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Global patterns and sources of dissolved organic matter export to the coastal zone: Results from a spatially explicit, global model

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[1] Here we describe, test, and apply a system of spatially explicit, global models for predicting river export of three dissolved organic matter (DOM) components: dissolved organic carbon (DOC), dissolved organic nitrogen (DON), and dissolved organic phosphorus (DOP). The DON and DOP models represent the first attempt to model DON and DOP export in a spatially explicit, global manner. DOC, DON, and DOP models explain 88%, 77%, and 91% of the variability in DOC, DON, and DOP yield (kg C, N, or P $\mathrm{km}^{-2}\ \mathrm{yr}^{-1}$) from validation basins, respectively, and all models are relatively bias free. When applied globally, these models predict that 170 Tg C yr^{-1}, 10 Tg N yr^{-1}, and 0.6 Tg P yr^{-1} are exported by rivers to the coastal zone as DOC, DON, and DOP, respectively. Because predicted spatial patterns of export for DOC, DON, and DOP are all largely driven by water runoff, geographic distributions of high and low fluxes are fairly consistent across elements, with high fluxes of DOC, DON, and DOP generally predicted for high runoff systems and low fluxes predicted for arid systems. However, there are important regional differences in predicted rates of DOC, DON, and DOP export due to anthropogenic inputs of DON and DOP and wetland influence on DOC.

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1. Introduction

[2] Dissolved organic matter (DOM) is a major component of the organic matter transported to the coastal zone by rivers [*Meybeck*, 1982; *Ludwig et al.*, 1996]. It influences aquatic food webs, controls the availability of dissolved nutrients and metals, and affects the optical properties of aquatic systems [*Findlay and Sinsabaugh*, 2003]. In addition to controlling ecosystem-level processes, DOM is also important from regional and global biogeochemical perspectives, as DOM constitutes an important pathway for carbon (C), nitrogen (N), and phosphorus (P) transport from land to sea. In systems for which data on both inorganic and organic dissolved species are available, dissolved organic N (DON) and dissolved organic P (DOP) are frequently more abundant than dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP) [*Eyre and Pont*, 2003; *Alexander et al.*, 1996]. Furthermore, input ratios of DIN:DON and DIP:DOP may have important impacts on coastal ecosystem response to nutrient loading. A significant portion of the DON exported to estuaries is thought to be bioavailable [*Seitzinger and Sanders*, 1997], and the growth of bacteria and some harmful algal species is thought to be stimulated to differing degrees by DIN and DON [*Berg et al.*, 1997; *Glibert et al.*, 2001; *Anderson et al.*, 2002]. The source and composition of DON can also influence microbial response [*Seitzinger et al.*, 2002]. Much less is known about the impacts of DOP loading, though some work indicates that DOP can be bioavailable in coastal and marine systems [*Stepanauskas et al.*, 2002; *Bjorkman and Karl*, 2003], and that it can control phytoplankton and bacterial growth and dynamics in coastal systems [*Benitez-Nelson and Buesseler*, 1999; *Poder et al.*, 2003].

[3] Several attempts have been made to estimate global patterns and magnitudes of DOC export [e.g., *Meybeck*, 1982; *Ludwig et al.*, 1996], and at least one study has estimated global river DON and DOP export [*Meybeck*, 1982]. However, no previous study has estimated global patterns or magnitudes of DON or DOP in a spatially

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explicit manner. Nor has any previous study developed internally consistent DOC, DON, and DOP export models.

[4] Here we describe, test, and apply spatially explicit, global models for the prediction of DOC, DON, and DOP export. These models were developed as part of an international, interdisciplinary effort to model river export of multiple bioactive elements (C, N, and P) and elemental forms (dissolved/particulate, inorganic/organic) called Global Nutrient Export from Watersheds (Global NEWS). Because of this, we hereinafter refer to the DOC, DON, and DOP models as NEWS-DOC, NEWS-DON, and NEWS-DOP, respectively. Collectively, we refer to this suite of models as NEWS-DOM.

[5] NEWS-DOM models include several innovations and advantages over previous global DOM export models. For NEWS-DOC, these include increased spatial resolution ($0.5^\circ \times 0.5^\circ$) of global input data sets and watershed delineations, inclusion of a consumptive water use term, use of a larger calibration database with better spatial distribution than past models, model validation with data not used in model formulation, inclusion of a wetland component, and inclusion of a non-linear response of DOC export to runoff. NEWS-DON and NEWS-DOP are also based on $0.5^\circ \times 0.5^\circ$ global input data sets, include anthropogenic inputs, and non-linear responses to runoff, and were validated using data that wasn't used for model formulation or calibration. The NEWS-DOC, NEWS-DON, and NEWS-DOP models were designed to be internally consistent and compatible with other NEWS models [e.g., *Harrison et al.*, 2005; *Dumont et al.*, 2005]. Additionally, each of these models can be used to examine the relative importance of different land-use types and inputs in terms of their contributions to DOC, DON, or DOP export.

2. Methods

2.1. Model Descriptions

2.1.1. NEWS-DOC Model

[6] Building on past work by *Ludwig et al.* [1996] and by *Schlesinger and Melack* [1981], among others, we developed a new model to predict DOC yield (kg C km^{-2} yr^{-1}) called NEWS-DOC. NEWS-DOC predicts DOC yield (*DOC*) as a function of runoff, wetland area, and consumptive water use. The model's central equation is as follows:

$$DOC = \frac{(C_{wet} \times W) + \left(C_{dry} \times (1 - W)\right) \times R^a \times Q_{act}}{Q_{nat}}, \qquad (1)$$

where C_{wet} and C_{dry} represent the export coefficients (kg C km^{-2} yr^{-1} m runoff^{-1}) for wetlands and non-wetlands, respectively, W is the fraction of a basin that is wetland by area, R is average annual runoff (m), a is a unitless coefficient describing the shape of the relationship between runoff and DOC yield, and Q_{act}/Q_{nat} is the ratio of present-day annual average discharge (Q_{act}) to pre-dam annual average discharge (Q_{nat}). NEWS-DOM models included the Q_{act}/Q_{nat} correction factor because R is derived from models that don't account for consumptive water use (described in section 2.2.2). Coefficients a, C_{wet}, and C_{dry} were calibrated as described in section 2.2.3, and were set to equal 0.95, 12475, and 3883, respectively. For this and all subsequent NEWS-DOM models, area-weighted basin average values were used for model inputs.

[7] The model formulation represented by equation (1) is consistent with published regional analyses showing strong relationships between runoff and DOC export [*Ludwig et al.*, 1996] and between basin percent wetland area and DOC export [*Dillon and Molot*, 1997; *Gorham et al.*, 1998; *Mulholland*, 2003; *Raymond and Hopkinson*, 2003]. On the basis of preliminary analysis of our data and literature [e.g., *Schlesinger and Melack*, 1981], agricultural and natural landscapes appeared to have similar DOC export coefficients (kg C km^{-2} yr^{-1} m runoff^{-1}), so they were lumped together in NEWS-DOC. Sewage is a source of DOC to surface waters, but inclusion of sewage in preliminary versions of NEWS-DOC did not improve model fit to data, and so was not included in the final model formulation of NEWS-DOC.

[8] The magnitudes of wetland and non-wetland DOC were calculated as follows:

$$DOC_{\mathrm{wetland}} = \frac{(C_{wet} \times W) \times R^a \times Q_{act}}{Q_{nat}} \qquad (2)$$

$$DOC_{\mathrm{non\text{-}wetland}} = \frac{\left(C_{dry} \times (1 - W)\right) \times R^a \times Q_{act}}{Q_{nat}}, \qquad (3)$$

where DOC_{wetland} is DOC yield from wetland areas, $DOC_{\mathrm{non\text{-}wetland}}$ is DOC yield from non-wetland areas, and other symbols and coefficient values are the same as in equation (1) and the notation section.

2.1.2. NEWS-DON Model

[9] Using a combination of observed relationships between N application and DON export, and a multiple regression approach, we developed a model to predict DON yield (kg N km^{-2} yr^{-1}). This model (NEWS-DON) predicts DON yield (*DON*) as a function of sewage inputs, runoff, inorganic fertilizer N inputs, manure N inputs, and consumptive water use. NEWS-DON's central equation is as follows:

$$DON = \frac{\left(N_{sew} \times b + \left(d \times \left(N_{fe} + N_{am}\right) + N_{nat}\right)\right) \times R^c \times Q_{act}}{Q_{nat}}, \qquad (4)$$

where N_{sew} is sewage-derived (point source) N (kg N km^{-2} yr^{-1}) entering surface waters, b is a coefficient describing the fraction (0–1) of point source total N (TN) reaching the river mouth as DON, d (m runoff^{-1}) is a coefficient defining the fraction (0–1) of N applied as manure or inorganic fertilizer that is leached to surface waters, N_{fe} and N_{am} are the rates of inorganic N fertilizer application and N input from animal manure, respectively (both in kg N km^{-2} yr^{-1}), N_{nat} is the DON export coefficient for land prior to N fertilizer and manure inputs (kg N km^{-2} yr^{-1} m runoff^{-1}), R is annual runoff (m), c is a unitless coefficient defining the shape of the relationship between runoff and DON yield, Q_{act} is present-day discharge, and Q_{nat} is pre-dam discharge. Coefficients b, c, d, and N_{nat} were calibrated as described in section 2.2.3, and were set to equal 0.17, 1.05, 0.01, and 301, respectively.

[10] Though few studies have quantified the link between N fertilizer and manure application and DON leaching to surface waters, the model formulation represented by equation (4) is consistent with existing data, which show elevated DON losses from inorganic N-fertilized and manure-fertilized soils [*Neff et al.*, 2003; *Siemens and Kaupenjohann*, 2002; *McDowell et al.*, 2004] and with observational evidence that DON is approximately 3–30% of sewage point sources [*Seitzinger*, 1995]. There is some evidence that wetlands can exert a control on DON levels in streams at a local scale [*Pellerin et al.*, 2004]. However, inclusion of a wetland term in preliminary versions of NEWS-DON did not improve model fit, and a wetland effect is not likely to have been masked by covariance between anthropogenic activity and wetland area because correlation analysis shows no relationship between wetland area and anthropogenic activity (e.g., population density, agriculture, or pasture) in basins with DON data. For these reasons wetlands were assumed to have the same DON export coefficient (kg km^{-2} land-use yr^{-1} m runoff^{-1}) as non-wetland areas in NEWS-DON.

[11] The magnitudes of individual source contributions to DON export were calculated as follows:

$$DON_{\text{non-anthropogenic}} = \frac{\left(1 - Fr_{ag}\right) \times N_{nat} \times R^{c} \times Q_{act}}{Q_{nat}}, \qquad (5)$$

$$DON_{\text{point source}} = \frac{N_{sew} \times b \times Q_{act}}{Q_{nat}}, \qquad (6)$$

$$DON_{\text{diffuse anthropogenic}} = \frac{\left(Fr_{ag} \times N_{nat} + d \times \left(N_{fe} + N_{am}\right)\right) \times R^{c} \times Q_{act}}{Q_{nat}}, \qquad (7)$$

where Fr_{ag} is the fraction of a watershed that is agriculture as defined by *Bouwman et al.* [2005a, 2005b], $DON_{\text{non-anthropogenic}}$ is the DON yield attributable to non-human sources, $DON_{\text{point source}}$ is the DON yield attributable to anthropogenic point sources, and $DON_{\text{diffuse anthropogenic}}$ is the DON yield attributable to anthropogenic non-point sources. Otherwise, symbols and coefficient values are the same as in equation (4) and the notation section. Diffuse anthropogenic *DON* was defined as total DON originating in agricultural fields, not just excess DON due to fertilizer and manure inputs.

2.1.3. NEWS-DOP Model

[12] Using an approach similar to that used for the NEWS-DOC and NEWS-DON models, we developed a model to predict DOP yield (kg P km^{-2} yr^{-1}). This model (NEWS-DOP) predicts DOP yield (*DOP*) as a function of sewage inputs, runoff, inorganic fertilizer P inputs, manure P inputs, and consumptive water use. NEWS-DOP's central equation is identical to that of NEWS-DON and is as follows:

$$DOP = \frac{\big(\big(P_{sew} \times e\big) + \big(g \times \big(P_{fe} + P_{am}\big) + P_{nat}\big)\big) \times R^{f}\big) \times Q_{act}}{Q_{nat}}, \qquad (8)$$

where P_{sew} is sewage-derived (point source) total P (TP) (kg P km^{-2} yr^{-1}), e is a coefficient describing the fraction (0–1) of point source P exported as DOP, g is a coefficient defining the fraction (0–1) of diffusely applied (manure plus inorganic P fertilizer) P leached to surface waters (m runoff^{-1}), P_{fe} and P_{am} are the rates of inorganic P fertilizer application and P input from animal manure, respectively (both kg P km^{-2} yr^{-1}), P_{nat} is the export coefficient for *DOP* from land prior to fertilizer or manure inputs (kg P km^{-2} yr^{-1} m runoff^{-1}), respectively, R is annual runoff (m), f is a coefficient defining the shape of the relationship between runoff and DOP yield (unit-less), Q_{act} is present-day discharge, and Q_{nat} is pre-dam discharge. Coefficients e, f, g, and P_{nat} were calibrated as described in section 2.2.3, and were set to equal 0.02, 1.1, 0.02, and 16, respectively.

[13] The model formulation represented by equation (8) is consistent with field and laboratory studies, which show elevated DOP concentrations in inorganic P-fertilized and manure-fertilized soils [e.g., *Chardon et al.*, 1997; *Neff et al.*, 2003]. It is also consistent with mass balance calculations and data suggesting that sewage point sources can constitute a significant source of DOP to rivers [*Seitzinger*, 1995; *Chiswell et al.*, 1997]. As with NEWS-DON, explicit inclusion of wetlands in NEWS-DOP did not improve the fit between NEWS-DOP predictions and DOP measurement data. Also, as with DON, there was no correlation between percent wetland area and anthropogenic activities. Therefore, in NEWS-DOP, we treat DOP export from non-wetlands and wetlands as equivalent.

[14] The magnitudes of individual source contributions to DOP export were calculated as follows:

$$DOP_{\text{non-anthropogenic}} = \frac{\left(1 - Fr_{ag}\right) \times P_{nat} \times R^{f} \times Q_{act}}{Q_{nat}}, \qquad (9)$$

$$DOP_{\text{point source}} = \frac{P_{sew} \times e \times Q_{act}}{Q_{nat}}, \qquad (10)$$

$$DOP_{\text{diffuse anthropogenic}} = \frac{Fr_{ag} \times N_{nat} + g \times \left(P_{fe} + P_{am}\right) \times R^{f} \times Q_{act}}{Q_{nat}}, \qquad (11)$$

where $DOP_{\text{non-anthropogenic}}$ is the DOP yield attributable to non-human sources, $DOP_{\text{point source}}$ is the DOP yield attributable to anthropogenic point sources, and $DOP_{\text{diffuse anthropogenic}}$ is the DOP yield attributable to anthropogenic non-point sources. Otherwise, symbols and coefficient values are the same as in equations (5) and (8) and the notation section. As with DON, diffuse anthropogenic *DOP* was defined as total DOP originating in agricultural fields, not just excess DOP due to fertilizer and manure inputs.

2.2. Model Calibration, Validation, and Input Data

2.2.1. River Data

[15] To calibrate NEWS-DOM models, we collected DOM concentration and water discharge data from the most downstream monitoring stations of rivers worldwide (Appendices A, B, and C). We used data only from watersheds where both constituent concentration and discharge had been directly measured and limited our data set to basins that contained more than ten 0.5° × 0.5° grid cells

for reasons discussed by *Harrison et al.* [2005]. We were able to obtain runoff and DOC, DON, and DOP concentration data for 68 basins, 50 basins, and 40 basins, respectively (Appendices A, B, and C). When possible, we used flow-weighted mean DOC, DON, or DOP concentrations in our analysis (27, 28, and 30 cases, respectively). When this was not possible, we used median concentrations of DOC, DON, or DOP (41, 22, and 10 cases, respectively). DOC, DON, and DOP loads were calculated by multiplying flow-weighted mean or median concentration values by average discharge values for the same period. Yields were calculated by dividing loads by basin area. For some rivers (e.g., the Potomac and Susquehana), we were able to obtain more than 30 DOC, DON, and DOP concentration measurements per year, but in most cases data coverage was considerably sparser. In many cases there were only 3–4 measurements per year. DOC, DON, and DOP data sets were divided in half, and basins were assigned randomly to either a model calibration data set or a model validation data set (Figures 1, 2, and 3 in section 3, Table 1, and Appendices A, B, and C). Calibration data sets were used to calibrate NEWS-DOM model coefficients (section 2.3.1), whereas the validation data sets were reserved for model evaluation. The rivers in our DOC, DON, and DOP data sets make up 49, 36, and 29% of the global total discharge (37,400 km^3 yr^{-1} [*Meybeck*, 1982]), respectively. In all cases both calibration and validation data sets contain basins from temperate, tropical and boreal regions, as well as basins with diverse climates, and a range of dominant land-uses and land covers (Appendices A, B, and C).

2.2.2. Hydrological Input Data

[16] An updated version of the STN30-p global river network (STN30-p version 6.0 [*Vörösmarty et al.*, 2000a, 2000b]) was used to define basin boundaries for model runs at 0.5° × 0.5° resolution. We used modeled annual average runoff estimates from the water balance model (WBM) as described by *Vörösmarty et al.* [2000a, 2000b] to supply runoff values for model runs.

[17] To estimate the impact of consumptive water (and thus DOM) use on DOM export, we multiplied predicted DOC, DON, and DOP yields by the ratio of measured post-dam water discharge to measured pre-dam water discharge (Q_{act}/Q_{nat}). Values for Q_{act}/Q_{nat} were taken from *Meybeck and Ragu* [1996], and when unavailable were assumed to equal 1.

2.2.3. Anthropogenic DOM Sources and Land Cover Data

[18] We calculated net total N (TN) point source inputs to surface water as per *Bouwman et al.* [2005b] and net total P (TP) point source inputs to surface water as per *Harrison et al.* [2005] (Table 2). Per capita human N and P inputs to sewage systems were estimated as a function of per capita gross domestic product as described by *Van Drecht et al.* [2003] for N and by *Harrison et al.* [2005] for P. However, these estimates do not account for N and P removal via sewage treatment. In order to account for differential sewage treatment capacities globally we used a combination of sewage treatment data and regional estimates of sewage treatment [*World Health Organization/UNICEF*, 2001], as described in detail by *Bouwman et al.* [2005b]. Estimates of sewage point sources were then incorporated into equations (4), (6), (8), and (10).

[19] In NEWS-DON and NEWS-DOP, N and P inputs from inorganic N and P fertilizer (N_{fe} and P_{fe}, respectively) and animal manure (N_{am} and P_{am}, respectively) were calculated as per *Bouwman et al.* [2005a]. For fertilizer inputs, national N and P-use data were used and distributed across agricultural areas, maintaining different application rates for different crop types as per *Bouwman et al.* [2005a]. To calculate manure inputs (N_{am} and P_{am}), we used published N excretion rates along with N:P ratios of manure for various livestock species, including pigs, cows, chickens, sheep, goats, and horses [*Bouwman et al.*, 2005a] and multiplied excretion rates by number of animals per basin.

[20] Land use data were gathered from several sources. Wetland data came from a 1-minute resolution data set developed by *Lehner and Döll* [2004]. Data on basin percent agriculture, basin percent pasture, and population density for the year 1995 had 0.5° × 0.5° resolution, and came from the HYDE database [*Klein Goldewijk and Batjes*, 1997; *Klein Goldewijk*, 2001]. For continental analyses, continents were defined geographically as in the work of *Harrison et al.* [2005]. All input data sets were for 1995 conditions.

2.3. Model Development

2.3.1. Model Calibration

[21] Calibration of NEWS-DOM models was achieved by optimizing each model to attain the highest model efficiency (R^2) while maintaining coefficients within the range of literature values. Model efficiency (capital R^2, not the coefficient of determination (r^2)) is a metric ranging from 0 to 1 reflecting the degree of fit between measured and modeled values (described by *Nash and Sutcliffe* [1970]). When $R^2 = 1$, all points fall on the 1:1 line. When R^2 is 0, model error is equal to the variability in the data.

[22] For NEWS-DOC, we calibrated coefficients a, C_{wet}, and C_{dry}. Coefficients C_{wet} and C_{dry} were constrained to fall within 10,000–24,000 kg C km^{-2} yr^{-1} and 0–5000 kg C km^{-2} yr^{-1}, respectively, based on literature ranges for wetland and non-wetland DOC export coefficients [*Schlesinger and Melack*, 1981; *Mulholland*, 2003; *Dillon and Molot*, 1997]. We allowed these coefficients to vary with a step size of 1 kg C km^{-2} yr^{-1}. Coefficient a was allowed to vary between 0.05 and 2 with a step size of 0.05.

[23] For NEWS-DON we calibrated coefficients b, c, d, and N_{nat} (equation (4), notation section). To constrain our estimates of point source DON contributions (a function of b), we used data from 21 sewage outflows (both treated and untreated) in the eastern United States indicating that 3–30% of the TN in sewage is discharged as DON [*Seitzinger*, 1995]. We allowed coefficient b, describing the fraction of sewage exported as DON to vary between 0.03 and 0.40 with a step size of 0.01. We allowed coefficient d, describing the fraction of diffuse anthropogenic N inputs (inorganic fertilizer N plus manure N) exported as DON to vary between 0.01 and 0.1 with a step size of 0.01. This is consistent with a plot-level study that found 3–4% of N applied as inorganic fertilizer or manure was recovered as

DON in lysimiters [*Siemens and Kaupenjohann*, 2002]. Coefficient N_{nat}, describing the rate of DON export from unimpacted systems, was allowed to vary between 100 and 1000 kg N km^{-2} yr^{-1} (range based on a potential in-stream molar C:N range of 3.3–33), with a step size of 1 kg N km^{-2} yr^{-1}. Coefficient *c*, determining the shape of the relationship between runoff and DON export, was allowed to vary between 0.05 and 2 with a step size of 0.05.

[24] For NEWS-DOP we calibrated coefficients *e*, *f*, g, and P_{nat} (equation (8), notation section). To constrain our estimates of point source DOP contributions (a function of *e*), we used data from watersheds in the eastern United States showing that 0.7–28% of sewage is discharged as non-bioavailable DOP in those systems [*Seitzinger*, 1995]. We allowed coefficient *e* to vary between 0.01 and 0.40 with a step size of 0.01. We allowed coefficient *g*, representing the fraction of inorganic P fertilizer exported to the coastal zone, to vary between 0.01 and 0.1 with a step size of 0.01. This is consistent with the one plot-level study of DOP we were able to locate, where 1% of the P applied as manure was recovered in lysimiters as DOP [*Chardon et al.*, 1997]. Coefficient P_{nat}, describing the rate of DOP export from unimpacted systems, was allowed to vary between 1 and 40 kg P km^{-2} yr^{-1} (range based on a potential in-stream molar C:P range of 38–1503), with a step size of 1 kg km^{-2} yr^{-1}. Coefficient *f*, determining the shape of the relationship between runoff and DOP export, was allowed to vary between 0.05 and 2 with a step size of 0.05. A script created in MATLAB 6.1.0.450 was used to carry out all calibration procedures.

2.3.2. Model Uncertainty and Sensitivity Analyses

[25] We evaluated model precision and bias for all three NEWS-DOM models according to *Alexander et al.* [2002]. Prediction error (*K*) is expressed as by *Alexander et al.* [2002] as

$$K = \left[\frac{L - M}{M} \times 100\right], \tag{12}$$

where *L* is the model prediction, and *M* is the measured stream DOC, DON, or DOP export.

[26] Change in model efficiency (R^2) [*Nash and Sutcliffe*, 1970] (section 2.3.1) was determined upon removal of model components (e.g., runoff, consumptive water use, point and diffuse N and P sources for NEWS-DON and NEWS-DOP, and wetlands for NEWS-DOC). This change in model efficiency was then used to evaluate the relative importance of different model components in explaining DOM export. We also subjected the NEWS-DOM models to a sensitivity analysis in which we varied each model input and coefficient and each combination of inputs and coefficients (+5%) and quantified model response to these variations.

3. Results and Discussion

3.1. Model Performance

3.1.1. DOC Model

[27] NEWS-DOC explained 88% of the variability in DOC yield (kg C km^{-2} yr^{-1}) and 93% of the variability in DOC load (ton C basin^{-1} yr^{-1}) in validation basins (Figure 1; Table 1). NEWS-DOC's predictive capacity is comparable to that of a DOC export model developed by *Ludwig et al.* [1996] (Table 1). Overall, NEWS-DOC model bias is small, as indicated by the distribution of prediction error and by the median error (+4% and −18% for calibration and validation basins, respectively; Table 1). However, NEWS-DOC may slightly overestimate DOC export from systems with low DOC yields (Figure 1). Though proportional uncertainty (percent uncertainty) is fairly consistent across all basins, absolute uncertainty of NEWS-DOC is greater for high DOC-yield basins than for low DOC-yield basins, as evidenced by the similar scatter in data points relative to the 1:1 line over the entire range despite log-log axes (Figure 1). NEWS-DOC predictions were within a factor of 0.5 of measured yields over half the time (54% of basins), within a factor of 2 of measured yields in 84% of basins, and all but one of the measured DOC yield values were within a factor of 3 of predictions. NEWS-DOC's greatest overestimate (+162%) occurred in the Huang He basin, and the greatest underestimate (−76%) occurred in the North Dvina basin (Figure 1).

3.1.2. DON Model

[28] NEWS-DON explained 77% of the variability in DON yield (kg N km^{-2} yr^{-1}) and 70% of the variability in DON load (ton N basin^{-1} yr^{-1}) in validation basins (Figure 2; Table 1). The predictive capacity of NEWS-DON was quite high (Figure 1, Table 1), though not as high as for NEWS-DOC or NEWS-DOP. Overall model bias was small for NEWS-DON, as indicated by the distribution of prediction error and by the median error (−21% and −24% for calibration and validation basins, respectively; Table 1). NEWS-DON predictions were within a factor of 0.5 of measured yields in 37% of the basins with validation data, within a factor of 2 of measured yields in 67% of basins, and all but three measured DON yield values were within a factor of 3 of predictions. The exceptions were the St. Lawrence, Ganges, and Colville rivers, which NEWS-DON overestimated by 940% and 450%, and underestimated by 75%, respectively (Figure 2).

3.1.3. DOP Model

[29] Of the three NEWS-DOM models, NEWS-DOP demonstrated the best agreement between measurements and model predictions (Figure 3, Table 1). NEWS-DOP explained 91% of the variability in DOP yield (kg P km^{-2} yr^{-1}) and 94% of the variability in DOP load (ton P basin^{-1} yr^{-1}) in validation basins (Figure 3; Table 1). NEWS-DOP demonstrated almost no model bias, as indicated by the distribution of prediction error and by the median error (+2% and +5% for calibration and validation basins, respectively; Table 1). NEWS-DOP predictions are within a factor of 0.5 of measured yields in 54% of the basins with validation data, within a factor of 2 of measured yields in 88% of basins, and all of the predicted export values fall within a factor of 3 of measured values. Though relative (percent) uncertainty is quite constant over the entire range of observed DOP yields, there is an increase in absolute uncertainty with increased yields. NEWS-DOP's greatest overestimate occurred in the Khatanga River Basin (overestimated by 126%), and its

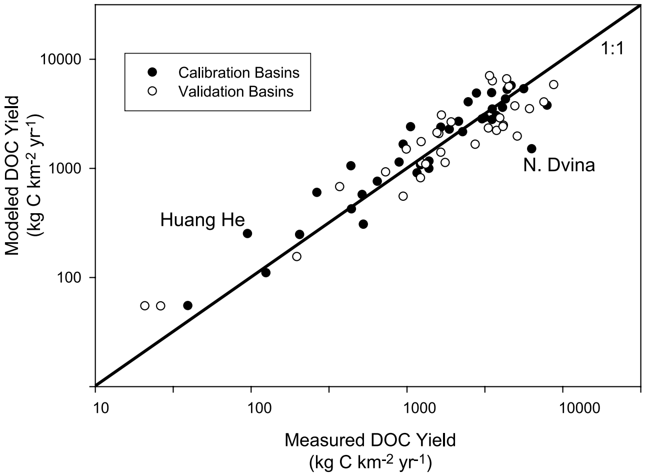

Figure 1. Comparison of measured and model-predicted DOC yield (kg C km^{-2} yr^{-1}). Calibration basins are represented by the solid circles, and validation basins are represented by the open circles. Dark diagonal line represents the 1:1 line. The two basins with the largest percent deviation from the 1:1 line are named.

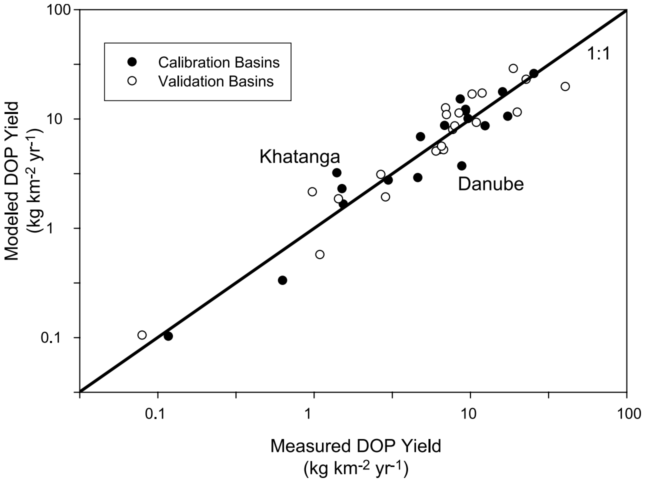

Figure 3. Comparison of measured and model-predicted DOP yield (kg P km^{-2} yr^{-1}). Calibration basins are represented by the solid circles, and validation basins are represented by the open circles. Dark diagonal line represents the 1:1 line. The two basins with the largest percent deviation from the 1:1 line are named.

greatest underestimate occurred in the Danube basin (underestimated by 58%; Figure 3).

3.2. Model Predictions

3.2.1. Global and Regional Rates of DOC, DON, and DOP Export

[30] In order to estimate global total DOC, DON, and DOP export, model-predicted DOC, DON, and DOP for individual basins (as defined by STN30-p described in section 2.2.2) were summed globally. According to NEWS-DOC, rivers export 170 Tg (10^{12}g) C yr^{-1} as DOC. This estimate of global river DOC export is somewhat lower than previous estimates, which range from 198 to 208 Tg C yr^{-1} [*Ludwig et al.*, 1996; *Meybeck*, 1982]. NEWS-DON predicts that globally, rivers export 10 Tg N yr^{-1} as DON. This agrees well with a previous estimate of global DON export by *Meybeck* [1982] of 11 Tg N yr^{-1}. NEWS-DOP predicts that globally, rivers export 0.6 Tg P yr^{-1} as DOP. This is somewhat lower than a previous estimate by *Meybeck* [1982] of 1.0 Tg P yr^{-1}, which was based simply on a constant global DIP:DOP value. Together, NEWS-DOM models imply a global molar DOC:DON:-DOP ratio of exported DOM equal to 732:36:1, though this ratio varies substantially by basin.

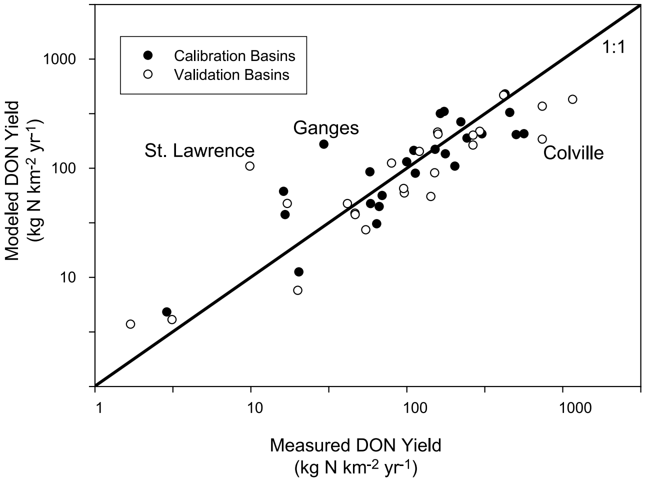

Figure 2. Comparison of measured and model-predicted DON yield (kg N km^{-2} yr^{-1}). Calibration basins are represented by the solid circles, and validation basins are represented by the open circles. Dark diagonal line represents the 1:1 line. The three basins with the largest percent deviation from the 1:1 line are named.

[31] NEWS-DOM models suggest that DON (10 Tg N yr^{-1}) and DOP (0.6 Tg P yr^{-1}) fluxes are somewhat lower than DIN and DIP fluxes at the global scale. Estimates of global river DIN export range from 12 to 25 Tg N yr^{-1} [*Meybeck*, 1982; *Seitzinger and Kroeze*, 1998; *Smith et al.*, 2003; *Green et al.*, 2004; *Dumont et al.*, 2005]. Estimates of global river DIP export range from 0.8 to 2.4 Tg yr^{-1} [*Pierrou*, 1976; *Meybeck*, 1982; *Richey*, 1983; *Wollast*, 1983; *Smith et al.*, 2003; *Harrison et al.*, 2005]. Using model predictions from other NEWS models (NEWS-DIN [*Dumont et al.*, 2005], and NEWS-DIP [*Harrison et al.*, 2005]) together with NEWS-DOP and NEWS-DON, modeled global DIP:DOP is 1.6, and modeled global DIN:DON is 2.5. However, the predicted pattern of export for DON and DOP differs substantially from the pattern predicted for DIN and DIP [*Dumont et al.*, 2005; *Harrison et al.*, 2005; S. P. Seitzinger et al., Sources and delivery of carbon, nitrogen, and phosphorus to the coastal zone, an overview of Global NEWS models, manuscript in preparation, 2005], so these predicted ratios vary substantially by basin.

[32] At the continental scale, NEWS-DOM models predict fairly consistent patterns for DOC, DON, and DOP export. In all cases, South America is predicted to be the

Table 1. Metrics of Model Performance for NEWS-DOC, NEWS-DON, and NEWS-DOP Models Validated With Data From a Global Data Set[a]

		DOM Yield				Prediction Errors, %				
Model	n	r^2	R^2	DOM Load r^2	IQR[b]	Minimum	25th	Median	75th	Maximum
NEWS-DOC-Calibration	36	0.87	0.87	0.93	52	−76	−13	4	38	162
NEWS-DOC-Validation	32	0.88	0.86	0.93	55	−62	−13	−18	42	160
NEWS-DON-Calibration	25	0.72	0.72	0.89	90	−64	−33	−21	57	454
NEWS-DON-Validation	24	0.77	0.76	0.70	71	−75	−43	−24	27	940
NEWS-DOP-Calibration	21	0.90	0.90	0.94	60	−59	−31	2	29	126
NEWS-DOP-Validation	22	0.91	0.89	0.94	58	−52	−18	5	40	117
Ludwig et al. [1996]-Calibration only (DOC model)	29	0.81	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
NEWS-DIP-Calibration[c]	56	0.72	0.68	0.74	178	−86	−31	98	148	1494
N-Model-Calibration (DIN)[d]	32	. . .	. . .	0.84	108	−77	−26	18	82	1205

[a] R^2, model efficiency as defined in section 2.3.1; r^2, the coefficient of determination. Measured runoff from basins containing more than ten 0.5° × 0.5° cells were used for all validation calculations. Global DIN model (N-Model) and global DIP model (NEWS-DIP) error statistics for calibration basins are also included for comparison with global DOM models. Errors are computed as the difference between the predicted and measured values of stream DOM yield (kg C, N, or P km^{-2} yr^{-1}) expressed as a percentage of the measured export (equation (12)). DOM load is ton C, N, or P $basin^{-1}$.

[b] Interquartile range (difference between the 25th and 75th percentiles of the distribution of errors).

[c] Values for NEWS-DIP Calibration from *Harrison et al.* [2005]. NEWSDIP is a global DIP export model.

[d] Values for *Seitzinger and Kroeze* [1998] N-model a global DIN export model from *Alexander et al.* [2002].

largest exporter of DOM to the coastal zone, followed by Asia (Figure 4). North America, Africa, and Oceania come next, and are approximately co-equal with respect to their contribution to global DOC, DON, and DOP export. Europe is predicted to export somewhat less DOM to coastal regions, with Australia exporting the least DOM to coastal zones (Figure 4). On a per-area yield basis, the ranking of continents is somewhat different. Oceania is predicted to have the greatest per-area rate of DOM export, followed, in order of decreasing export, by South America, North America, Asia, Europe, Australia, and Africa.

3.2.2. Global and Regional Sources of DOC, DON, and DOP

[33] In addition to estimating distribution and magnitudes of DOM flux to the coastal zone, NEWS-DOM models can also be used to estimate the relative importance of DOC, DON, and DOP sources in determining DOM export. These estimates are of necessity quite uncertain, and dependent upon model assumptions, but they represent our current best estimate of regional and global sources of DOM exported to the coastal zone.

[34] At the global scale, NEWS-DOM models suggest that DOM export is controlled mainly by non-anthropogenic factors. NEWS-DON and NEWS-DOP predict that globally, humans are responsible for 14% of DON export and 19% of DOP export by rivers. For both DON and DOP, diffuse anthropogenic sources (accounting for 11% and 17% of DON and DOP yields, respectively) were projected to be more important than point sources (3% and 2% of DON and DOP yields, respectively). These estimates of anthropogenic DON and DOP count all DON and DOP from agricultural soils as anthropogenically derived DOM. If just the increase in DON and DOP export due to fertilizer application, manure application, and sewage production is considered, then the anthropogenic contribution to river-exported DON and DOP would be 5% and 11%, respectively.

[35] NEWS-DOC predicts that globally, 23% of DOC exported to the coastal zone comes from wetlands, suggesting that changes in wetland area may have an important impact on river DOC export. The amount of DOC export NEWS-DOC attributes to wetlands, is a direct function of NEWS-DOC's calibrated wetland and non-wetland export coefficients (C_{wet}, and C_{dry}, respectively). NEWS-DOC estimates that wetlands export 3.2-fold more DOC than non-wetlands on a per-area basis. This is consistent with, though toward the low end of, previous estimates regarding the importance of wetlands in controlling DOC export. Previous estimates of the ratio of wetland to non-wetland DOC yield range 1.9 to 37 [*Dillon and Molot*, 1997; *Gorham et al.*, 1998; *Raymond and Hopkinson*, 2003]. If NEWS-DOC underestimates this ratio, then it also underestimates the contribution of wetlands to DOC export globally and the impact of changing wetland area on DOC export. Though a detailed analysis of the impact of

Table 2. Input Data Sets Used for NEWS-DOM Models

Data Set	Resolution	Year	Source
Basin delineations	0.5°	1960–present	STN30 [*Vörösmarty et al.*, 2000a, 2000b]
River networks	0.5°	1960–present	STN30 [*Vörösmarty et al.*, 2000a, 2000b]
Water runoff	0.5°	1960–present	STN30 [*Vörösmarty et al.*, 2000a, 2000b]
Wetland distribution	1 minute		Welarem [*Lehner and Döll*, 2004]
Population density	0.5°	1995	[*Klein Goldewijk*, 2001]
Fertilizer N inputs	0.5°	1995	[*Bouwman et al.*, 2005a, 2005b]
Manure N inputs	0.5°	1995	[*Bouwman et al.*, 2005a, 2005b]
Fertilizer P inputs	0.5°	1995	[*Bouwman et al.*, 2005a, 2005b]
Manure P inputs	0.5°	1995	[*Bouwman et al.*, 2005a, 2005b]
Landuse	0.5°	1995	[*Bouwman et al.*, 2005a, 2005b]
Pre-dam water discharge	137 rivers	NA	[*Meybeck and Ragu*, 1996]

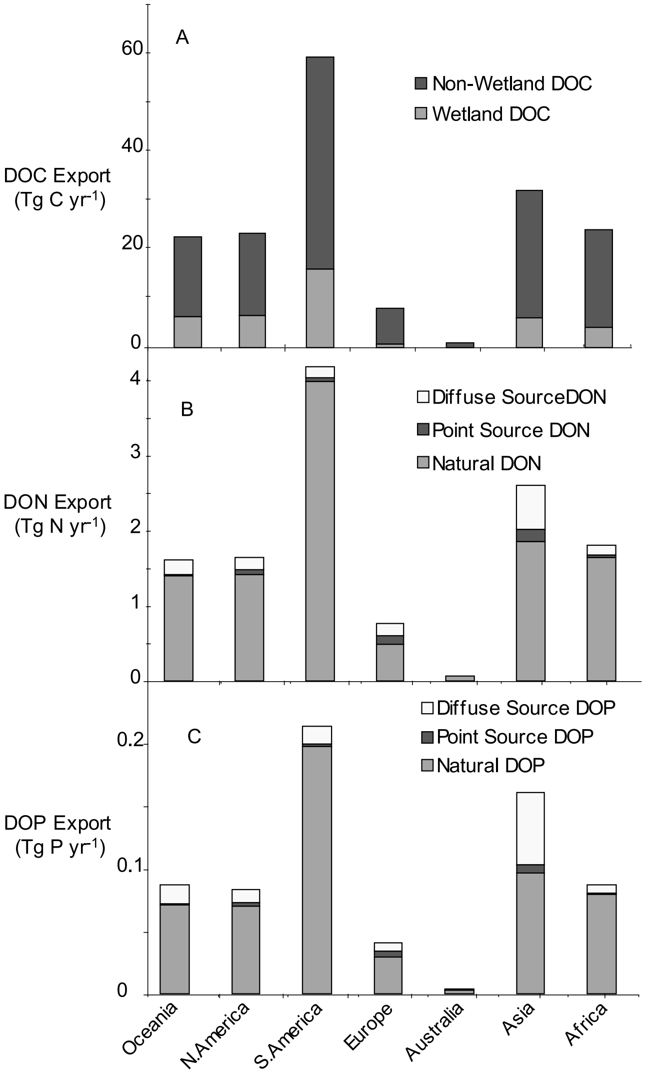

Figure 4. DOM export and sources by continent and by source: (a) distribution of DOC export (Tg C yr^{-1}) by continent and source, partitioned into wetland and non-wetland sources; (b) distribution of DON export by continent and source (Tg N yr^{-1}), partitioned into natural, and point and diffuse anthropogenic DON sources; and (c) distribution of DOP export by continent and source (Tg P yr^{-1}), partitioned into natural, and point and diffuse anthropogenic DOP sources.

wetland loss on DOC export is beyond the scope of this paper, it is worth noting that large-scale wetland conversion such as that seen in the United States (over 50% in the last 2 centuries [*National Research Council Committee on Characterization of Wetlands*, 1995]) is likely to have resulted in a marked decrease in river DOC transport.

[36] At the continental scale, NEWS-DOM models indicate that non-anthropogenic DOM sources dominate DON and DOP export on every continent (Figure 4). For DON, the contribution of DON point sources varies by continent, from 1% in Oceania to 13% in Europe. The contribution of anthropogenic diffuse sources to total DON export also varies by continent, from 3% in S. America to 22% in Asia (Figure 4). As calculated by NEWS-DOP, anthropogenic diffuse source contribution to DOP export ranges from 7% in South America to 36% in Asia, and point source contribution ranges from 0.8% in Oceania to 10% in Europe (Figure 4). On a per-continent basis, anthropogenic sources are predicted to play a slightly greater role in controlling DOP export than they play in controlling DON export (Figure 4).

3.2.3. Spatial Distribution of DOC, DON, and DOP Export

[37] The range of predicted DOM yields was large, spanning over 9 orders of magnitude for DOC and over 8 orders of magnitude for DON and DOP. NEWS-DOC-predicts high DOC yields in the humid tropics, particularly in Southeast Asia, Indonesia, West Africa, and tropical South America (Figure 5a). NEWS-DOC also predicts hot spots for DOC export along the west and east coasts of Canada, at the northern fringe of Europe, in Japan, eastern China, eastern Russia, and New Zealand (Figure 5a). The highest predicted DOC yield (29,267 kg C km^{-2} yr^{-1}) occurred in eastern Burma. NEWS-DOC predicted the lowest DOC yields (1×10^{-5} kg C km^{-2} yr^{-1}) in the Hai Ho basin in northern China, an arid region with little runoff. NEWS-DOC also predicted low rates of DOC export in other low-runoff basins in regions such as western Australia, the southwestern United States, western Mexico, northern Chile, the Arabian Peninsula, Northern Africa, and parts of southern Africa (Figure 5a).

[38] Predicted DON yields follow a pattern similar to that of predicted DOC yields because both are frequently components of the same compounds and also because predicted yields of both DON and DOC are influenced greatly by runoff. However, there are also differences in patterns of predicted DON yield from patterns of predicted DOC yield. These differences result from human influence on DON yield. For example, regions with a lot of intensive agriculture or high population densities such as Europe, and Southeast Asia demonstrate elevated DON yields in comparison to DOC (Figures 4a and 4b). The highest predicted DON yield (2172 kg N km^{-2} yr^{-1}) occurs in western Colombia. The lowest predicted yield (0.00002 kg N km^{-2} yr^{-1}) occurs in southwest Angola, in the region of Iona National Park. In general, low predicted DON yields tend to occur in relatively dry areas with low levels of anthropogenic influence.

[39] Highest predicted DOP yields tend to follow a pattern similar to that of DON, clustering in high runoff areas or in areas with a high degree of human activity (Figure 5c). The highest predicted DOP yield (236 kg P km^{-2} yr^{-1}) occurs in central Japan, in the area around the city of Kumatsu. The lowest predicted yield (7×10^{-6}) occurs in the same low-flow basin in western Angola as the lowest predicted DON flux. As with DON, low predicted DOP yields tend to occur in areas with low levels of anthropogenic influence and in relatively dry regions.

[40] The patterns of predicted coastal DOC, DON, and DOP loads (ton C, N, or P basin^{-1} year^{-1}) differ from the pattern of predicted DOC, DON, and DOP yields (kg C, N, or P km^{-2} yr^{-1}). The five highest yield systems account for

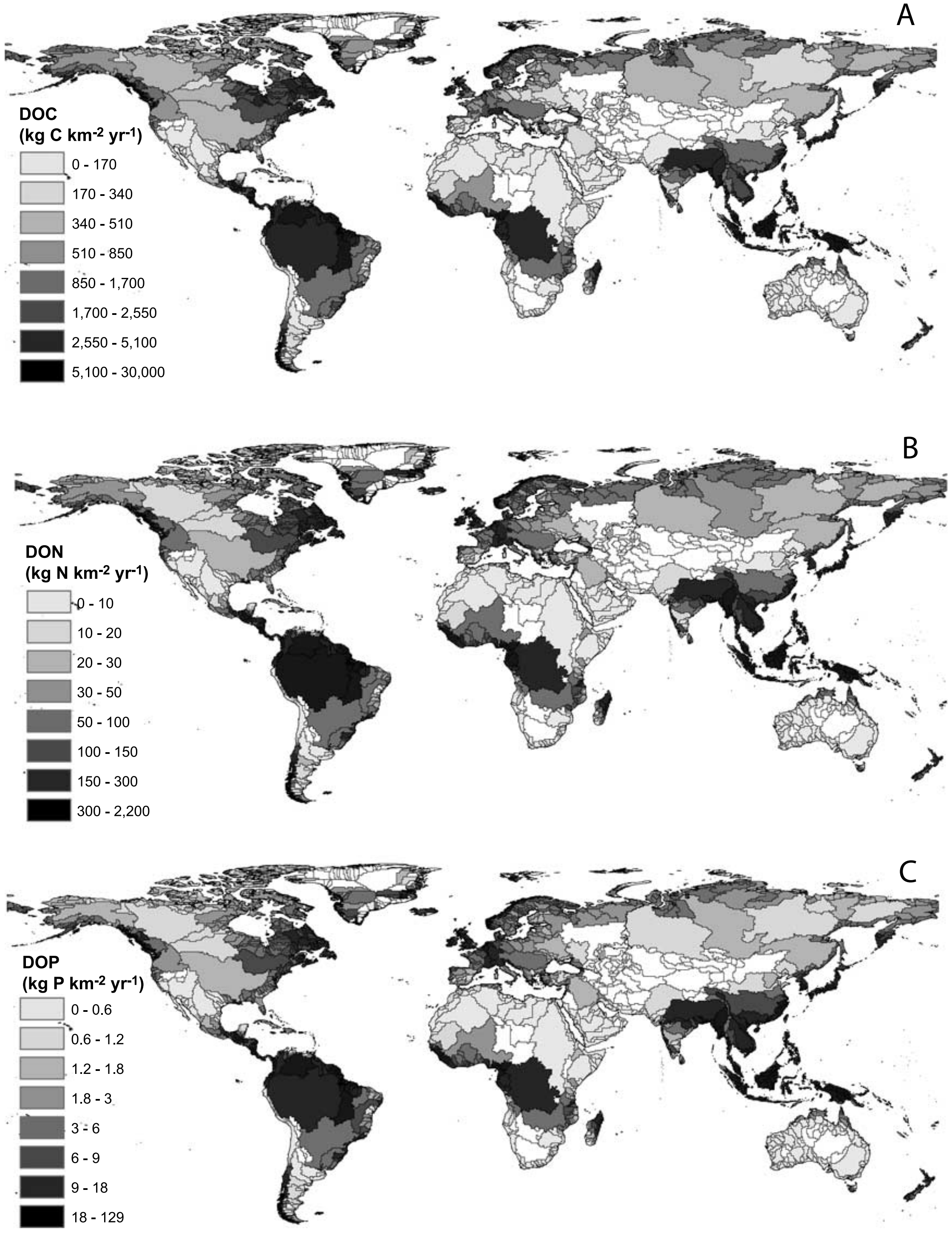

Figure 5. Model-predicted DOM yield by watershed. (a) DOC yield by watershed (kg C km^{-2} yr^{-1}). (b) DON yield by watershed (kg N km^{-2} yr^{-1}). (c) DOP yield by watershed (kg P km^{-2} yr^{-1}). White basins are endoreic. See color version of this figure at back of this issue.

just 0.3% of the total DOC, DON, and DOP export to the coastal zone. However, the five rivers with the highest predicted loads (Amazon, Zaire, Orinocco, Tocantins, and Ganges) together account for 33%, 38%, and 31% of the predicted global DOC, DON, and DOP export, respectively. The largest 10% of river basins (area-wise) as defined by STN30 account for 75%, 74%, and 73% of the globally exported DOC, DON, and DOP, respectively and a similar proportion of the total runoff.

3.2.4. Spatial Distribution of DON and DOP Sources

[41] In addition to estimating distribution and magnitudes of DOM flux to the coastal zone, NEWS-DOM models can

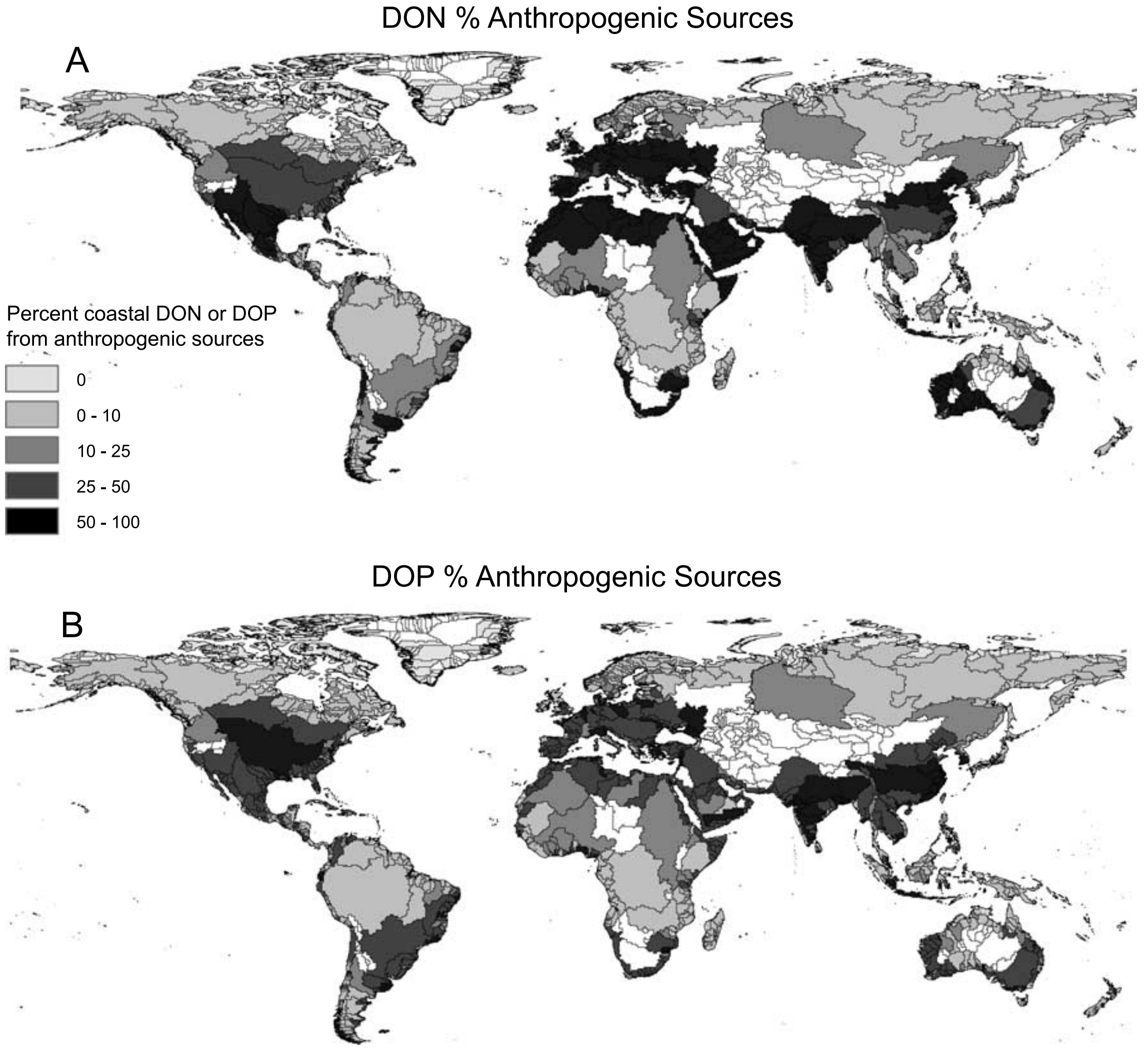

Figure 6. Percent anthropogenic contribution to (a) DON and (b) DOP export from exoreic basins worldwide. White basins are endoreic. See color version of this figure at back of this issue.

also be used to estimate the relative importance of anthropogenic sources of DOC, DON, and DOP export to the coastal zone for individual basins. Though NEWS-DOM models suggest that the role of humans in determining global DOM export is not dominant (section 3.2.2, and Figure 4), NEWS-DON and NEWS-DOP also predict that humans have an important impact on river DON and DOP export in a number of specific regions (Figure 6). The dominance of human activity in many arid basins is largely attributable to the low predicted contribution from natural and anthropogenic diffuse DON and DOP sources in dry systems. In such arid systems, NEWS-DOM models predict that DON and DOP export is controlled largely by anthropogenic point sources. However, there are exceptions to this rule, as NEWS-DOM and NEWS-DOP predict a substantial human contribution to DON and DOP export in quite a few mesic basins as well. For example, non-arid basins with a substantial (>50%) human contribution to exported DON include much of Europe, South Asia, northern China, and several basins on the east coast of the United States (Figure 6a). These tend to be basins with high population densities and/or a significant amount of intensive agriculture. For DOP, non-arid basins with a substantial (>50%) human contribution include the Mississippi River Basin, several European river basins, several basins in the eastern United States, much of China, South Asia, and Japan (Figure 6b).

3.3. Model Sensitivity, Model Efficiency, and Future Directions

[42] A model sensitivity analysis in which all model coefficients and input parameters were increased by 5% and response of model predictions was assessed suggests that NEWS-DOM models are generally fairly stable (Table 3). NEWS-DOC was most sensitive to changes in consumptive water use and the coefficient *a*, the exponent describing the shape of the relationship between runoff and DOC export. NEWS-DOC was also relatively sensitive to changes in the fraction of a basin that is wetland and to changes in the non-wetland DOC export coefficient.

Table 3. Results of a Sensitivity Analysis Indicating Mean Change in Predicted DIP Yield as a Function of Increasing Input Data Sets and Model Parameters by +5%

Treatment	Parameter or Input	Mean Change in Predicted DOM,[a] %
	NEWS-DOC	
+5%	consumptive water use (Q_{act}/Q_{nat})	5
+5%	runoff (m) (R)	0.63
+5%	percent wetland (W)	4.7
+5%	export coefficient for wetlands (C_{wet})	0.92
+5%	export coefficient for non-wetlands (C_{dry})	4.08
+5%	a	6.6
	NEWS-DON	
+5%	consumptive water use (Q_{act}/Q_{nat})	5
+5%	runoff (m) (R)	4.72
+5%	point source DON (N_{sew})	0.51
+5%	diffuse source DON (N_{fe})	0.14
+5%	natural DON export coefficient (N_{nat})	4.35
+5%	b	0.51
+5%	c	−7.28
+5%	d	0.14
	NEWS-DOP	
+5%	consumptive water use (Q_{act}/Q_{nat})	5
+5%	runoff (m) (R)	5.07
+5%	point Source DOP (P_{sew})	0.18
+5%	diffuse source DOP (P_{fe})	0.02
+5%	natural DOP export coefficient (P_{nat})	0.24
+5%	e	0.02
+5%	f	−0.33
+5%	g	0.24

[a] Predicted DOM is kg C, N, or P km^{-2} yr^{-1}.

NEWS-DON was most sensitive to changes in coefficient *c,* the runoff exponent. NEWS-DOP predictions were most sensitive to changes in runoff and consumptive use estimates. In all, the sensitivity analysis suggests that at the global scale NEWS-DOM predictions are fairly sensitive to small changes in hydrologic inputs, and relatively insensitive to changes in anthropogenic inputs. However, in individual basins with large proportional anthropogenic DOM contribution, NEWS-DOM predictions can be quite sensitive to anthropogenic inputs.

[43] A model efficiency analysis in which individual model components were sequentially removed to test their impact on model fit, indicates that runoff alone accounts for most of the explanatory power of NEWS-DOM models. Removal of anthropogenic input terms from NEWS-DON and NEWS-DOP models decreased model efficiency by less than 5% in all cases. These results, together with the results of the model sensitivity analysis, suggest that predictions of DOM export may be improved markedly through improved understanding of the hydrologic elements of DOM export, specifically through improved runoff estimates, improved estimates of consumptive water use, and improved understanding of the relationship between runoff and DOM export.

[44] Though NEWS-DOM models represent our best current understanding of global and regional DOC, DON, and DOP export, there are a number of uncertainties that remain. For example, NEWS-DOM's source attributions are quite uncertain. These attributions are based on assumptions in NEWS-DOM models that DON and DOP export to coastal regions are increased by agricultural and sewage inputs, but that DOC export is not. NEWS-DOM models also treat wetlands as an important driver of DOC export, but treat wetlands and non-wetlands as equal with respect to their influence on DON and DOP yield. These assumptions imply that DOC:DON and DOC:DOP ratios will be higher in DOM exported from wetlands than in DOM exported from non-wetland surfaces. This assumption is consistent with observations in at least one regional study [*Gorham et al.*, 1998], but needs to be tested further by future work. Similarly, by omitting sewage-derived DOC from NEWS-DOC, and by assuming equal DOC export coefficients for agricultural and non-agricultural systems, we imply that regions with high population densities and lots of intensive agriculture will tend to have lower DOC:DON and DOC:DOP ratios than regions with low population densities and little or no agriculture. This prediction is largely consistent with existing observations [*Alexander et al.*, 1996; N. F. Caraco et al., Natural and anthropogenic controls on river borne dissolved organic carbon, nitrogen and phosphorus in the U.S., manuscript in preparation, 2005], but further testing is warranted in more regions. Assumptions about wetland and anthropogenic contributions to DOM export should be revisited as more and better data on the relationships between wetlands and DOM and human activities and DOM become available.

[45] Another source of uncertainty in NEWS-DOM models is in-stream DOM processing. In-stream production and uptake of DOC, DON, and DOP may be quite important

in determining DOM export to the coastal zone. However, in-stream transformations, production, and loss of DOM are not included explicitly in NEWS-DOM models. Presumably, in-stream transformations will be affected greatly by DOM quality, a factor that is likely to vary with DOM source [*Seitzinger et al.*, 2002; *Stepanauskas et al.*, 2002]. Future modeling efforts should more explicitly address in-stream DOM processing.

[46] Finally, though we have made use of all of the available measurement data we could find, a great need for additional, high-quality DOC, DOP, and DON data remains. It would be particularly useful to have DON and DOP data for some large Asian rivers, as there are currently no DON or DOP concentration data available for these important systems.

Appendix A

[47] Model input and validation data for NEWS-DOC are included in Table A1. Included are river name, river location (continent), whether the basin was used to calibrate or validate NEWS-DOC (Cal or Val, respectively), basin area (km^2), average annual basin runoff (m y^{-1}), average DOC concentration (mg C L^{-1}), data source, the percent wetland coverage in the watershed, and NEWS-DOC-predicted DOC export (kg C km^{-2} yr^{-1}).

Appendix B

[48] Model input and validation data for NEWS-DON are included in Table B1. Included are river name, river location (continent), whether the basin was used to calibrate or validate NEWS-DON (Cal or Val, respectively), basin area (km^2), average annual basin runoff (m y^{-1}), average DON concentration (mg N L^{-1}), data source, rates of sewage, manure, and inorganic fertilizer N inputs (kg N km^{-2} yr^{-1}), and NEWS-DON-predicted DON export (kg N km^{-2} yr^{-1}).

Appendix C

[49] Model input and validation data for NEWS-DOP are included in Table C1. Included are river name, river location (continent), whether the basin was used to calibrate or validate NEWS-DOP (Cal or Val, respectively), basin area (km^2), average annual basin runoff (m y^{-1}), average DOP concentration (mg P L^{-1}), data source, rates of sewage, manure, and inorganic fertilizer P inputs (kg P km^{-2} yr^{-1}), and NEWS-DOP-predicted DOP export (kg P km^{-2} yr^{-1}).

Notation

[50] The notation list gives definitions of variables for NEWS-DOM models.

DOC	DOC yield, kg C km^{-2} yr^{-1}.
DON	DON yield, kg N km^{-2} yr^{-1}.
DOP	DOP yield, kg P km^{-2} yr^{-1}.
Q_{act}	measured discharge after dam construction, km^3 H_2O yr^{-1}.
Q_{nat}	measured discharge prior to dam construction, km^3 H_2O yr^{-1}.
R	runoff, m H_2O yr^{-1}.
W	percent of the land area within a watershed that is wetland.
C_{wet}	export coefficient for DOC from wetland soils, kg C km^{-2} yr^{-1}; for NEWS-DOC C_{wet} was set equal to 12475.
C_{dry}	export coefficient for DOC from non-wetland soils, kg C km^{-2} yr^{-1}; for NEWS-DOC C_{wet} was set equal to 3883.
N_{nat}	export coefficient for DON from unimpacted soils, kg N km^{-2} yr^{-1}; for NEWS-DON N_{nat} was set equal to 301.
P_{nat}	export coefficient for DOP from unimpacted soils, kg P km^{-2} yr^{-1}; for NEWS-DOP P_{nat} was set equal to 16.
N_{fe}	N applied to watersheds as inorganic fertilizer, kg N km^{-2} yr^{-1}.
N_{am}	N applied to watersheds as manure, kg N km^{-2} yr^{-1}.
P_{fe}	P applied to watersheds as inorganic fertilizer, kg P km^{-2} yr^{-1}.
P_{am}	P applied to watersheds as manure, kg P km^{-2} yr^{-1}.
Fr_{ag}	fraction of a watershed that is agricultural land.
a	unitless coefficient defining how non-point DOC export responds to runoff; for NEWS-DOC a was set equal to 0.95.
c	unitless coefficient defining how non-point DON export responds to runoff; for NEWS-DON c was set equal to 1.05.
f	unitless coefficient defining how non-point DOP export responds to runoff; for NEWS-DOP f was set equal to 1.1.
b	unitless coefficient defining the fraction of sewage DON making it to the coast; for NEWS-DON b was set equal to 0.17.
e	unitless coefficient defining the fraction of sewage DOP making it to the coast; for NEWS-DOP e was set equal to 0.02.
d	unitless coefficient defining the fraction of nonpoint DON making it to the coast; for NEWS-DON d was set equal to 0.01.
g	unitless coefficient defining the fraction of nonpoint DOP making it to the coast; for NEWS-DOP g was set equal to 0.02.

Table A1. Model Input and Validation Data for NEWS-DOC

River	Continent	Cal/Val	Basin Area, km^2	Runoff, m yr^{-1}	DOC, mg C L^{-1}	Source[a]	Percent Wetland	NEWS-DOC, kg C km^{-2} yr^{-1}
Alabama	North America	Cal	56,894	0.59	6.0	2	4.4	2769
Altamaha	North America	Cal	35,224	0.42	5.5	2	8.1	2140
Amazon	South America	Cal	6,112,000	1.08	4.1	1	8.0	5235
Apalachacola	North America	Cal	44,548	0.63	6.0	2	5.7	3018
Aux Outar	North America	Cal	19,100	0.66	4.8	1	0.9	2885
Brahmaputra	Asia	Cal	580,000	0.88	3.2	1	15.1	4834
Brazos (Texas)	North America	Cal	116,568	0.08	5.3	2	5.1	420
Chang Jiang	Asia	Cal	1,808,000	0.51	2.1	1	3.7	2379
Colorado (California)	North America	Cal	638,951	0.01	7.1	2	1.6	55
Colorado (Texas)	North America	Cal	108,787	0.02	5.2	2	3.4	109
Columbia	North America	Cal	669,000	0.35	2.7	1	3.1	1646
Colville	North America	Cal	53,535	0.62	7.6	2	57.3	5678
Connecticut	North America	Cal	25,019	0.65	3.8	2	22.3	4018
Danube	Europe	Cal	817,000	0.25	5.5	1	1.1	1152
Dnepr	Europe	Cal	504,000	0.11	4.9	1	5.2	570
Don	Europe	Cal	422,000	0.05	4.2	1	0.2	245
Elbe	Europe	Cal	146,000	0.16	4.0	1	1.0	753
Fraser	North America	Cal	220,000	0.51	3.7	1	0.8	2255
Gambia	Africa	Cal	42,000	0.12	2.3	1	3.1	595
Ganges	Asia	Cal	1,050,000	0.47	4.6	1	15.1	2664
Huang He	Asia	Cal	752,000	0.05	1.8	1	1.1	250
Hudson	North America	Cal	20,953	0.7	6.2	2	21.7	4277
Indus	Asia	Cal	916,000	0.06	8.5	1	2.4	304
Klamath	North America	Cal	31,339	0.49	3.4	2	5.2	2356
Kobuk (Alaska)	North America	Cal	24,657	0.69	8.2	2	40.4	5306
Kuban	Europe	Cal	57,900	0.23	1.9	1	0.1	1044
Kuskokwim	North America	Cal	80,549	0.68	5.2	2	34.2	4877
Lena	Asia	Cal	2,490,000	0.21	6.6	1	1.7	987
Loire	Europe	Cal	112,000	0.23	5.3	1	1.2	1065
MacKensie	North America	Cal	1,787,000	0.17	5.2	1	22.5	1127
Manicuagan	North America	Cal	45,800	0.59	5.2	1	5.2	2810
Mississippi	North America	Cal	2,926,507	0.17	6.7	2	7.6	898
Moise	North America	Cal	19,200	0.81	4.4	1	0.2	3453
Moose	North America	Cal	109,000	0.4	20.0	1	57.3	3745
North Dvina	Europe	Cal	348,000	0.32	20.1	1	2.5	1494
Natashquan	North America	Cal	16,100	0.83	5	1	0.8	3576
Niger	Africa	Val	1,200,000	0.13	2.9	1	5.6	672
Nueces	North America	Val	39,956	0.03	7.2	2	1.1	154
Nushagak	North America	Val	25,511	1.06	3.2	2	29.1	6986
Ob	Asia	Val	2,990,000	0.14	9.1	1	12.5	810
Ogooe	Africa	Val	205,000	0.73	8.4	1	5.9	3479
Orange	Africa	Val	1,000,000	0.01	2.3	1	1.2	54
Orinoco	South America	Val	1,100,000	1.03	4.4	1	14.6	5567
Parana	South America	Val	2,783,000	0.2	6.1	1	11.2	1113
Pechora	Europe	Val	324,000	0.4	12.7	1	5.6	1954
Pee Dee	North America	Val	22,870	0.44	9.6	2	13.9	2455
Petit	North America	Val	19,600	0.83	6	1	2.5	3696
Po	Europe	Val	70,000	0.7	2.4	1	0.8	3046
Potomac	North America	Val	30,000	0.32	3.1	1	2.1	1484
Rhine	Europe	Val	224,000	0.31	5.4	1	0.2	1388
Rio Grande (Texas)	North America	Val	456,700	0.01	4.1	2	1.4	54
Sabine	North America	Val	18,982	0.51	7.8	2	14.9	2870
Sacramento	North America	Val	60,870	0.44	3.6	2	4.6	2102
San Joaquin	North America	Val	35,058	0.11	8.8	2	3.2	549
Sanaga	Africa	Val	119,300	0.46	3.5	1	1.1	2056
Savannah	North America	Val	25,511	0.44	7.5	2	10.2	2315
Scheldt	Europe	Val	11,400	0.53	7.9	1	2.0	2392
Seine	Europe	Val	78,600	0.2	3.7	1	0.3	917
St. Johns	North America	Val	18,373	0.6	12.6	2	28.0	4014
St. Lawrence	North America	Val	1,020,000	0.33	3.8	1	9.3	1734
Stikine	North America	Val	51,593	1.38	6.4	2	0.7	5792
Susitna	North America	Val	50,246	1.2	3.0	2	12.9	6267
Susquehanna	North America	Val	70,189	1.43	3.1	2	5.5	6542
Trinity (Texas)	North America	Val	44,512	0.22	6.0	2	4.1	1079
Uruguay	South America	Val	240,000	0.6	3.2	1	0.9	2635
Yenisei	Asia	Val	2,590,000	0.24	7.4	1	1.7	1119
Yukon	North America	Val	831,387	0.36	10.6	2	19.4	2201
Zaire	Africa	Val	3,698,000	0.32	8.5	1	7.9	1646

[a] Sources for DOC and runoff data: *Meybeck and Ragu* [1996]; 2, *Alexander et al.* [1996]. For sources of DOC inputs, see Table 2.

Table B1. Model Input and Validation Data for NEWS-DON

River	Continent	Cal/Val	Basin Area, km^2	Runoff, $m\ yr^{-1}$	DON, $mg\ N\ L^{-1}$	Source[a]	Sewage N, $kg\ N\ km^{-2}\ yr^{-1}$	Manure N, $kg\ N\ km^{-2}\ yr^{-1}$	Inorganic Fertilizer N, $kg\ N\ km^{-2}\ yr^{-1}$	NEWS-DON, $kg\ N\ km^{-2}\ yr^{-1}$
Alabama	North America	Cal	56,894	0.59	0.41	2	27.2	837.7	733.5	186.6
Amazon	South America	Cal	6,112,000	1.08	0.16	1	2.7	26.5	18.4	327.3
Anabar	Asia	Val	78,800	0.17	0.25	1	0.0	0.0	0.0	46.8
Apalachicola	North America	Val	44,548	0.63	0.25	2	64.9	1273.7	1210.4	211.6
Brazos (TX)	North America	Val	116,568	0.08	0.66	2	22.0	2264.8	557.5	27.0
Colorado (CA)	North America	Val	638,951	0.01	0.56	2	9.8	50.5	2.9	4.1
Colorado (TX)	North America	Val	108,787	0.02	0.83	2	13.0	1490.9	690.8	7.5
Colville	North America	Val	53,535	0.62	1.21	2		0.0	0.0	182.2
Connecticut	North America	Val	25,019	0.65	0.25	2	61.7	0.0	53.9	202.3
Copper	North America	Cal	62,678	1.54	0.28	2	0.2	0.0	0.0	473.7
Danube	Europe	Val	817,000	0.25	0.60	1	84.4	1472.0	718.9	89.7
Ganges	Asia	Cal	1,050,000	0.47	0.06	1	42.4	3426.5	1097.3	163.9
Indigirka	Asia	Cal	362,000	0.17	0.35	1	0.1	0.0	0.0	46.8
Khatanga	Asia	Val	364,000	0.23	0.41	1	0.1	0.0	0.0	64.3
Klamath	North America	Cal	31,339	0.49	0.31	2	6.4	662.7	142.1	147.2
Kobuk	North America	Cal	24,657	0.69	0.44	2	0.0	0.0	0.0	203.9
Kolyma	Asia	Cal	660,000	0.2	0.35	1	0.2	0.0	0.0	55.6
Kuskokwim	North America	Cal	80,549	0.68	0.74	2	0.2	0.0	0.0	200.8
Lena	Asia	Val	2,490,000	0.21	0.46	1	1.6	0.0	0.0	58.7
MacKenzie	North America	Val	1,787,000	0.17	0.10	1	0.6	21.2	6.1	47.0
Mississippi	North America	Val	2,926,507	0.17	0.82	2	18.1	2542.3	331.2	54.4
Niger	Africa	Cal	1,200,000	0.13	0.13	1	9.7	42.3	90.5	37.1
Nile	Africa	Val	2,870,000		0.01	1	11.3	94.6	94.6	1.9
Nueces	North America	Cal	39,956	0.03	0.75	2	15.8	1782.8	1464.6	11.1
Nushugak	North America	Cal	25,511	1.06	0.44	2	0.3	0.0	0.0	320.0
Olenek	Asia	Cal	219,000	0.16	0.41	1	0.1	0.0	0.0	44.0
Orange	Africa	Val	1,000,000	0.01	0.15	1	7.5	106.7	12.9	3.7
Orinoco	South America	Cal	1,100,000	1.03	0.16	1	7.7	86.4	49.7	313.2
Parana	South America	Cal	2,783,000	0.2	0.08	1	23.8	292.7	232.2	60.6
Pee Dee	North America	Cal	22,870	0.44	0.26	2	59.2	724.6	807.7	143.6
Po	Europe	Cal	70,000	0.7	0.32	1	158.1	3271.4	895.5	262.5
Potomac	North America	Val	29,966	0.67	0.44	2	73.7	351.6	371.8	215.0
Rio Coatzacoalcos	North America	Cal	29,497	0.65	0.87	3	33.0	1140.3	18.6	204.5
Rio Grande (TX)	North America	Cal	456,701	0.01	0.57	2	13.7	283.3	115.0	4.8
Roanoake	North America	Val	22,458	0.36	0.22	2	31.5	191.5	297.4	110.0
Sabine	North America	Val	18,982	0.51	0.52	2	18.1	1024.9	882.4	160.9
Sacramento	North America	Cal	60,870	0.44	0.41	2	13.6	620.5	403.5	133.8
San Joaquin	North America	Val	35,058	0.11	0.44	2	35.6	1132.4	300.9	37.1
Savannah	North America	Val	25,511	0.44	0.27	2	32.7	1030.7	907.0	140.9
Sebou	Africa	Cal	38,492	0.07	0.90	3	67.4	628.2	467.4	30.6
Seine	Europe	Cal	78,600	0.2	0.50	1	250.5	6378.0	1677.3	113.0
St. Johns	North America	Val	18,373	0.6	0.44	2	89.7	269.9	909.3	198.2
St. Lawrence	North America	Val	1,020,000	0.33	0.03	1	39.8	634.1	105.7	103.0
Stikine	North America	Val	51,593	1.38	0.84	2	0.1	0.0	0.0	422.1
Susitna	North America	Val	50,246	1.2	0.62	2	3.3	0.0	0.0	365.1
Susquehanna	North America	Val	70,189	1.43	0.29	2	40.8	604.5	478.2	460.9
Trinity	North America	Cal	44,512	0.22	0.52	2	120.5	1921.8	1471.4	88.8
Yana	Asia	Val	238,000	0.14	0.33	1	0.2	0.0	0.0	38.2
Yukon	North America	Cal	831,387	0.36	0.57	2	0.5	0.0	0.0	103.1
Zaire	Africa	Cal	3,698,000	0.32	0.18	1	2.7	3.6	5.3	91.5

[a] Sources for DON and runoff data are as follows: 1, *Meybeck and Ragu* [1996]; 2, *Alexander et al.* [1996]; 3, GEMS-Water Trienniel Reports. For sources of DON inputs, see Table 2.

DOC_{wetland}	estimated DOC yield from wetland areas, kg C $km^{-2}\ yr^{-1}$.
$DOC_{\text{non-wetland}}$	estimated DOC yield from non-wetland areas, kg C km^{-2} yr.
$DON_{\text{non-anthropogenic}}$	estimated DON yield from non-human sources, kg N km^{-2} yr.
$DON_{\text{point source}}$	estimated DON yield from anthropogenic point sources, kg N km^{-2} yr.
$DON_{\text{diffuse anthropogenic}}$	estimated DON yield from anthropogenic non-point sources, kg N km^{-2} yr.
$DOP_{\text{non-anthropogenic}}$	estimated DOP yield from non-human sources, kg P km^{-2} yr.
$DOP_{\text{point source}}$	estimated DOP yield from anthropogenic point sources, kg P km^{-2} yr.

Table C1. Model Input and Validation Data for NEWS-DOP

River	Continent	Cal/Val	Basin Area, km^2	Runoff, m yr^{-1}	DOP, mg P L^{-1}	Source[a]	Sewage P, kg P km^{-2} yr^{-1}	Manure P, kg P km^{-2} yr^{-1}	Inorganic Fertilizer P, kg P km^{-2} yr^{-1}	NEWS-DOP, kg P km^{-2} yr^{-1}
Alabama	North America	Cal	56,894	0.59	0.016	2	10.4	99.0	180.3	12.1
Altamaha	North America	Cal	35,224	0.42	0.030	2	12.2	109.5	202.6	8.6
Amazon	South America	Cal	6,112,000	1.08	0.015	1	1.1	2.0	3.5	17.5
Anabar	Asia	Cal	78,800	0.17	0.000	1	0.0	0.0	0.0	2.3
Apalachicola	North America	Cal	44,548	0.63	0.014	2	24.7	156.2	294.5	15.0
Brazos (TX)	North America	Cal	116,568	0.08	0.019	2	8.6	74.4	451.2	1.6
Colorado (CA)	North America	Cal	638,951	0.01	0.021	2	3.7	1.4	4.1	0.1
Colorado (TX)	North America	Cal	108,787	0.02	0.026	2	5.0	103.1	317.2	0.3
Columbia	North America	Cal	665,368	0.4	0.012	2	2.9	13.0	118.9	6.8
Connecticut	North America	Cal	25,019	0.65	0.015	2	24.0	0.0	0.0	10.0
Copper	North America	Cal	62,678	1.54	0.017	2	0.0	0.0	0.0	25.7
Danube	Europe	Cal	817,000	0.25	0.035	1	30.5	12.7	32.2	3.7
Hudson	North America	Cal	20,953	0.7	0.013	2	48.2	37.9	26.1	11.7
Indigirka	Asia	Cal	362,000	0.17	0.009	1	0.0	0.0	0.0	2.3
Khatanga	Asia	Cal	364,000	0.23	0.006	1	0.0	0.0	0.0	3.2
Klamath	North America	Cal	31,339	0.49	0.014	2	2.4	33.0	111.6	8.6
Kolyma	Asia	Cal	660,000	0.2	0.015	1	0.0	0.0	0.0	2.7
Kuskokwim	North America	Cal	80,549	0.68	0.026	2	0.0	0.0	0.0	10.5
Lena	Asia	Cal	2,490,000	0.21	0.022	1	0.3	0.0	0.0	2.9
Mississippi	North America	Val	2,926,507	0.17	0.015	2	7.0	39.6	238.2	3.1
Nueces	North America	Val	39,956	0.03	0.040	2	7.3	192.6	350.7	0.6
Nushagak	North America	Val	25,511	1.06	0.011	2	0.0	0.0	0.0	17.1
Olenek	Asia	Val	219,000	0.16	0.006	1	0.0	0.0	0.0	2.1
Orinoco	South America	Val	1,100,000	1.03	0.010	1	2.8	1.9	6.8	16.7
Pee Dee	North America	Val	22,870	0.44	0.018	2	22.7	89.9	163.7	8.5
Po	Europe	Val	70,000	0.7	0.010	1	61.0	8.3	116.6	12.5
Potomac	North America	Val	29,966	0.67	0.030	2	28.3	28.6	58.7	11.4
Rio Grande (TX)	North America	Val	456,701	0.01	0.016	2	5.3	11.7	13.8	0.1
Roanoke	North America	Val	22,458	0.36	0.018	2	12.1	20.2	36.7	5.6
Sabine	North America	Val	18,982	0.51	0.017	2	6.9	132.9	242.1	11.2
Sacramento	North America	Val	60,870	0.44	0.018	2	5.3	43.8	133.2	7.9
San Joaquin	North America	Val	35,058	0.11	0.027	2	13.7	30.0	255.0	1.9
Savannah	North America	Val	25,511	0.44	0.025	2	12.6	97.7	237.2	9.2
St. Johns	North America	Val	18,373	0.6	0.012	2	34.5	79.7	70.3	10.8
St. Lawrence	North America	Val	773,889	0.32	0.021	2	13.6	33.6	71.2	5.2
Stikine	North America	Val	51,593	1.38	0.017	2	0.0	0.0	0.0	22.8
Susitna	North America	Val	50,246	1.2	0.034	2	0.3	0.0	0.0	19.6
Susquehana	North America	Val	70,189	1.43	0.013	2	16.4	47.4	117.1	28.6
Trinity	North America	Val	44,512	0.22	0.027	2	46.1	186.9	340.4	5.0
Yana	Asia	Val	238,000	0.14	0.010	1	0.0	0.0	0.0	1.8
Yukon	North America	Val	831,387	0.36	0.018	2	0.1	0.0	0.0	5.2

[a] Sources for DOP and runoff data: 1, *Meybeck and Ragu* [1996]; 2, *Alexander et al.* [1996]. For sources of DOP inputs, see Table 2.

$DOP_{\text{diffuse anthropogenic}}$ estimated DOP yield from anthropogenic non-point sources, kg P km^{-2} yr.

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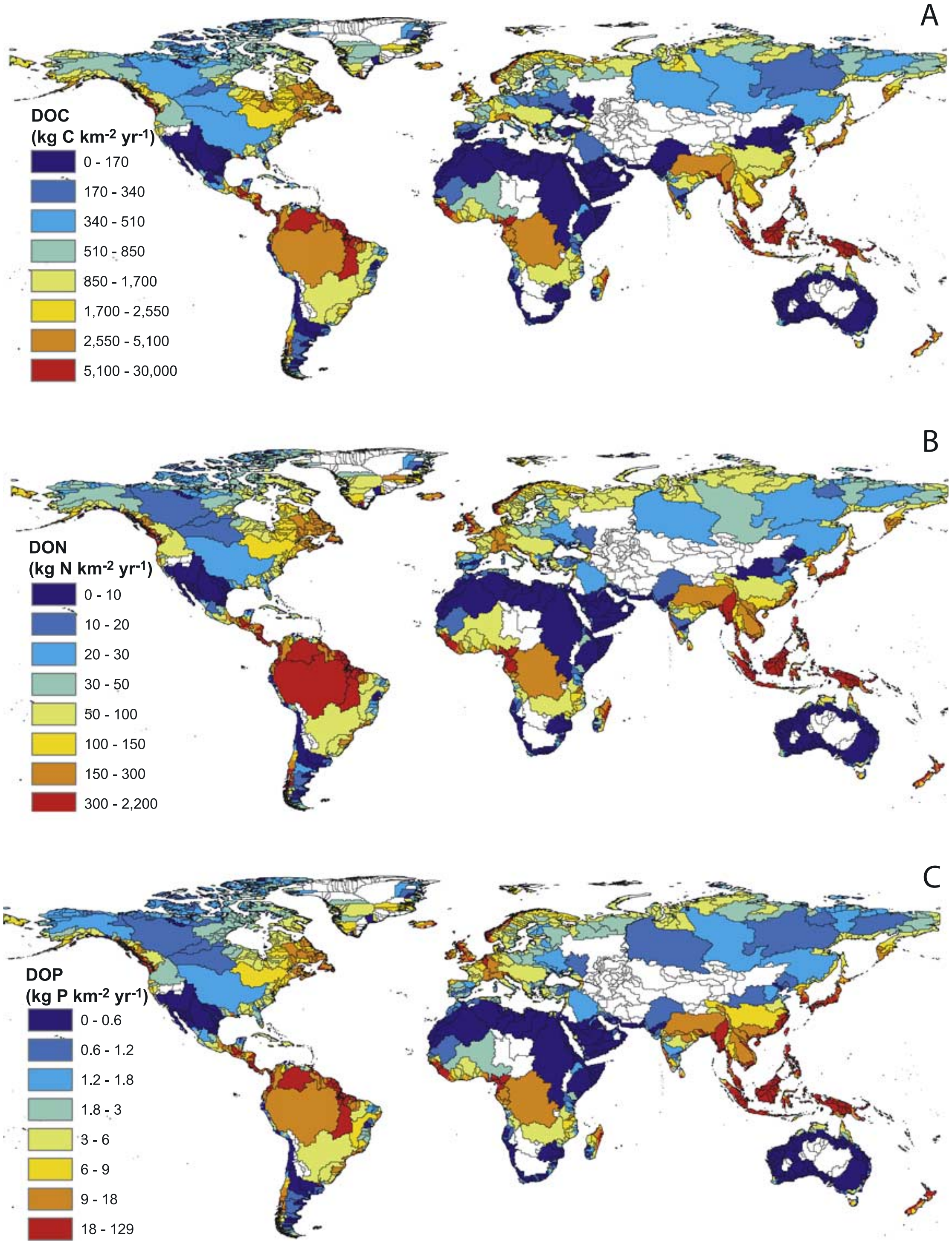

Figure 5. Model-predicted DOM yield by watershed. (a) DOC yield by watershed (kg C km^{-2} yr^{-1}). (b) DON yield by watershed (kg N km^{-2} yr^{-1}). (c) DOP yield by watershed (kg P km^{-2} yr^{-1}). White basins are endoreic.

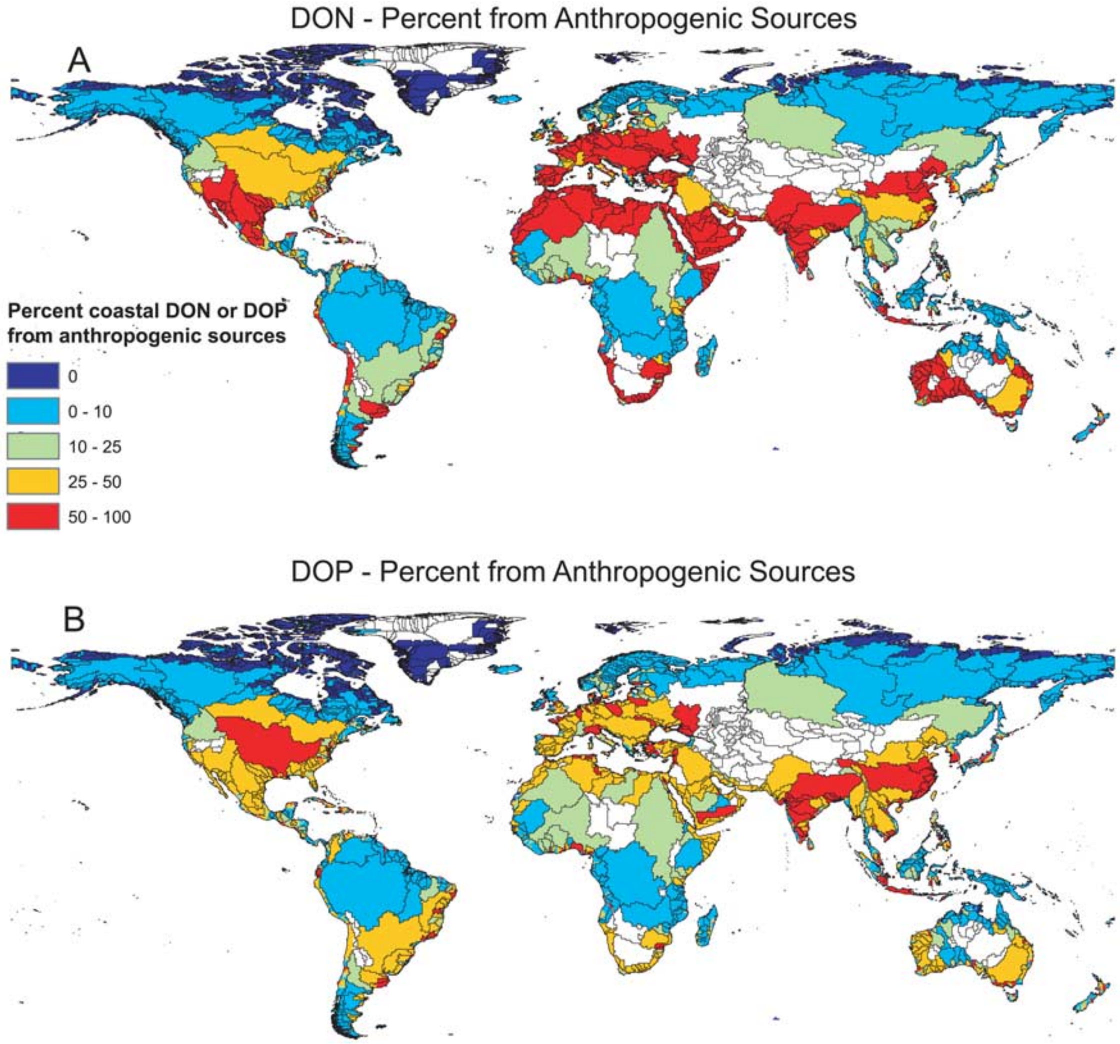

Figure 6. Percent anthropogenic contribution to (a) DON and (b) DOP export from exoreic basins worldwide. White basins are endoreic.