisturbed transport, thus affecting the fractions of organic C compounds that are in situ metabolized or exported downstream.

## Environmental controls of organic carbon export and concentration

Variables controlling TOC and DOC export differ. Statistical relationships only share the relative extent of croplands and heathlands in catchments, and population density as predictor variables (Table 4 in Electronic supplementary material). Total organic C export is largely unexplained by environmental variables compared with DOC export. Upland POC yield in small mountainous rivers has locally been reported to be high and likely controlled by erosion rate (Carey et al. 2005; Coynell et al. 2005; Lyons et al. 2002), but a lack of data on erosion for many catchments limits our ability to generate global erosion rates. Because sediment yield is well explained by runoff and basin area (Milliman and Syvitski 1992), these variables might be useful for predicting POC export at local or regional scales; the authors have also shown that POC export is poorly explained by environmental variables worldwide (Table 4 in Electronic supplementary material). Furthermore, fossil POC (i.e. ancient POC trapped in the sedimentary rock matrix) is a fraction that could be mobilized and hence responsible for an important fraction of POC yield downstream, at least in sedimentary catchments (Blair et al. 2003; Hilton et al. 2008). The biogeochemical role of fossil POC is so far not well known, but further research seems warranted to gain a better understanding of riverine C metabolism and transport.

TOC export is influenced by rainfall, runoff, population number and land use (urban areas, croplands, pastures, peatlands and heathlands). It is likely that differences in variables controlling TOC and DOC export might be related to the still poorly known role of stream POC and its transformations. Afforestation has been suggested to increase DOC export (Tate and Meyer 1983; Neal and Hill 1994), but this is at variance with the view of Schlesinger and Melack (1981) who reported higher OCE from forested catchments compared with catchments with other land, and with the results of this study (Fig. 3c). Furthermore, the share of croplands in catchment landscapes only explains OCE in crop-dominated catchments (Table 10 in Electronic supplementary material).

Although the authors used the same environmental variables of OCE as in local-scale studies such as watershed size, slope and precipitation (Clair et al. 1994; Hope et al. 1997; Correll et al. 2001; Stutter et al. 2006), the explained variability in most of our worldwide models was not high (Tables 7, 10 in Electronic supplementary material). Similar findings were reported by Alvarez-Cobelas et al. (2008, 2009) for global N and P exports. Models built on the scale of climatic areas and biomes weakly predict OCE, except in warm temperate and arid climates and in agricultural areas (Table 7 in Electronic supplementary material). The reason for this poor explanative power of most empirical models of OCE is that broadened spatial scales inevitably increase environmental variability. This increases noise in the data set which leads to less robust models of OCE. Therefore, case-by-case (i.e. local) approaches (Kalff 1991) may be more useful for determining OCE controls. Also the consideration of other important variables, which are rarely measured for explaining nutrient export (e.g. groundwater inputs, rates of erosion, etc.), could increase the predictability of OCE, particularly in upland catchments (Stutter et al. 2006). Other frequently suggested variables to explain OCE, such as wetland percentage area in catchments, did not explain OCE significantly in our models (Tables 7, 10 in Electronic supplementary material).

Relationships of OCE with discharge or runoff were not very strong in this study (Table 4 in Electronic supplementary material); this contrasts with observations made in other studies (Brinson 1976; Saunders and Lewis 1988; McDowell and Asbury 1994; Newbold et al. 1995; Mulholland 2003; Royer and David 2005), where strong relationships at local scales were reported. Most of these studies, however, have been carried out in areas where (1) discharge and runoff are relatively strongly linked to rainfall, (2) the baseflow is important for hydrographs, and (3) soil organic leachates are easily exported because of heavy and evenly year-round distributed rainfall. This provides further evidence that local and regional studies can reveal patterns that are not readily detected at either the global or the biome scale. C metabolism in rivers ($CO_2$ outgassing and sedimentary immobilization of settling material) accounts for a good fraction of OCE (Cole et al. 2007). Both approaches (i.e. organic C export downstream and in situ metabolism) should be considered jointly to improve OCE models. Therefore, controls of OCE are inherently multivariate, but controlling factors and their weight change among climatic regions and biomes (Table 7 in Electronic supplementary material, and Mulholland 2003). Our analysis of OCE worldwide and at the scale of biomes and climatic areas suggests that discharge is perhaps the single most important environmental variable controlling OCE at broader spatial scales.

Hydrological effects (e.g. shifting patterns of rainfall or changes in evapotranspiration with land use) are likely to influence OCE to a greater extent than biological processes, such as for example those impinging on soil C and N contents. Despite local studies showing that soil C and N contents explain a good fraction of OCE variability (Aitkenhead and McDowell 2000; Aitkenhead-Peterson et al. 2007), the global analysis by the authors does not support this contention (Fig. 5).

## Stoichiometry of nutrient export from catchments

Organic C export is weakly related to total N and P export (Table 12 in Electronic supplementary material). Dissolved organic C export also shows a weak relationship with the export rates of dissolved organic N and nitrate. The relationship between DOC and nitrate concentrations was weakly positive (Table 12 in Electronic supplementary material). Goodale et al. (2005) and Konohira and Yoshioka (2005) have reported stronger but inverse relationships between the concentrations of these fractions in forested catchments. This worldwide relationship may arise from the interplay of many processes whose weight might change either locally or regionally. For example, low denitrification rates may result from low DOC availability, thus maintaining high nitrate contents as has been shown in USA rivers (Mulholland et al. 2009). However, it is unclear if this relationship holds true in other geographic areas where DOC concentration is not limiting $N_2$ volatilization.

Ratios of organic C to other elements show that the former is clearly in excess in most catchment outlets (Fig. 6). If inorganic C data were available, which is not often the case, then total C:N and C:P ratios would even be higher downstream, thus resulting in shortage of N and P relative to C for primary producers. These ratios have been either unrelated to most environmental predictors (Table 12 in Electronic supplementary material) or the variability explained by these variables was low (e.g. relationship between OC:N and forest cover). These results contrast with the findings of McGroddy et al. (2008), showing that climatic and geological factors explain exports of C, N and P in first-order, forested streams of New Zealand. This again points to the fact that spatial scale mediates the biogeochemical fate of elemental ratios.

The distribution of estimated total N:P ratios at the outlet of catchments (Fig. 6) was left-skewed. This suggests that most catchments (ca. 80%) export excess N compared to P, with the ratio being on average twofold higher than that shown in earlier reports (Downing and MacCauley 1992). Thus, on a global scale the export of riverine nutrients is likely to imbalance P requirements for plant growth, thereby limiting primary production in coastal areas (Justic et al. 1995). This also supports the notion that the N-limitation of coastal ecosystems must be viewed with caution (Elser et al. 2007). Furthermore, our data suggest that catchments receiving point and/or diffuse C sources contribute to an increased imbalance of nutrient ratios. While this implies that degraded catchments export proportionally more N than P, this proportionality must be evaluated considering different biogeochemical transformation processes of both nutrients (e.g. P immobilization in sediments).

Percentages of crops, forests, urban areas and lentic areas in catchments also explained a low amount of variability ($R^2 < 20\%$) in N:P stoichiometry (Table 12 in Electronic supplementary material), which precludes their use as good predictors of that ratio. In this study, this can be attributed again to the high variability of our broad-scale data set. Gergel (2005) highlights the importance to consider nutrient sources and sinks associated with the degree of spatial heterogeneity, and land use fractions to accurately predict nutrient export in heterogeneous catchments with different land use practices. Furthermore, the strong buffer capacity of soils (Turner and Rabalais 2003), the size and nature of soil pores and bedrock fractures of catchments (Mulholland and Hill 1997) and differing erosion patterns in catchments (Donnelly et al. 1998) influence element delivery to streams through different pathways and time lags, but these features are hardly considered in P export and P in-stream dynamics. More specifically, the role and behaviour of particle-bound P is still not well known in terrestrial systems (Frossard et al. 1995). The linkage between C, N and P export from catchments thus appears to be weaker than previously believed (Mackenzie and Lerman 2006). Also, catchment stoichiometry is more variable than previously expected and hence clearly deserves more scientific consideration.

## Ways forward

Our study suggests that local and narrow regional approaches can be better suitable for predicting OCE with environmental controlling variables in empirical models instead of using either worldwide, climate or biome approaches. Although these models might be improved by adding further environmental variables (e.g. groundwater discharge, rates of erosion, water retention and better characterization of catchment chemistry of soils), it is likely that the variability explained would not greatly increase, and their addition will certainly be more expensive. Our study has also demonstrated the importance of hydrology on OCE. More detailed spatio-temporal data on hydrology, with greater spatial resolution and runoff patterns (responses to storms and droughts), which can easily be measured automatically, could improve OCE models.

Further improvements will also be obtained by including data on in situ organic C transformations and retention (e.g. $CO_2$ and $CH_4$ degassing and organic C burial in stream sediments). Studies dealing with these processes along with OCE are mostly lacking, and they must be encouraged in order to improve our knowledge about OCE.

Another frequent drawback in OCE studies is their low temporal resolution, which adds uncertainty to estimations of annual fluxes, not only for organic C but also for N and P export (Harris and Heathwaite 2005; Johnes 2007), particularly when floods and droughts affect streamflow (Eimers et al. 2008; Worrall and Burt 2008). Clearly, sampling with more detailed temporal resolution is needed, particularly during thaw and storm flows.

Among the uncertainties, the POC fraction of C export is far from being well known and more efforts to measure POC with methods other than differencing TOC and DOC will be rewarding to improve knowledge of OCE. Furthermore, catchments and landscapes where OCE studies are undertaken are usually poorly described; more detailed data on soil types, their C, N and P concentrations in the soil profile, and land use might enable improvements in the knowledge of the environment–OCE relationship.

Furthermore, other types of OCE models (heuristic or predictive) should incorporate in situ processes in a quasi-empirical, mechanistic way. Such models have been used for studying nutrient export (Billén et al. 2001) and N export (Caraco and Cole 1999). It is likely that such models perform better, also having the advantage of being more realistic.

Finally, more data are needed concerning the stoichiometry of nutrient export. Therefore, it is necessary to measure C (including inorganic C), and dissolved and particulate forms of N and P simultaneously in more catchments across the world. Particularly, no data on total elemental ratios are available for polar and subpolar basins.

This article shows the current state of research of organic C export on a worldwide basis. The synthesis shown in this article reveals many gaps in our knowledge, which currently limit a thorough understanding of the biogeochemical fate and role of OCE. Further studies addressing these research gaps hold potential to gain better insight into the functioning of global biogeochemical cycles and how they may be altered by global environmental change.

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