# Atmospheric fluxes of organic N & P to the global ocean



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- C/N/P cycles are coupled, mainly through photosynthetic fixation of these elements by biological activity.
- Biological productivity relies on the availability nutrients
- There is increasing evidence that significant fractions of N and P deposition occur as organic nitrogen (ON) and organic phosphorus (OP).
- Human activities have modified the atmospheric content and deposition fluxes of OC, ON and OP
- Critical biogeochemical feedbacks might exist between chemistry/climate/terrestrial and marine biosphere that involve the coupling of the C/N/P cycles.

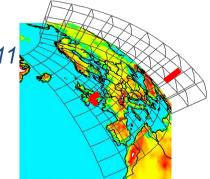


# 3-d global modeling of atmospheric deposition & data compilation

Use the global 3-d Chemistry Transport Model TM4-ECPL VOC /NOx/oxidants chemistry & all major aerosol components including primary & secondary OC, coupled with ISORROPIA II.

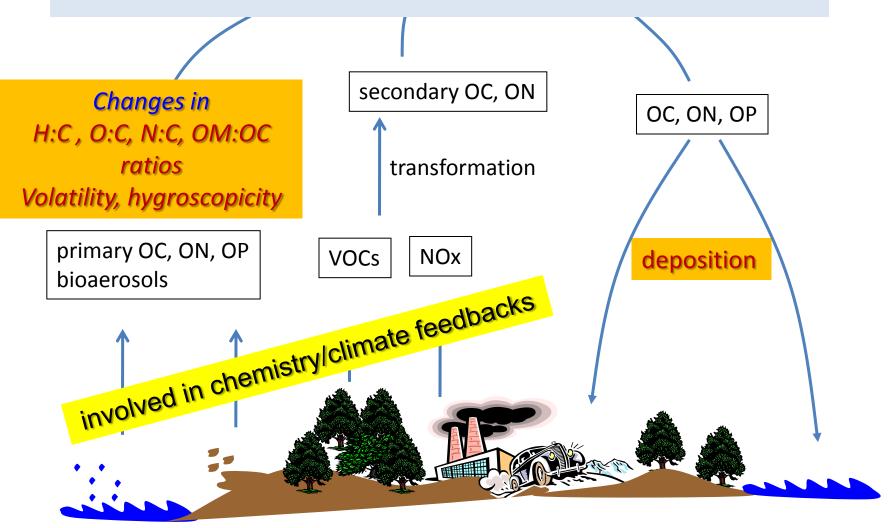
Myriokefalitakis et al., Atmos. Chem. Phys., 2008, Advances in Meteorology 2010, Atmos. Chem. Phys., 2011

Explicitly calculate IN gases and particles and ON in the gas phase

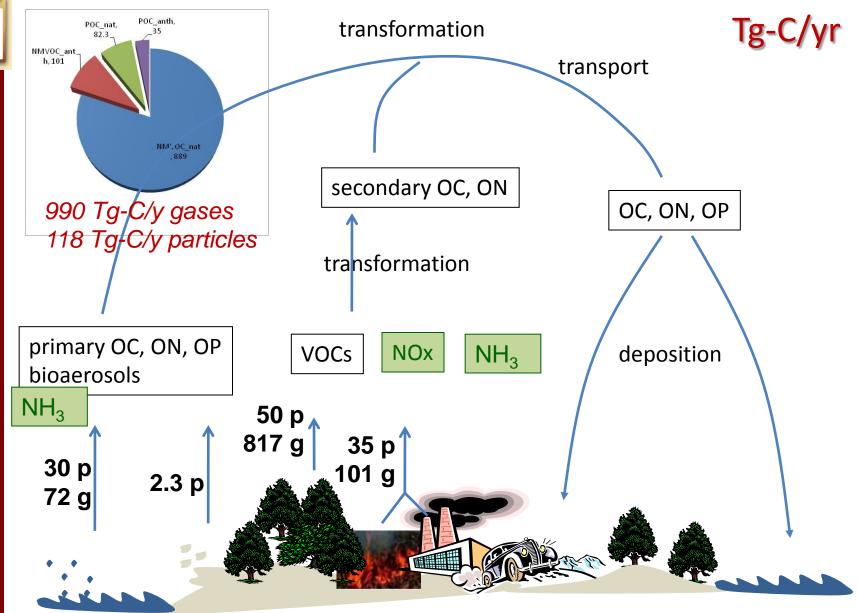


- Use observed ON/OC and OP/OC ratios in aerosols to calculate ON and OP in the particulate phase
- Present day simulations as in Kanakidou, et al. Global Biogeochemical Cycles, 2011GB004277, 2012 (anthropogenic CIRCE, biomass burning gfedv2, biogenic emissions POET)

Aim: Provide an updated picture of the role of organics in transporting nutrients particularly N and P to the oceans.



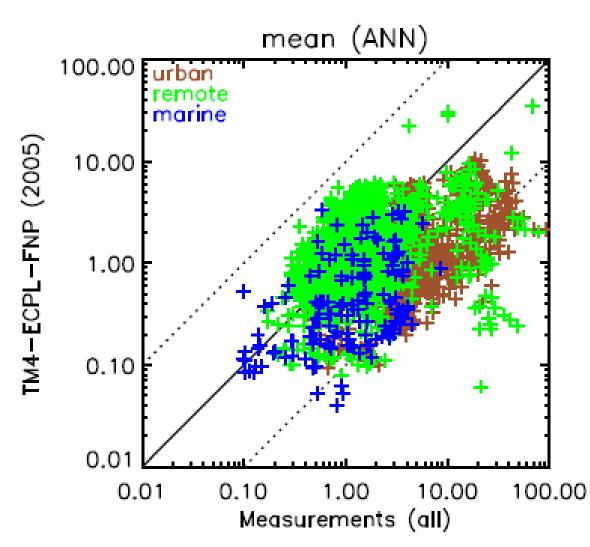
## Organic Carbon in the global atmosphere



Kanakidou et al., GBC, 2012



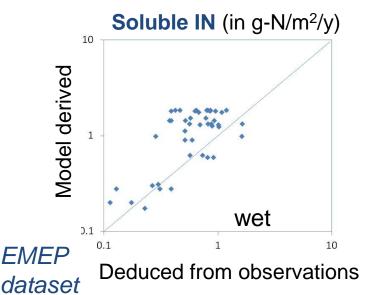
### Aerosol - Organic Carbon simulations versus observations (PM<sub>2.5</sub>)



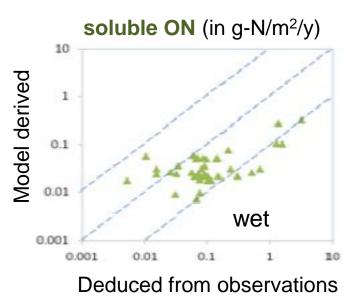
Evaluation as part of the AEROCOM – OA intercomparison – Tsigaridis et al in preparation

### Deposition of soluble IN,ON and OP comparison to observationally derived fluxes

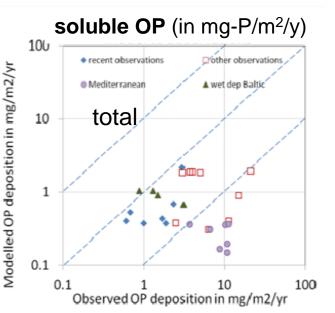
<u>E</u>



Depending on location, the observed water soluble ON fraction ranges from ~3% to 90% (median of ~35%) of total soluble N in rainwater; Soluble OP fraction ranges from ~20-83% (median of ~35%) of total soluble P.

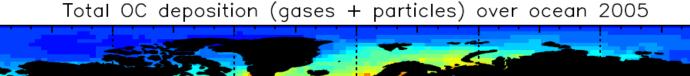


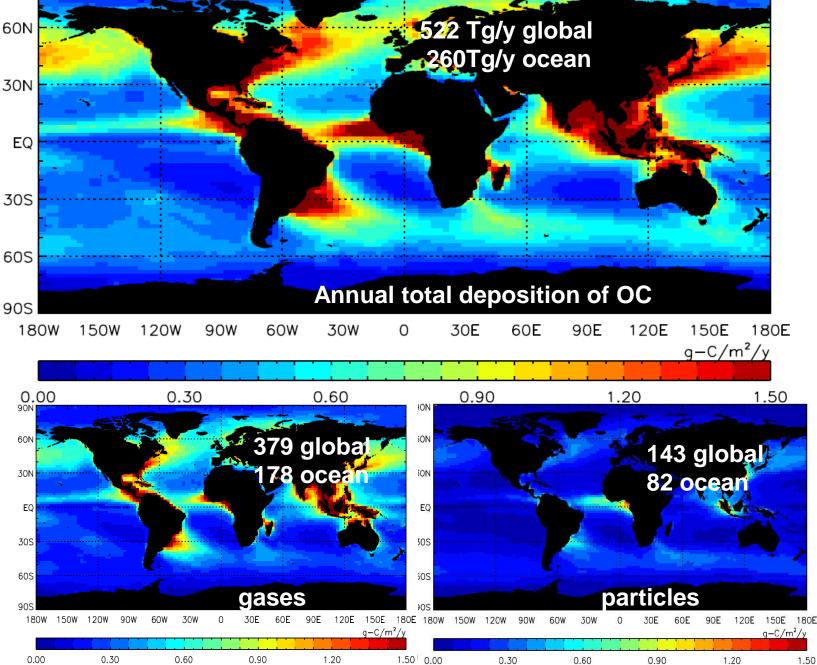
Kanakidou et al., GBC 2012



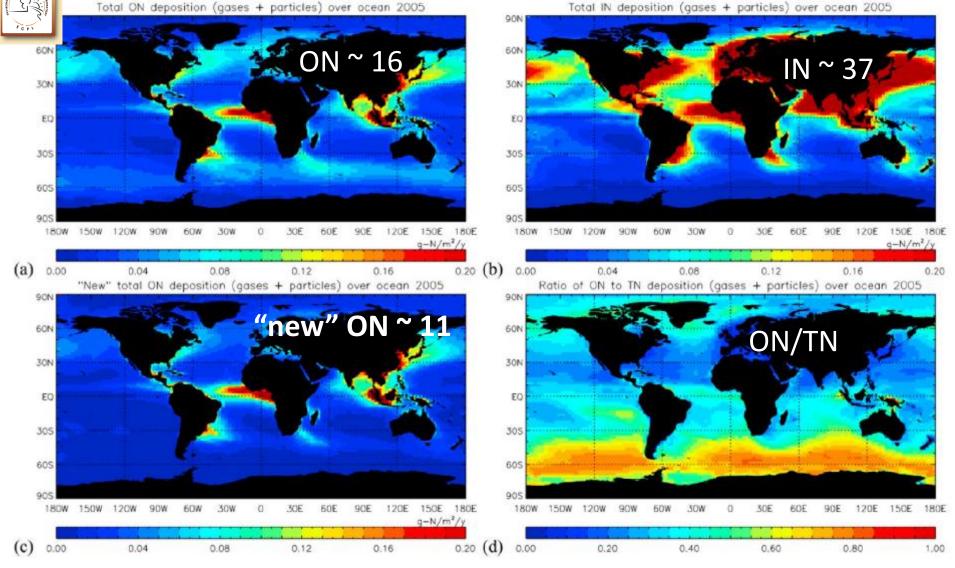


90N





### Soluble Nitrogen deposition over the ocean Tg-N/yr



Kanakidou, et al. GBC, 2011GB004277, 2012

CTITUE RSTITUE CTITUE CT

#### Organic Phosphorus Deposition

Deposition over sea 0.35Tg/y

6% anthropogenic 4% terrestrial natural 90% ocean recycling

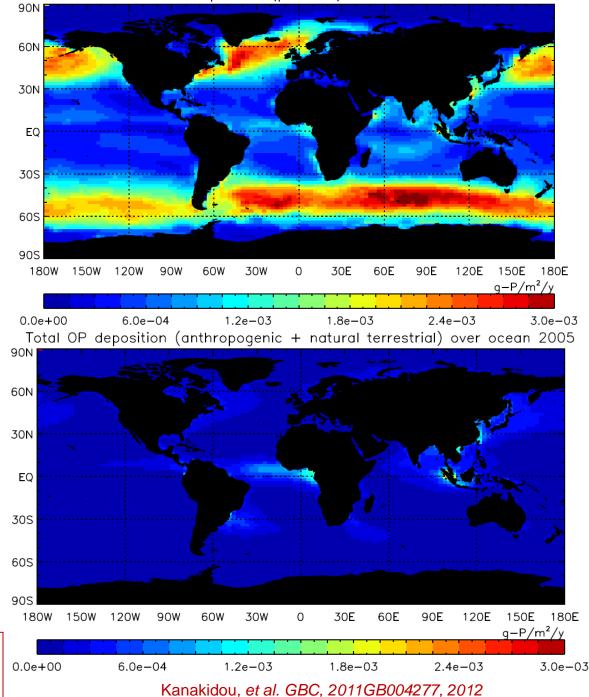
*Turn overtime 3.8 days* 

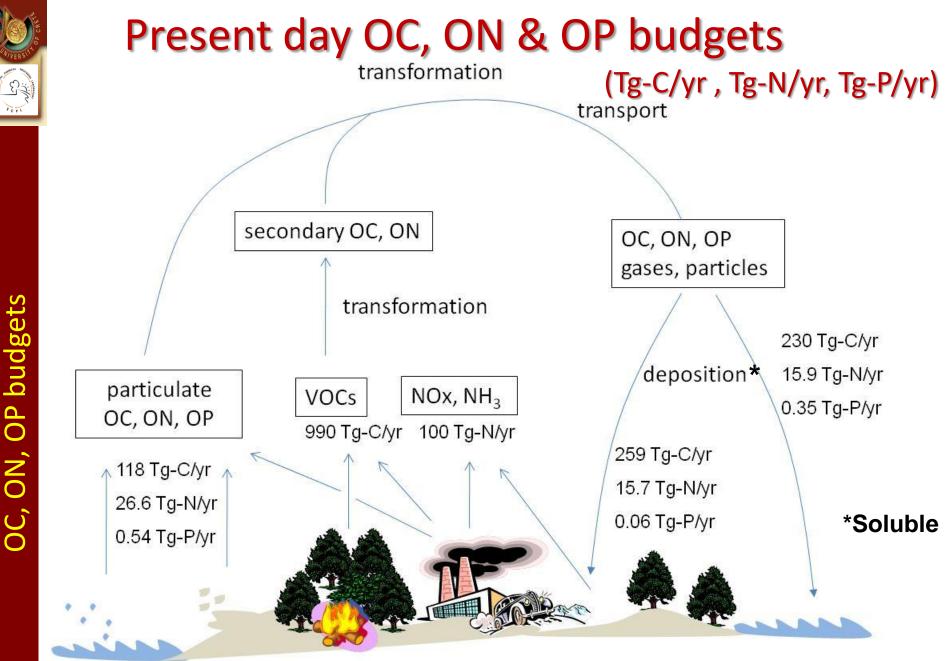
**'New' Organic Phosphorus Deposition** 

Deposition over sea 0.04Tg/y

Uncertainty at least an order of magnitude

Total OP deposition (particles) over ocean 2005





Kanakidou et al., GBC, 2012, doi 10.10.1029/2011GB004277

OC, ON, OP budgets



# Conclusions

- Present day global ON deposition is ~32 Tg-N/yr (~ 1/4 of TN)
- 4 ~40% of the ON deposition and ~45% of the total ON atmospheric source are associated with anthropogenic activities.
- 4 ~6% of the OP deposition and ~10% of the total OP atmospheric source are associated with anthropogenic activities.
- The model-derived present-day soluble ON and OP deposition to the global ocean is estimated to be ~16 Tg-N/yr and ~0.35 Tg-P/yr respectively with an order of magnitude uncertainty. Of these amounts 33% (ON) and 90% (OP) are recycled oceanic materials.
- Anthropogenic emissions might modify the N:P composition of atmospheric deposition of nutrients.

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# Recommendations

- The exact deposited amounts of the ON and OP to the global ocean and their assimilation by marine organisms are still an open question.
- **4** ON & OP should be taken into account in impact studies.
- Need for : More ON, OP observations & standardized
- Targeted observational experiments to parameterize the bounding of N & P on OC under clean and polluted atmospheres.

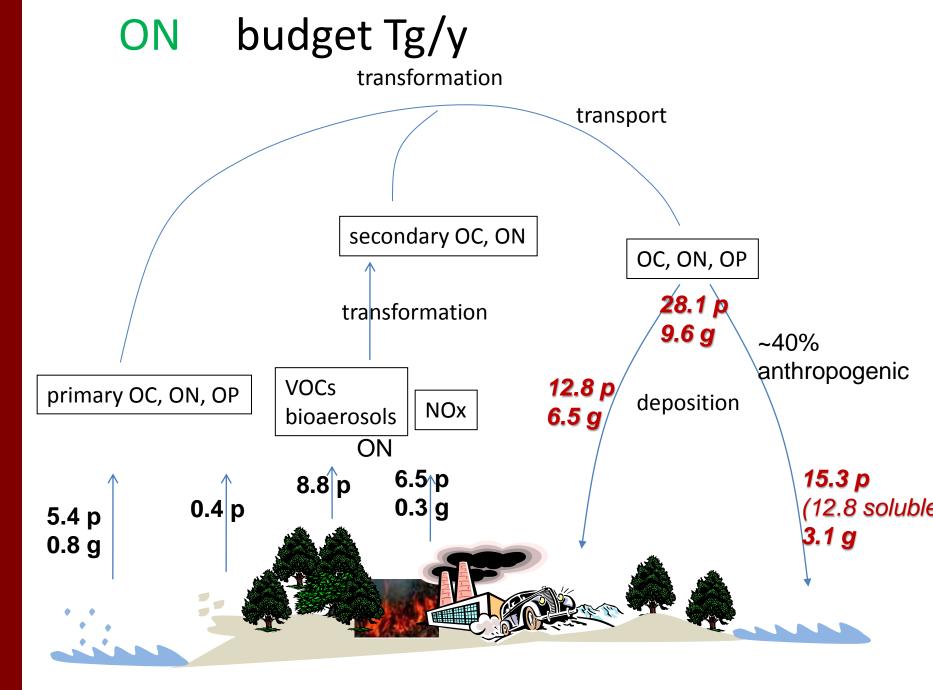
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#### GESAMP WG 38 team

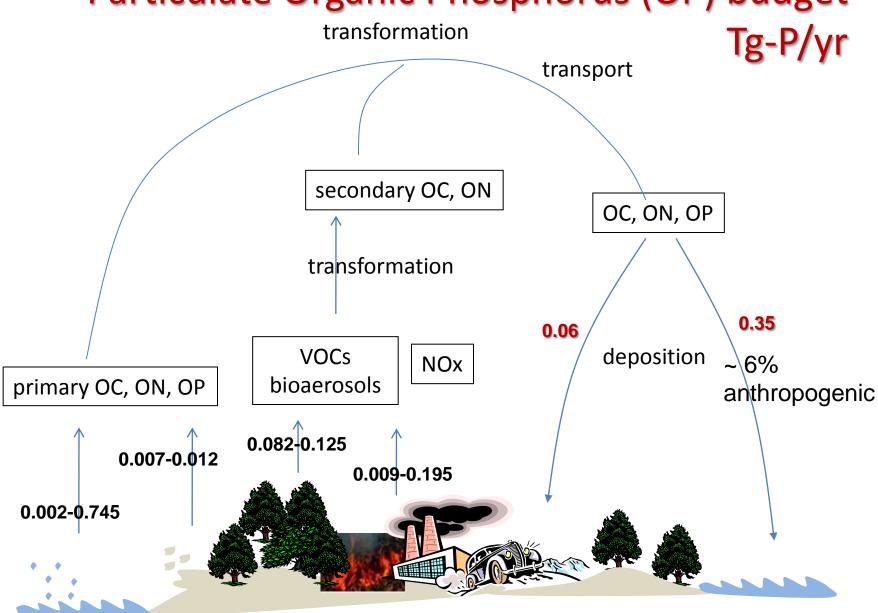
University of Crete PERSEUS – EU – FP7 project 7 h

CITYZEN – EU- FP6 project PEGASOS –EU-FP7 project ECLIPSE – EU- FP7 project



Kanakidou et al., GBC, 2012

#### Particulate Organic Phosphorus (OP) budget



Kanakidou et al., GBC, 2012

#### Table 1. NMOC Emissions

Emissions Tg/yr	Stevenson et al. 2006 IPCC TAR		Fiore et al. 2009 This work	
	Tg/yr	Tg/yr	Tg-C/yr	Tg-C/yr
biomass burning	31	42		37 <sup>&amp;</sup>
vegetation isoprene	580 *	249		442
terrestrial terpenes &other reactive VOC	295 *	144		375**
oceans biosphere- DMS	20 (Tg S/yr)	24		72 <sup>\$&amp;</sup>
Anthropogenic Emissions	116 -176	161		64 <sup>&amp;</sup>
Total NMVOC	1042-1102		630 ± 221	995

a) Global Anthropogenic, Biomass Burning and Natural Annual NMVOC Emissions - used in global models

 b) Global Anthropogenic, Biomass Burning and Natural Annual POC Emissions – used in TM4-ECPL and comparison with literature estimates, in Tg-C/yr except if differently indicated.

Emissions	Range in literature	This work
Biomass burning, biofuel, fossil fuel,	17 - 77ª	35
Primary biogenic particles (PBP)	7.5 – 82.5 <sup>b</sup>	50 <sup>&amp;</sup>
soil organic matter on dust	1.3- 34.5 <sup>c</sup>	2.3 <sup>&amp;</sup>
ocean	2-75	30.6 <sup>&amp;</sup>
Total POC Tg-C/yr	27.8 – 269 <sup>d</sup>	118

#### **Gaseous Organic Nitrogen**

 $VOC \rightarrow \rightarrow RONO2$ , PAN –like, SOA\_N

#### Particulate Organic Nitrogen emissions Tg-N/yr

Emissions	best estimate	estimated range <sup>\$</sup>
Biomass burning, biofuel, fossil fuel,	6.5	0.3-14.4
Primary biogenic particles (PBP)	8.8	0.1-16.4
soil organic matter on dust	0.4 <sup>&amp;</sup>	0.01-6.04
ocean PON	5.4 <sup>&amp;</sup>	0.3-13.2
Total PON Tg-N/yr	21.1	0.71-50.4
Ocean amines Tg N/yr	0.8	
CH₃CN (not accounted here)	0.28	

### Particulate Organic Phosphorus (OP) emissions

Sources	Range Tg-P/y	Best estimate	Estimated from TSP <sup>#</sup>
Biomass burning, biofuel, fossil fuel,	0.008-0.719	0.195	0.009
Primary biogenic particles (PBP)	0.001-0.825	0.125	0.082
soil organic matter on dust	0.003-0.138	0.007	0.0115
ocean	0.048-1.826	0.745 <sup>&amp;</sup>	0.0015
	0.8-3.2*	(1.6*)	
Total POP Tg-P/yr	0.060-4.882	1.072	0.072
Anthropogenic fraction <sup>\$</sup>		18%	12%

\* Based on Na content in the seawater, see text; <sup>&</sup> based on OC emissions and assuming a Redfield ratio; <sup>\$</sup> including biomass burning; <sup>#</sup> based on PO<sub>4</sub><sup>3-</sup> estimate by *Mahowland et al* [2008] and Table 8 observational data on OP/TSP.



# Comparison with literature

Soluble Nitrogen deposition Tg-N/y Global Ocean

	this work	Neff et al 2002	this work	Duce et al 2008 & Dentener et al 2005
ON	~32 (48% *)	9 -50	~16 (38%*)	20 (10-30)
	~10 (g) 22( p)		~ 3 (g) ~ 13 (p)	
IN	~ 91 ~ 62 (g) ~ 29 (p)	~ 84	~ 37 ~ 26 (g) 11 (p)	47 (28-66)
TN	~ 122	~ 93	~ 53	67 (38-96)
ON/TN	0.26	0.10	0.30	0.30

\* Anthropogenic contribution

# **Comparison with literature**

### **Organic Carbon – Emissions and Deposition**

Emissions Tg-C/yr	This work TM4-ECPL model	Goldstein& Galbally 2007	Hallquist et al 2009	
OC gases	990	1300	1334	
OC particles	118		16	
OC gas+ particles	1108			
Deposition Tg-C/yr Global (ocean)	This work TM4-ECPL model	Goldstein& Galbally 2007	Hallquist et al 2009	Jurado et al. (2008) (soluble)
	TM4-ECPL		•	
Global (ocean)	TM4-ECPL model	Galbally 2007	2009	(2008) (soluble)

