Atmospheric fluxes of organic N and P to the global ocean

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[1]   The global tropospheric budget of gaseous and particulate non-methane organic matter (OM) is re-examined to provide a holistic view of the role that OM plays in transporting the essential nutrients nitrogen and phosphorus to the ocean. A global 3-dimensional chemistry-transport model was used to construct the first global picture of atmospheric transport and deposition of the organic nitrogen (ON) and organic phosphorus (OP) that are associated with OM, focusing on the soluble fractions of these nutrients. Model simulations agree with observations within an order of magnitude. Depending on location, the observed water soluble ON fraction ranges from $\sim$3% to 90% (median of $\sim$35%) of total soluble N in rainwater; soluble OP ranges from $\sim$20–83% (median of $\sim$35%) of total soluble phosphorus. The simulations suggest that the global ON cycle has a strong anthropogenic component with $\sim$45% of the overall atmospheric source (primary and secondary) associated with anthropogenic activities. In contrast, only 10% of atmospheric OP is emitted from human activities. The model-derived present-day soluble ON and OP deposition to the global ocean is estimated to be $\sim$16 Tg-N/yr and $\sim$0.35 Tg-P/yr respectively with an order of magnitude uncertainty. Of these amounts $\sim$40% and $\sim$6%, respectively, are associated with anthropogenic activities, and 33% and 90% are recycled oceanic materials. Therefore, anthropogenic emissions are having a greater impact on the ON cycle than the OP cycle; consequently increasing emissions may increase P-limitation in the oligotrophic regions of the world's ocean that rely on atmospheric deposition as an important nutrient source.

1. Introduction

[2]   In the early 1980s, *Duce et al.* [1983] provided the first assessment of global tropospheric OM budgets that characterizes the sources and fates of OM from the marine and terrestrial biospheres and emphasizes their importance. Since then, atmospheric OM has attracted extensive attention from the scientific community because of the impact on the environment: air quality through interactions with ozone and the formation of secondary aerosol, acids, and persistent organic pollutants [*Houweling et al.*, 1998; *Poisson et al.*, 2000; *Kanakidou et al.*, 2005]; the oxidizing capacity of the atmosphere [*Monks et al.*, 2009]; visibility [*Seinfeld and Pandis*, 1998]; climate [*Intergovernmental Panel on Climate Change*, 2007]; and human health [*Dawson et al.*, 2010; *Delfino et al.*, 2010]. There is increasing interest in the impact of atmospheric OM on marine and terrestrial ecosystems via

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nutrient deposition in the form of organic N and P [*Duce et al.*, 1991; *Cornell et al.*, 2003; *Mahowald et al.*, 2005]. However, the atmospheric chemistry of OM is highly complex. Atmospheric OM is emitted in both the particulate and gas phases and it often undergoes further physico-chemical transformations during transport. Thus, a substantial fraction of OM remains unidentified [*Goldstein and Galbally*, 2007].

[3] In this work we use the term "organic matter" OM to describe the atmospheric organic matter pool, here defined as total mass of H-containing organic compounds and their oxidation products excluding methane. We use the term "organic carbon" (OC) to refer to the mass of C in the OM. Likewise, we use the terms organic nitrogen (ON) and organic phosphorus (OP) to refer to the N and the P in the OM. Atmospheric ON includes a broad array of chemical species with widely different chemical functionality and reactivity and with atmospheric lifetimes that range from seconds to weeks [*Neff et al.*, 2002] and even months [*Poisson et al.*, 2000]. Atmospheric ON includes species such as amines, urea, amino acids, amides, organic nitrates, and azarenes (N-heterocycles), and related species in their reduced, partially oxidized, or fully oxidized forms in both the gas and particulate phases [*Milne and Zika*, 1993; *Neff et al.*, 2002; *Cornell et al.*, 2003; *Matsumoto and Uematsu*, 2005, and references therein; *Ge et al.*, 2011]. In atmospheric aerosols and in deposition samples, the ON concentration is typically measured as the difference between the total N concentration and the measured inorganic N (IN). This procedure can lead to large errors in the ON determination because the difference between total N and IN is often small [*Cornell et al.*, 2003; *Lesworth et al.*, 2010; *Cape et al.*, 2011]. Thus, the sources, atmospheric loading and environmental impacts of ON are poorly characterized and little understood.

[4] Atmospheric OP has been less studied than ON. It appears to be present largely as a byproduct of both marine and terrestrial organisms, e.g., bacteria, viruses, fungi and spores, and plant debris; it is also emitted from a wide range of anthropogenic activities, such as agricultural fertilization, coal, fuel and waste burning and open fire [e.g., *Graham and Duce*, 1979; *Food and Agriculture Organization of the United Nations (FAO)*, 2001; *Benitez-Nelson*, 2000; *Ruttenberg*, 2003]. Most measurements of atmospheric OP are limited to particulate OP; as was the case with ON, OP is usually measured by the chemically defined difference between the total P and the inorganic P (IP). Because of limitations in analytical procedures, many IP compounds may go unmeasured and end up in the OP pool [*Benitez-Nelson*, 2000; *Paytan and McLaughlin*, 2007]. OP is likely comprised of a wide range of organic compounds [*Benitez-Nelson*, 2000; *Turner et al.*, 2002; *Kaiser et al.*, 2003; *Paytan and McLaughlin*, 2007]. In rainwater samples from New Jersey, *Altieri et al.* [2009] identified 49 organophosphorus compounds with structures containing CHONP (29), CHONSP (8), CHOP (7), and CHOSP (5).

[5] Human activities have modified the atmospheric content and deposition of OM by both increasing emissions and altering the tropospheric chemistry in gaseous and particulate OM. Interactions between natural and anthropogenic emissions are known to nonlinearly enhance the presence of organic aerosols in the atmosphere and to chemically bind anthropogenically emitted species, including N, to OM [*Kanakidou et al.*, 2000, 2005; *Hallquist et al.*, 2009].

Additionally, climate change can affect OM concentrations; changes in temperature, humidity, and radiation will modulate biogenic emissions, which are a primary source of many OM compounds [*Duce et al.*, 1983; *Arneth et al.*, 2010]. Because of the multiple biogeochemical feedbacks between the C/N/P cycles and the terrestrial and marine biospheres, anthropogenic activity could significantly affect the future transport of atmospheric OM.

[6] Atmospheric deposition has been proposed as an important source of nutrients for the marine environment [*Duce et al.*, 2008; *Okin et al.*, 2011]. In a warmer climate increasing ocean stratification and shallower mixing depths are expected to enhance the impact of atmospheric inputs in the surface ocean. Changes in atmospheric OM composition and deposition could affect nutrient ratios in seawater, and further alter ecosystem diversity and community structure [*Arrigo*, 2005]. The magnitude of the impact of atmospheric deposition may be underestimated because earlier studies of the atmospheric input of N and P to marine ecosystems were largely focused on inorganic forms and generally did not account for temporal and spatial variability. However, there is increasing evidence that a significant fraction of N and P deposition occurs as ON [e.g., *Neff et al.*, 2002; *Cornell et al.*, 2003; *Lesworth et al.*, 2010; *Cape et al.*, 2011, and references therein] (see also section S3.1 in Text S1 in the auxiliary material) and OP [e.g., *Graham and Duce*, 1981, 1982; *Mahowald et al.*, 2008; *Markaki et al.*, 2010, and references therein] (see also section S4 in Text S1 in the auxiliary material).[1] Knowledge about the speciation of N and P is critical as several studies have shown that ON and OP are directly assimilated by marine organisms. For example, *Seitzinger and Sanders* [1999] have shown that dissolved ON from rainwater can stimulate productivity of coastal-marine bacteria and phytoplankton as well as influence community structure. Furthermore, bioavailability of dissolved ON depends on its sources. Urban/suburban sources provide a higher proportion of bioavailable dissolved ON (59% ± 11) compared to agricultural pastures (30% ± 14) and forests (23% ± 19) [*Seitzinger et al.*, 2002]. Several anthropogenic organophosphates have been shown to serve as P sources for bacteria [*Cook et al.*, 1978, and references therein]. In the surface North Pacific dissolved OP is the source of 30–50% of the biologically available P, an amount equivalent to 7–15% of the total dissolved OP pool [*Björkman and Karl*, 2003]. *Lomas et al.* [2010] estimated that dissolved OP supports more than 25% of annual primary production in the subtropical North Atlantic. Despite the potential importance of these organically associated nutrients for ocean biota, the composition, deposition rates, and their environmental impact is still an open question because of the dearth of observational data. Consequently it is difficult to achieve a global assessment.

[7] Here we present a global picture of the ON and OP atmospheric cycles using a 3-dimensional global chemistry-transport model that simulates OC atmospheric distributions and deposition. The model results are extensively compared to measurements of soluble ON and OP components. The deposited material that originates from anthropogenic sources is distinguished from that originating from natural terrestrial and oceanic sources that is recycled via the atmosphere. To our

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Table 1a. Global Annual Emissions of Gaseous Non-Methane OC (OC(g)) Used in TM4-ECPL and in Other Global Models, in Tg-C/yr[a]

Sources	STEV2006[b]	IPCC TAR[b]	FIOR2009	TM4-ECPL[c]
Biomass burning	24	32		37[d]
Terrestrial biosphere isoprene	512[e]	220		442
Terrestrial terpenes + other reactive VOC	227[e]	111		375[f]
Oceans biosphere + DMS	30	35		72[g]
Anthropogenic emissions	56–135	124	96.8 ± 41.8	64[h]
Total OC(g)	849–928	522[§]	630 ± 221	990

[a]STEV2006: *Stevenson et al.* [2006]; FIOR2009: *Fiore et al.* [2009].

[b]STEV2006 and IPCC-TAR, which were reported in Tg-OM/yr, have been converted to Tg-C/yr, using the isoprene stoichiometry and a mean OM:OC mass ratio of 1.3 for all other emissions.

[c]Details and references for the emission inventories used in TM4-ECPL are given in section S1 in Text S1 in the auxiliary material.

[d]Estimate for the year 2005 [*van der Werf et al.*, 2006].

[e]Isoprene = 220–631 TgC/yr; terpenes = up to 260 TgC/yr; methanol = 107 Tg-C/yr.

[f]For chemical speciation see text.

[g]Includes dimethylsulfide (DMS), amines, other OC(g), and DMS land emissions.

[h]Estimate for the year 2005 [*Doering et al.*, 2009].

knowledge these simulations are the first effort to provide global OP and ON atmospheric deposition maps that include both gases and particles.

2. Model Description

[8] We used the TM4-ECPL model [*Myriokefalitakis et al.*, 2008, 2010, 2011] to simulate oxidant, methane and OC chemistry, as well as all major primary and secondary aerosol components. Tables 1a and 1b summarize the global annual anthropogenic, biomass burning, and natural emissions of OC used in TM4-ECPL (henceforth, TM4) and compare them with earlier modeling studies. They also provide information on the uncertainties reflected in the range of global estimates. Sections S1 and S2 and Tables S1 and S2 in Text S1 in the auxiliary material provide more comprehensive data on the emissions compiled from the literature or calculated here. In TM4, the photochemical degradation of volatile organic compounds (VOCs) in the atmosphere forms secondary organic products, carbon monoxide, and ultimately carbon dioxide as illustrated in Figure 1. Also produced are semi-volatile and low volatility organic products that are subsequently transferred to the particulate phase in the atmosphere. Thus, only part of the emitted OC is ultimately

deposited to the surface by dry or wet processes in the gas or particulate form. Deposition parameterizations in TM4 use solubility estimates for the compounds [*Myriokefalitakis et al.*, 2011; *Tsigaridis and Kanakidou*, 2003; Table 1b] (see also section S1 in Text S1 in the auxiliary material). OC in the particulate phase is simulated in the model by using 20 tracers linked to various origins. These can be grouped as: i) primary OC particles from fossil fuel, biofuel and biomass burning; ii) primary OC particles from the ocean [*Myriokefalitakis et al.*, 2010]; iii) secondary OC particles from semi-volatile OC formed by anthropogenic and natural gaseous OC oxidation in the gas phase or formed by multiphase chemistry [*Myriokefalitakis et al.*, 2011]; and iv) aged primary and secondary OC particles [*Tsigaridis and Kanakidou*, 2003]. TM4 has been further improved to account for primary biogenic particles of terrestrial origin and for OC associated with dust particles. The global distributions of the atmospheric burden and deposition of OC are derived as the sum of the corresponding terms of the individual OC model tracers calculated by TM4 using OC emissions (Tables 1a and 1b), chemical transformation, transport in the atmosphere, and deposition. Simulated particulate $PM_{2.5}$ OC concentrations are compared with observations in Figure S1 in Text S1 in the auxiliary material.

Table 1b. A Comparison of Literature Estimates and Global Annual Emissions of Particulate OC (OC(p)) Used in the TM4-ECPL Model, in Tg-C/yr[a]

Sources	Range in Literature	TM4-ECPL	Soluble Fraction[a]
Biomass burning, biofuel, fossil fuel	17–77[b]	35	0.5
Primary biogenic particles (PBP)	7.5–82.5[c]	50[d]	0.3
Soil organic matter on dust	1.3–34.5[e]	2.3[d],[e]	0.1
Ocean	2–75	30.6[d]	[f]
Total OC(p) Tg-C/yr	27.8–269	118	
Total OC(g + p)	427–1371	1108	

[a]The modeled soluble OC fraction of emissions is also shown.

[b]*Bond et al.* [2004].

[c]Range based on estimates for organic matter (OM) in Tg-OM/yr by *Andreae and Rosenfeld* [2008], *Mahowald et al.* [2008], *Winiwarter et al.* [2009], and *Heald and Spracklen* [2009]. Up to 1000 Tg-OM/yr estimated by *Jaenicke* [2005] and assuming OM:OC in PBP of 2 [*Winiwarter et al.*, 2009].

[d]Neglected in most modeling studies and approximated in the present study; details are given in section S1 in Text S1 in the auxiliary material.

[e]No estimate available; here derived from the global dust emissions data set, available from the AEROCOM modeling experiments [*Dentener et al.*, 2006b], assuming 0.25% OM content of dust and an OM:OC ratio of 1.72 (see details in section S2 in Text S1 in the auxiliary material); associated with a 49% uncertainty in dust emissions [*Textor et al.*, 2006].

[f]Fine mode OC = 0 [*Facchini et al.*, 2008]; coarse mode OC = 0.8.
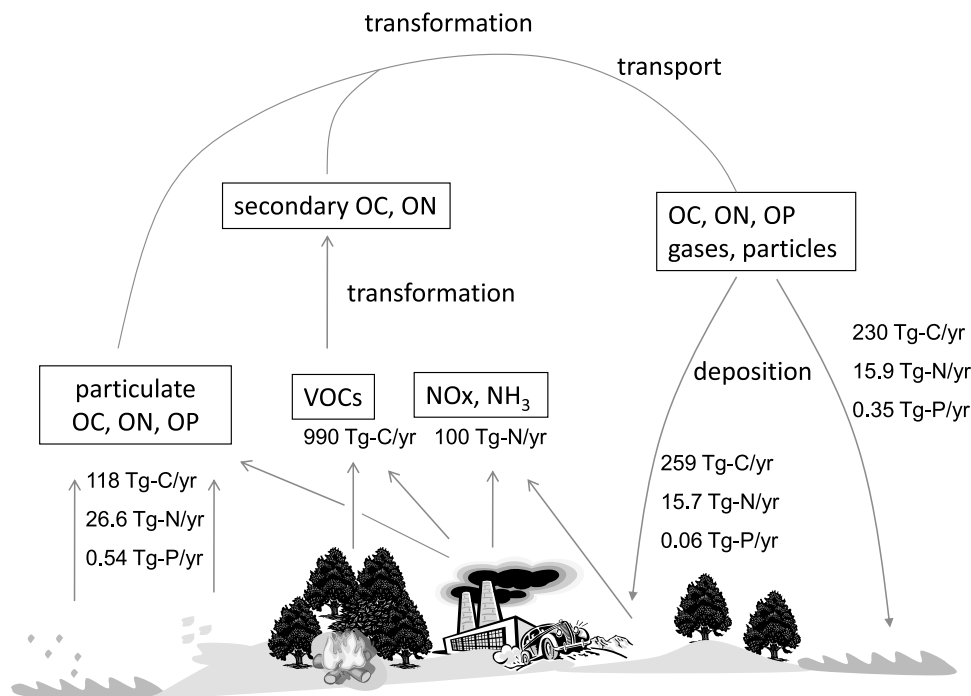
Figure 1. Simplified illustration of the atmospheric cycle of organic matter showing the various sources of particulate OC, ON and OP, OC gases (VOC) and (N oxides and NH₃), the transformation during transport, and the deposition of OC, ON and OP as gases and particles to the land and to the ocean. Total emissions are those used as input in the model (except amine emissions, which are not shown). The deposition fluxes shown are of major soluble species as determined by the model. Deposition fluxes include material recycled from the ocean.

Measured values fall within a factor of ten of the modeled values although the model tends to be biased toward lower values; the model seems to perform better at remote locations, most of them located over USA.

[9] The model uses primary non-marine emissions of N oxides, ammonia and a small amount of amine emitted from the oceans [*Van Neste et al.*, 1987; *Facchini et al.*, 2008] that form amine salts (Table 2a). Most global atmospheric chemistry transport models account for the formation of organic nitrate during oxidation of volatile OC using chemical schemes of various complexity [*Dentener et al.*, 2006a]. They do not explicitly account for the production of other forms of ON, particularly those associated with the primary and secondary particulate OM, thus underestimating the atmospheric burden of ON and its deposition to the surface. In this paper we make such an estimate. The model explicitly calculates the chemically produced gaseous organic nitrates and oxygenated IN compounds both in the gas and particulate phases [*Myriokefalitakis et al.*, 2008, 2011].

[10] In addition, N and P concentrations were linked to source-specific particulate OC tracers using varying N:C or P:C molar ratios as measured in the OM from different source types (Tables 1b, 2b, and details in section 3.3.1 and sections S2 and S3 in Text S1 in the auxiliary material). Specifically, for the OC emissions of terrestrial primary biogenic particles, we apply a mean N:C molar ratio of 0.15, which is typical for living organisms given a factor of two uncertainty (based on mid-range ratios for bacteria [*Neff et al.*, 2002] and pollen grains [*Descolas-Gros and Schölzel*, 2007]). For soil OC on dust, a mean N:C molar ratio of 0.1 (0.07–0.12) [*Cleveland*

and Liptzin, 2007] was used. Similarly, the N:C Redfield molar ratio of 0.15 (ranging from 0.12 to 0.30) [*Arrigo*, 2005] was used for the primary marine organic particles and amino acid emissions over the ocean [*Milne and Zika*, 1993]. ON has also been observed in pollution aerosols and secondary organic aerosol (SOA) from biogenic precursors [*Hallquist et al.*, 2009; *Aiken et al.*, 2008; *Lim and Ziemann*, 2005]. A mean N:C molar ratio of 0.3 (with uncertainty of at least a factor of 3) was used here for the anthropogenic sources. This ratio is within the range reported for individual compounds in

Table 2a. A Comparison of Annual NO$_x$ and NH$_3$ Emissions Used in This Work (TM4-ECPL) With Literature Values (Tg-N/yr)[a]

NO$_x$ (Tg N/yr)	STEV2006	IPCC TAR	FIOR2009	TM4-ECPL
Biomass burning	10.2	7.1		5.3
Soils	7[b]	5.6		7.6
Lightning	5[b]	5		6.5
Anthropogenic emissions	27.8	33	32.5 ± 6.0	32
Aviation	0.8			0.8
Total NOx	50.8	50.7	46.5 ± 5.7	52.2

NH$_3$ (Tg N/yr)[c]	STEV2006	IPCC TAR	FIOR2009	TM4-ECPL
Biomass burning	4.9	5.7		3.9
Soils	2.4	2.4		3.6
Anthropogenic emissions	49	36		40.4
Total non-marine NH$_3$	56.3	44.1		47.9

[a]STEV2006: *Stevenson et al.* [2006]; FIOR2009: *Fiore et al.* [2009].
[b]Range for various model input data: 3.7–7 Tg-N/yr from lightning, 5.5–8.0 Tg-N/yr from soils.
[c]Marine NH$_3$ emissions are not shown as they do not result in new nutrient additions to the ocean.

Table 2b. Global Emissions of Organic Nitrogen (ON) (Tg-N/yr)[a]

Sources	TM4-ECPL[b]	Uncertainty Range[c]	Used N:C[d]
Biomass burning, biofuel, fossil fuel	12.3	1–46.2	0.3 (0.05–0.6)
Primary biogenic particles	8.7	0.6–18.6	0.15 (±50%)
Soil organic matter on dust	0.2	0.1–4.2	0.1 (0.07–0.12)
Ocean ON(p)	5.4	0.3–22.5	0.15 (0.12–0.30)
Total ON(p)	26.6	1.7–91.4	
Ocean amines	0.8[e]	0.4–4	
Total ON	27.4[f]	2.1–95.4	
Anthropogenic fraction of ON emissions[g]	46%	1–94%	

[a]Particulate ON (ON(p)) emissions and uncertainty range are derived from OC(p) emissions in Table 1b and the source specific N:C molar ratios reported in the table (see section 2).

[b]For soluble ON calculation apply the soluble fractions as for OC in Table 1b.

[c]The uncertainty range is calculated based on the uncertainty in N:C ratios given in parentheses in the last column and the emissions used in the model and given in Table 1b; the uncertainty in OC emissions will further increase this range.

[d]Molar ratio. See section S3 in Text S1 in the auxiliary material.

[e]*Myriokefalitakis et al.* [2010].

[f]CH$_3$CN emissions of 0.28 Tg-N/yr [*Holzinger et al.*, 2001] are not included in the model.

[g]For simplicity, all biomass burning emissions are counted in the anthropogenic fraction.

biomass burning aerosols, 0.03 to 0.5 [*Laskin et al.*, 2009]; however, it is higher than the N:C molar ratio reported for fresh urban aerosols, 0.08 to 0.2 [*Wang et al.*, 2010] based on aerosol mass spectrometer observations of submicron particles, a technique that detects fractions of ON, like organic nitrates or amides, as inorganic fragments [*Aiken et al.*, 2008]. For SOA produced by gas-to-particle conversion, the model uses a N:C molar ratio of 0.1 ± 0.05 (a value close to that of humic compounds) [*Lin et al.*, 2010] with a 50% uncertainty. For simplicity, a similar N:C ratio was assumed for the SOA from anthropogenic sources in both gaseous and particulate phases. In the model all OP emissions are primary and reside in the particulate phase. The P:C molar ratios used in the model to estimate the OP emissions to the atmosphere are discussed in section 3.3.1. This approach implies that the particulate ON and OP have a solubility behavior similar to the particulate OC with which they are associated. Soluble OC fractions are given in Table 1b, *Myriokefalitakis et al.* [2010], and *Tsigaridis et al.* [2006]. The insoluble OC particles are converted to soluble material during atmospheric aging as described in *Tsigaridis and Kanakidou* [2003]. Further details on the model are provided in section S1 in Text S1 in the auxiliary material.

3. Results and Discussion

3.1. OC in the Atmosphere

3.1.1. Emissions of OC

[11] The TM4 model uses total emissions of 990 Tg-C/yr of natural and anthropogenic OC gases (Tables 1a and 1b).

Overall, the emission rate is 10 to 130% higher than those used in most global chemistry-transport models as reported in *Fiore et al.* [2009] (see Table 1a). However, the TM4 rate is about 20% lower than estimates by *Goldstein and Galbally* [2007] and *Hallquist et al.* [2009] (Table 3). In addition, in the present study, TM4 uses a total of 118 Tg-C/yr for OC particle emissions with the soluble fractions of the emitted particles varying between 10% and 50% depending on the source (Table 1b). The annual overall OC emissions (gases and particles) in TM4 amount to 1108 Tg-C/yr. The model-estimated mean residence time of total OC is 5.2 days.

3.1.2. Deposition of OC to the Ocean

[12] Using TM4 we determine that a total of ~528 Tg-C/yr are deposited at the Earth's surface as total OC gases and particles. Wet deposition accounts for ~60% to the OC deposition and the remaining ~40% is removed by dry deposition. The model-determined global total OC deposition is well within the range of 305–645 Tg-C/yr estimated by *Goldstein and Galbally* [2007] but lower than the 950 Tg-C/yr estimated by *Hallquist et al.* [2009] (Table 3). Although more than 90% of the total OC is emitted from the land and less than 10% from the oceans (Table 1a), almost half of the total OC deposition occurs to the oceans, as calculated by TM4 (Table 3). Over the ocean, TM4 yields a total OC deposition flux of 246 Tg-C/yr that compares well with the total OC deposition to the oceans of 245 Tg-C/yr estimated by *Jurado et al.* [2008].

[13] Of the model-derived global total OC deposition flux, 489 Tg-C/yr are soluble OC, of which 230 Tg-C/yr are

Table 3. Annual OC Budget Terms Used in or Determined by the TM4-ECPL Model and Some Literature Values[a]

|	Emissions	Burden	DRY	WET	TOTgl	TOTo
OC gases	990	14	148 (148)	233 (233)[b]	381 (381)	166 (166)
OC particles	118	3	65 (36)	82 (73)	147 (109)	80 (64)
OC (g+p)	1108	17	213 (183)	315 (306)	528 (489)	246 (230)
OC[c]	1300 (g)				130–270 (g) 175–375 (p)	
OC[d]	1334 (g) 16 (p)				800 (g) 150 (p)	
OC[e]						187 (g) 58 (p)

[a]Fluxes are in Tg-C/yr; burdens are in Tg-C. Soluble OC is given in parentheses. DRY, dry deposition; WET, wet deposition; TOTgl, global total deposition; TOTo, total deposition to the oceans.

[b]Includes also semi-volatile precursors of SOA; (p), OC particles; (g), OC gases.

[c]*Goldstein and Galbally* [2007].

[d]*Hallquist et al.* [2009].

[e]*Jurado et al.* [2008].
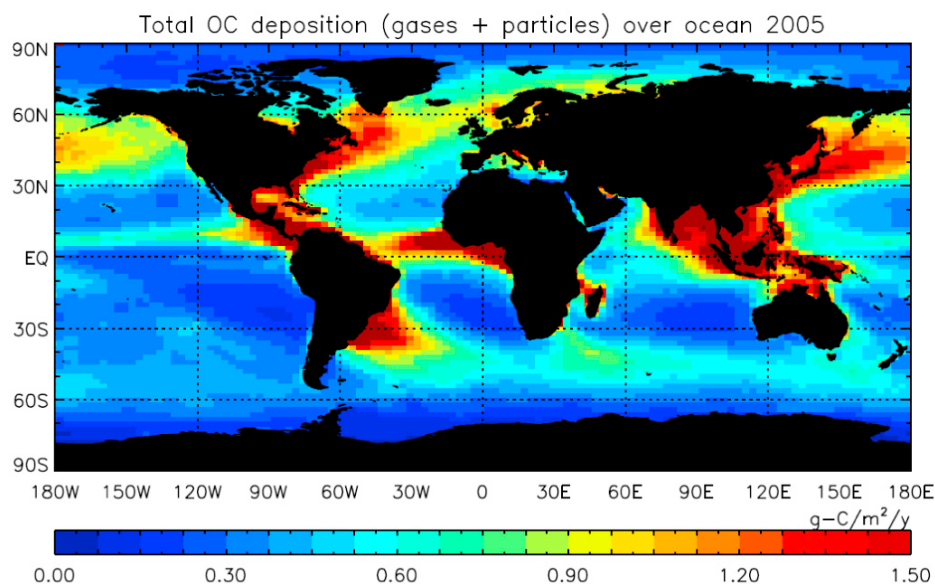
Figure 2. Deposition of soluble OC gases and particles to the oceans as computed by the TM4 model for the year 2005 (units g-C/m^2/yr).

deposited to the oceans. Figure 2 shows the annual global distribution of the deposition rates of all soluble OC components over the oceans; Figure S2 in Text S1 in the auxiliary material presents the rates of gaseous and particulate OC separately. The model-calculated global wet deposition of soluble OC, 306 Tg-C/yr (Table 3 and Figure S2 in Text S1 in the auxiliary material), compares well with an earlier estimate by *Willey et al.* [2000], 430 ± 150 Tg-C/yr, which was based on measured precipitation deposition of dissolved OC.

3.2. ON in the Atmosphere

[14] Available observations of ON in rainwater and aerosols are summarized in Tables S1 and S2 and in Figure S5 in Text S1 in the auxiliary material; they build upon recent compilations by *Cornell* [2010] and *Zamora et al.* [2011] which suggest that soluble ON contributes 10–80% of soluble total nitrogen.

3.2.1. Sources of ON

[15] We here estimate emissions of particulate ON (Table 2b) based on the OC emissions used in TM4 (Table 1b)

and using N:C molar ratios consistent with previous observations (Table 2b, discussion in section 2 and in Table S3 in Text S1 in the auxiliary material). Combined, the primary emissions of ON used in the model are ∼27.4 Tg-N/yr with a large uncertainty range, 2.1–95.4 Tg-N/yr. Of this total ∼46% is anthropogenic (Table 2b). Overall, model primary emissions total ∼128 Tg-N/yr which is comprised of both IN species (NO$_x$: 52.2 Tg-N/yr and NH$_3$: 47.9 Tg-N/yr, Table 2a) and organic N (27.4 Tg-N/yr, Table 2b). The chemical production of ON by gas phase chemistry followed by SOA formation is calculated to yield ∼10 Tg-N/yr.

3.2.2. Deposition of ON to the Ocean

[16] Based on the ON emissions in Table 2a and including the ON bound in gaseous OC oxidation products and in SOA compounds, TM4 yields a global atmospheric soluble ON deposition rate of 31.6 Tg-N/yr of which 15.9 Tg-N/yr (50%) (Table 4 and Figure 1) goes to the ocean (Figure 3a). ON gases contribute 30% to the global atmospheric soluble ON deposition. TM4 yields a global IN deposition rate of

Table 4. Calculated Annual Global Deposition Fluxes (in Tg-N/yr) of Soluble ON, Inorganic (IN), and Total (TN) Nitrogen[a]

|	TOTgl[b]	WETgl[b]	TOTo[b]	WETo[b]	TOTgl[c]	TOTo[d]
ON[e]	31.6 (48%)	19.3 (63%)	15.9 (38%)	9.4 (61%)	9.1 (up to 50)	20 (10–30)
	9.6 (g)	4.0 (g)	3.1(g)	1.0 (g)		
	22.0 (p)	15.3 (p)	12.8 (p)	8.4 (p)		
IN	90.7	61.1	36.6	27.5	83.8	47 (28–66)
	62.3 (g)	36.1 (g)	25.6 (g)	17.9 (g)		
	28.4 (p)	25.0 (p)	11.0 (p)	9.6 (p)		
TN[e]	122.3	80.4	52.5	36.9	92.9	67 (38–96)
ON/TN	0.26	0.24	0.30	0.25	0.10	0.30

[a]Soluble ON deposition fluxes are associated with at least a factor of 3 uncertainty in the emissions (Table 2b). For this work, the percent anthropogenic fraction of soluble ON deposition is in parentheses. TOTgl, global total deposition; TOTo, total deposition to the oceans; WETgl, global wet deposition; and WETo, wet deposition to the oceans. Range of earlier estimates is also provided in parentheses. Here (g): gases and (p): particles.
[b]This work.
[c]*Neff et al.* [2002].
[d]*Duce et al.* [2008].
[e]Including material of oceanic origin.
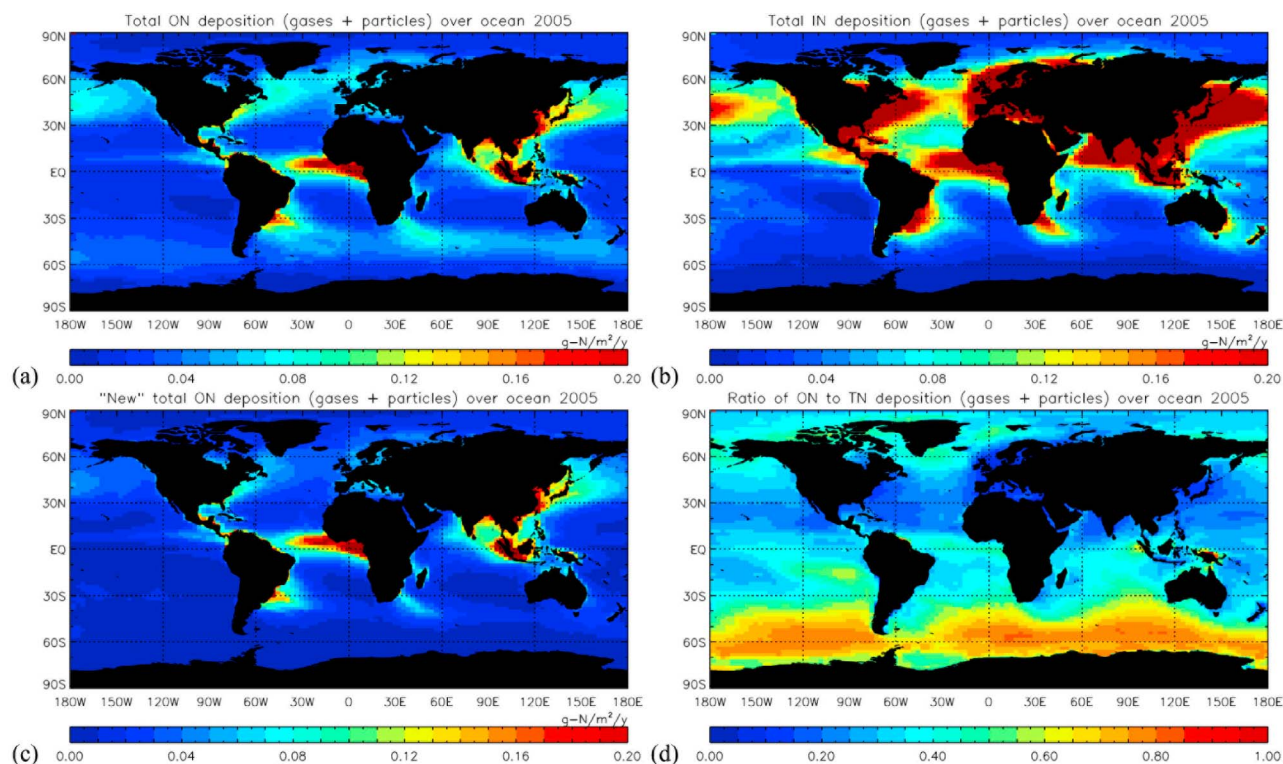
Figure 3. Deposition of N to the oceans as computed by the TM4 model for the year 2005 in g-N/m^2/yr: (a) Soluble ON (total 15.9 Tg-N/yr to the oceans), (b) IN not originating from the ocean (total 36.6 Tg-N/yr to the oceans), (c) 'new' soluble ON of terrestrial origin deposition to the oceans (total 10.7 Tg-N/yr to the oceans), and (d) ratio of soluble ON to soluble total N deposition.

90.7 Tg-N/yr of which 36.6 Tg-N/yr (40%) goes to the oceans (Table 4). The total N deposition to the oceans is 52.5 Tg-N/yr; of this, ~70% is IN and ~30% is soluble ON. These ON deposition estimates are uncertain by a factor of 5. The largest sources of uncertainty are in emission estimates, most notably those from combustion sources, as shown in Table 2b, and in the deposition velocities. Biomass burning global carbon emission estimates may vary by a factor of two due to the accumulation of associated uncertainties [*Keywood et al.*, 2012]. Major improvements in these estimates would be achieved by constraining estimates of combustion source of primary ON particles and the solubility of the ON species.

[17] Model OC tracers yield information on the origin of the deposited ON. Over the oceans, 38% of the soluble ON deposition (6.0 Tg-N/yr) is anthropogenic based on the origin of the N in OM and including the SOA from anthropogenic OC gases. An additional 29% (4.7 Tg-N/yr) is derived from non-oceanic natural emissions, and the remaining 33% (5.2 Tg-N/yr) is N recycled from the oceans. The TM4-calculated soluble ON deposition to the oceans is about 15.9 Tg-N/yr, a value close to that estimated by *Duce et al.* [2008], 20 Tg-N/yr (10–30 Tg-N/yr with 16 (8–24) Tg-N/yr attributed to human activities), and by *Neff et al.* [2002] for the global atmospheric ON deposition (between ~9 and 50 TgN/yr; Table 4). Figures 3a, 3b, and 3d depict the simulated annual global distributions of soluble ON and IN deposition to the oceans and the ratio of soluble ON to the soluble total N deposition, which includes both N-containing gases and particles. Figure 3c shows the annual distribution of terrestrially derived soluble ON deposited to the ocean; the terrestrial ON provides 'new' organic nutrients to marine ecosystems and thus supports new oceanic production in addition to that which might be supported by IN deposition. These figures clearly demonstrate the outflow of atmospheric pollution in the midlatitudes of the northern hemisphere and of biomass burning emissions, primary biogenic particles, and soil dust from the tropics that carry ON over the ocean. A comparison of the calculated and measured soluble ON deposition fluxes indicates that the model captures the observations within an order of magnitude (section S3 and Figure S5 in Text S1 in the auxiliary material).

[18] Table 5 provides the major budget terms for ON in the TM4 model. Although most (97%) of the primary ON is emitted as particles, the modeled atmospheric ON burden is equally shared between gases and particles. This results in an overall ON atmospheric turnover time of about 12 days that is twice as long as that of OC, most probably due to the lower solubility of the species in the ON pool.

3.3. OP in the Atmosphere

[19] Measurements of atmospheric OP are relatively few (summarized in Table S2 in Text S1 in the auxiliary material) and analytical methods require much improvement. Nonetheless, observations suggest that OP can be a significant component (up to 83%) of total P in rain and aerosol samples. Observed OP aerosol concentrations at coastal locations range from 0.01 to ~30 ng/m^3. Because of these limitations

Table 5. ON and OP Budget Terms Used in the TM4[a]

	Emission	Burden	CHEM	DRY	WET	TOTgl	TOTo
ON (g)	0.8	0.6	8.4	5.7 (5.7)	4.0 (4.0)	9.6 (9.6)	3.1 (3.1)
ON (p)	26.6	0.6	1.6	11.4 (7.0)	16.6(15.3)	28.1(22.0)	15.3(12.8)
ON(g + p)	27.4	1.2	10.0	17.1 (12.7)	20.7(19.3)	37.8(31.6)	18.5(15.9[$])
OP (p)	0.54	0.005	0.08[b]	0.36 (0.30)	0.18(0.10)	0.54(0.41)	0.43(0.35)[c]

[a]Fluxes are in Tg-N/yr and Tg-P/yr and burdens are in Tg-N and Tg-P for ON and OP, respectively; (g): gases and (p): particles. In parentheses are the calculated deposition values for soluble ON and OP. Deposition of gases is calculated based on solubility. CHEM, chemical production; DRY, dry deposition; WET, wet deposition; TOTgl, global total deposition; TOTo, total deposition to the oceans.
[b]Conversion of insoluble to soluble particles.
[c]Here 67% of ON deposition and 10% of OP deposition to the oceans is material of terrestrial natural and anthropogenic origin, thus providing new nutrients to the marine environment.

there are large uncertainties in the OP deposition estimates constructed and discussed here. In order to construct a more accurate global view of atmospheric OP cycling, we need measurements of OP emission factors from various P sources, systematic observations of atmospheric OP concentrations and properties (size distribution, solubility, and bioavailability), and deposition rates.

3.3.1. Sources of Atmospheric OP

[20] Based on the 50 Tg-OC/yr of primary emissions from the terrestrial biosphere (Table 1b), and a P:C molar ratio of 0.001 (Table 6 and section S4 in Text S1 in the auxiliary material), we estimate a global source of total OP of ~0.13 Tg-P/yr (0.01–4.26 Tg-P/yr). This value is comparable to the 0.16 Tg-P/y attributed to primary biogenic particles by *Mahowald et al.* [2008]. Considering that about half of this P is in a form readily available for plant uptake [*Doskey and Ugoagwu*, 1992], the soluble OP source is estimated to be ~0.06 (<0.01–2.13) Tg-P/yr.

[21] We estimate the soil dust source of OP based on both OC soil emissions (Table 1b) and soluble IP emissions associated with dust. Based on the soil-associated OC emissions and their uncertainty range (Table 1a), and an OP:OC molar ratio of 0.005 (Table 5) [*Cleveland and Liptzin*, 2007] (section S4 in Text S1 in the auxiliary material), we estimate the global OP soil-dust source to be 0.03 Tg-P/yr of which 10% is soluble (Table 1b). A slightly higher, but comparable, estimate of 0.04 Tg-P/yr (0.02–0.06) is computed from: a.) the correlation between dissolved IP and dust aerosol mass observed by *Zamora* [2010] at Miami and Barbados during dust events: b) the mean ratio of dissolved OP to

soluble total P of 16% (Table S3); and c.) the soluble fraction of the global dust source. The dust source strength used in TM4 was 1523 Tg/yr, a value comparable to the median of the 15 models in the AeroCom dust model intercomparison, 1123 Tg/yr [*Huneeus et al.*, 2011].

[22] The ocean is a major source of OP that is contained in the marine biota and is transferred to the atmosphere by sea-spray. Dissolved OP has been reported as the major soluble P component of aerosols in areas affected by oceans [*Graham and Duce*, 1979], although, as mentioned, measured dissolved OP can also contain inorganic polyphosphates. While OP recycled from the ocean does not provide new P to the marine ecosystem for fueling new oceanic production, it is calculated since it is an important part of the OP atmospheric cycle. Details of these calculations are provided in section S4 in Text S1 in the auxiliary material, and these estimates converge in the range of 0.19–0.66 Tg-P/yr.

[23] Measurements of anthropogenic sources have concentrated on the observation of total P and consequently information specific to OP is very limited (section S4 in Text S1 in the auxiliary material). There is a clear need for targeted observations of OP emitted from combustion sources. In the absence of more robust quantitative information on OP, we used a total P anthropogenic emissions estimate of 0.07 Tg-P/yr from *Mahowald et al.* [2005]. We further assume that OP is at most 50% of the total P emissions. Thus, the anthropogenic combustion source of OP is estimated to be <0.035 Tg-P/yr. Organophosphates are used in agricultural insecticides, ~0.07 Tg/yr for 1990–1998 [*FAO*, 2001]. We estimate this source using an OM:OP mass ratio of 5.5,

Table 6. Global Annual Particulate OP(p) Emissions (Tg-P/yr) Used in the TM4 Model Based on OC(p) Sources and the OP:OC Molar Ratios With the Uncertainty Range Given in Parentheses (see section 3.3.1)

Sources	Estimated From OC	Emission Range[a]	OP:OC Molar Ratio
Anthropogenic emissions[b]	0.05[c]	0.02–0.11	
Primary biogenic particles	0.06[c]	0.002–2.13	0.001 (0.0002–0.02)
Soil organic matter on dust	0.03[c,d]	0.01–0.15	0.005 (0.002–0.009)
Ocean	0.40[e]	0.19–0.80	
Total OP(p) Tg-P/yr	0.54	0.22–3.29	
Anthropogenic fraction	9%	1–77%	

[a]Based on uncertainties in OC emissions. (Table 1b) and element OP:OC ratios (this table).
[b]Based on total P estimates from *Mahowald et al.* [2005]; includes also agriculture–organophosphorus insecticides use, see text.
[c]Soluble fraction to be applied as for OC, Table 1b.
[d]An independent estimate of 0.04 (0.02–0.06) can be derived from dust emissions and correlations observed by *Zamora* [2010] as explained in the text.
[e]Based on the OP:Na mass ratio in marine aerosols and the global sea-salt emission (Na). Value adopted here; see section 3.3.1 and section S4 in Text S1 in the auxiliary material.
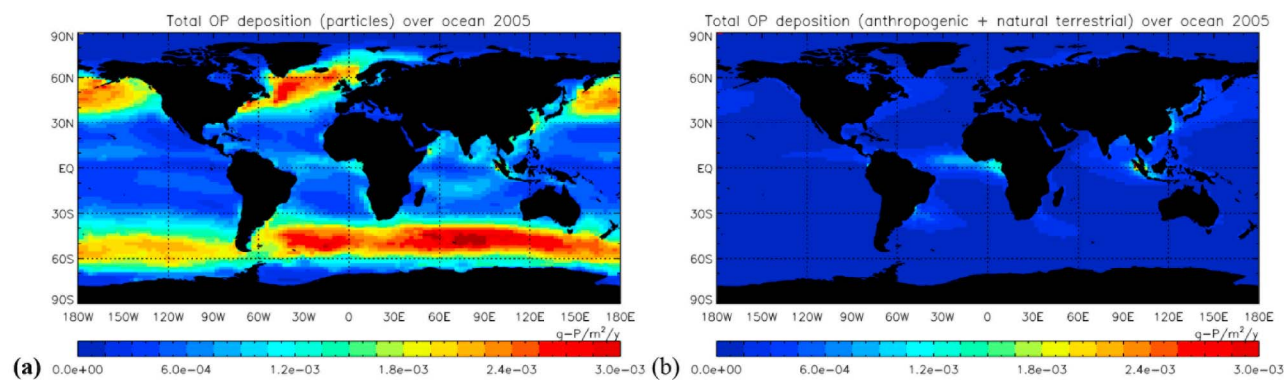
Figure 4. Deposition of soluble OP to the oceans as computed by the TM4 model for the year 2005 in g-P/m^2/yr: (a) Including soluble recycled OP (total 0.35 Tg-P/yr) and (b) using only 'new' soluble OP deposition to the oceans from anthropogenic and natural terrestrial sources; total 0.035 Tg-P/yr.

the mid-value of the range of values (3 to 8) derived from *Cook et al.* [1978]; this suggests that insecticides contribute an additional ~0.01 Tg-P/yr. Combined, these two anthropogenic sources of OP are estimated to be ~0.05 Tg-P/yr, with an order of magnitude uncertainty. They were incorporated in TM4 using the anthropogenic emission distributions of particulate OC. Overall, atmospheric sources of OP are calculated to be ~0.54 (0.22–3.29) Tg-P/yr of which ~0.33 (0.03–2.96) Tg-P/yr is soluble OP (Table 6 and Figure 1). An alternative picture of the soluble OP global source (0.13 Tg-P/yr) can be constructed based on the dissolved IP cycle evaluated by *Mahowald et al.* [2008] and the observed dissolved OP to dissolved total P ratio shown in Table S3. This estimate is about one third of that calculated here, although it lies within the uncertainty range shown in Table 6.

3.3.2. Deposition of OP to the Ocean

[24] Based on the TM4 OC simulations, we have constructed the OP atmospheric cycle (Figure 1) and deposition distribution over the oceans (Table 5 and Figure 4). The global OP burden is calculated to be 0.005 Tg-P (Table 5) of which ~40% is soluble; the mean turnover time due to deposition is 3.3 days. Wet deposition is responsible for about 36% of the OP removal and dry deposition is the main removal pathway (64%). The annual soluble OP deposition distribution over the oceans is shown in Figure 4 and is ~0.35 Tg-P/yr with another ~0.06 Tg-P/yr deposited on land. A comparison of the computed with measured OP deposition fluxes indicates that, as for ON, the model captures the magnitude of the observations but largely underestimates them (Figure S6 in Text S1 in the auxiliary material). Of the total soluble OP deposition to the ocean, ~6% is derived from pollution sources and ~3% from terrestrial emissions. Thus, ~10% of the soluble OP atmospheric deposition (~0.04 Tg-P/yr) constitutes 'new' P (Figure 4b), while the remaining 90% is recycled and as such does not support new oceanic production. An order of magnitude uncertainty is associated with these numbers as discussed earlier and depicted in Table 6. Interestingly, the ocean also impacts terrestrial ecosystems via the atmosphere. According to our model, transport and deposition of marine aerosols also provide about 28% of the OP deposited over land. This potential fertilizing effect of marine aerosols on coastal terrestrial ecosystems was previously suggested by *Graham and Duce* [1981]. Although the

calculated "new" OP deposition over the ocean is relatively small, it does provide external P to marine ecosystems and thus can support primary production in P-limited systems [*Okin et al.*, 2011].

4. Conclusions

[25] This work provides an updated picture of the role of OM in the global atmospheric transport and deposition of the nutrients N and P to the ocean (Figure 1). There is increasing observational evidence that a significant fraction of the atmospheric N and P deposition to the ocean occurs as ON and OP. Although the literature on ON and OP measurements is limited it suggests that the soluble ON fraction of total soluble N in rainwater ranges from ~3 to 90% (median ~35%) depending on location. While there are few studies of the bioavailability of atmospheric ON, they suggest that ~20 to 75% of the ON in atmospheric deposition is soluble and, thus, likely to be bioavailable. For P, the observed fraction of dissolved OP relative to dissolved total P in deposition ranges from ~20–83% (median ~35%). We hypothesize that this OP is likely bioavailable as well given the enzymatic capabilities of a multitude of phytoplankton to breakdown OP [*Benitez-Nelson*, 2000; *Paytan and McLaughlin*, 2007].

[26] Using global 3-dimensional chemistry transport TM4 model simulations, we estimate that ~70% of the global ON atmospheric source is derived from primary emissions while the remaining ~30% is chemically formed in the atmosphere. Our results also suggest that the global ON budget has a strong anthropogenic component, ~45% of the total source. In contrast, only ~10% of the OP is derived from human activities. We estimate the present-day deposition of soluble ON and IN to the global ocean to be about 16 Tg-N/yr and 37 Tg-N/yr respectively, of which about 40% of the ON and 80% of the IN are emitted from anthropogenic sources. Soluble OP deposition to the oceans is estimated to be 0.35 Tg-P/yr with ~6% being associated with anthropogenic activities and another ~3% with other terrestrial sources. For comparison, *Mahowald et al.* [2008] estimate IP deposition to the ocean at 0.24 Tg-P/yr with a ~14% anthropogenic contribution. Therefore it is expected that increasing anthropogenic emissions of N to the atmosphere will impact the ON cycle more rapidly than that of OP. Consequently the ratio of ON:OP will increase in atmospheric deposition to

the ocean and to terrestrial ecosystems, as will the inorganic N:P ratio [*Duce et al.*, 2008; *Okin et al.*, 2011]. These trends in atmospheric N:P deposition ratios are likely to contribute to shifts toward P-limitation of marine productivity [*Karl et al.*, 2001], with consequent effects on marine ecosystem diversity and community structure. Therefore, the emissions and atmospheric transport of both ON and OP should be incorporated in ocean biogeochemistry/climate models.

[27] There is very little observational data of atmospheric ON and OP concentration and composition and their deposition rates. Moreover there is little standardization in measurement protocols. Comprehensive information on the primary emissions of ON and OP to the atmosphere, in particular from anthropogenic sources, is needed. Innovative techniques should be developed to elucidate the origin and fate of nutrients, e.g., the use of isotopes [e.g., *Kelly et al.*, 2005; *Emeis et al.*, 2010]. The determination of the chemical nature of ON and OP deposition will provide information on the sources of ON and OP and their potential environmental impact. To this end it would be expedient to maximize the use of existing networks to incorporate the measurement of ON and OP in aerosols and deposition supplemented where possible by additional measurements of atmospheric gases and aerosols. There are national and international programs (e.g., SOLAS - Surface Ocean - Lower Atmosphere Study) whose objectives include the development of a better quantitative understanding of the key biogeochemical-physical interactions and feedbacks between the ocean and atmosphere. Measurements of ON and OP could logically find a place in these programs.

[28] It is especially important to make measurements at locations where high ON and OP deposition fluxes might be expected. These include those regions that are impacted by emissions from highly industrialized nations (e.g., the western and eastern North Atlantic and the western North Pacific) and regions heavily impacted by the transport of biomass burning emissions (e.g., the outflow from tropical Africa over the eastern tropical Atlantic, and the ocean bounding the islands and continental regions of Southeast Asia). However, we also need measurements in remote ocean regions where anthropogenic impacts are expected to be small. Such data are important to characterize "background" values and also to detect any trends over time that might indicate the growing (of waning) impact of anthropogenic sources. It is especially important to obtain measurements in the Southern Hemisphere which at this time is relatively little impacted. Figures 2, 3, and 4 can serve as guidance for the development of sampling strategies.

[29] Ultimately the impact of N and P deposition to the oceans will depend on how these materials are assimilated by marine organisms. The effectiveness of these atmospheric inputs in stimulating marine productivity will depend on their bioavailability, the time and location of the deposition, and the biogeochemical interactions in the surface waters [*Zamora et al.*, 2010]. Accordingly, we need well designed laboratory and field investigations of how, and under what circumstances, ON and OP are assimilated by marine ecosystems. Since the impact of atmospheric deposition depends on oceanic community structure and on the limiting factors in the region (light, nutrients, etc.), it is essential that measurements be made that take into consideration differences in season, organism community structure, circulation patterns, etc. Such information is critical in view of the large

anthropogenic contribution to the atmospheric N cycle and the more moderate anthropogenic contributions to the atmospheric P cycle. This increasing impact of human activity on nutrient deposition to the oceans is expected to alter the responses of the ecosystems and favor the growth and sustainability of species that are able to adapt and utilize atmospherically deposited ON and OP.

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