The impact of the atmospheric deposition of chemicals to the ocean

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What I Will Try To Do

- A little history - where we’ve come from in our understanding of deposition to the ocean and its measurement.

- Some examples of the impact of atmospheric deposition to the ocean, including the nutrients iron and nitrogen compounds as well as heavy metals, and other chemicals.

- The significant role played by GESAMP in this area.

- Where do we go next?
In the late 1980s great interest arose over John Martin’s suggestion that iron was a limiting nutrient for primary biological productivity in many regions of the world ocean. Questions then were raised about where the nutrient iron was coming from. Early studies indicated that it was coming primarily through the atmosphere in many regions. As far as the atmospheric source was concerned, it was soon clear that both iron (and another nutrient, phosphorus) largely enter the ocean from the atmosphere associated with mineral matter, or dust.

We will first consider the case of iron.

We will now consider some facts about atmospheric mineral matter, or dust.
A dust cloud coming off west Africa
Dust

There are old records dating back more than 2000 years in China about severe dust storms there.


“Finally I may remark, that the circumstance of such quantities of dust being periodically blown, year after year, over so immense an area in the Atlantic Ocean, is interesting, as showing by how apparently inefficient a cause a widely extended deposit may be in process of formation; …” Darwin, The Beagle, 1833
April, 1998 dust cloud from China moving across the Pacific Ocean. From Husar et al. (2001)
Predominant dust source regions and transport routes.

From Pye (1987) as reported in Jickells and Spokes (2001)
# Estimates of Global Dust Production

(Tg/yr)

<table>
<thead>
<tr>
<th>Reference</th>
<th>Emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Judson (1968)</td>
<td>60-360</td>
</tr>
<tr>
<td>Peterson &amp; Junge (1971)</td>
<td>500</td>
</tr>
<tr>
<td>SMIC (1971)</td>
<td>100-500</td>
</tr>
<tr>
<td>Joseph et al. (1973)</td>
<td>130-200</td>
</tr>
<tr>
<td>Jeanicke &amp; Matthias (1992)</td>
<td>1500-2000</td>
</tr>
<tr>
<td>Tegen &amp; Fung (1994)</td>
<td>3000</td>
</tr>
<tr>
<td>Andreae (1994)</td>
<td>1500</td>
</tr>
<tr>
<td>Ginoux et al. (2001)</td>
<td>1800</td>
</tr>
<tr>
<td>Zender et al. (2003)</td>
<td>1500</td>
</tr>
<tr>
<td>Tegen et al. (2004)</td>
<td>1800</td>
</tr>
<tr>
<td>Luo et al. (2003)</td>
<td>1650</td>
</tr>
<tr>
<td>Jickells et al. (2005)</td>
<td>1800</td>
</tr>
<tr>
<td>Grini (?)</td>
<td>2610</td>
</tr>
<tr>
<td>Mahowald (2007)</td>
<td>4500</td>
</tr>
</tbody>
</table>
Measurements of Dust in the Marine Environment

Joe Prospero began measuring dust on nylon meshes in Barbados in the mid-1960s.

This is a picture of Jarvis Moyers on a very early air/sea chemistry sampling tower in Hawaii in 1966.
Serendipity in the Pacific:

Dust observed at Enewetak Atoll at about 12°N in the west central North Pacific as part of the SEAREX Program in 1979.

(Duce et al., 1980, Science)
The first large scale dust monitoring network operated by the SEAREX Program and Hokkaido University, Japan in the 1980s.
Dust Sampling Towers in the Pacific

Hawaii

Samoa

Enewetak Atoll
The north tip of the North Island, New Zealand
Air sampling on board the R/V Moana Wave

(Picture taken in Honolulu Harbor)
Some Dust Results from the Pacific

Seasonal dust variability at Midway Island
AEROCE Network Sampling Sites in the Atlantic
Dust Sampling Towers in the Atlantic

Bermuda

Barbados

Mace Head, Ireland
Some Dust Results from the Atlantic


Courtesy of Joe Prospero
Episodic Character of the Dust

Mineral Dust (ug/m³)

Barbados: Daily Samples 2000

 Courtesy of
Joe Prospero
Episodic Character of Dust Fluxes

The atmospheric dust input to the ocean is very episodic, on daily, seasonal, and annual bases.

For example, at Midway, over 50% of the annual dust input occurred during three 1 week intervals.

At Miami, 22% of the annual input occurred in 1 day, and 68% of the annual input occurred in 4 days.
Certainly one of the reasons for the increased interest in dust has been the realization of the impact dust and its chemical components might have on marine biogeochemistry.

As mentioned earlier, particularly important in this regard has been iron.

While nitrogen has been generally considered to be the limiting nutrient in the ocean, it is useful to look at nitrogen in surface ocean productivity.
Surface Ocean Productivity

New production from NO$_3^-$ and N$_2$ fixation and atmospheric input

Phytoplankton

Regenerated production via NH$_4^+$, urea, amino acids, etc.

Animals and heterotrophic microorganisms

Export as sinking particles, fish catch, guano, etc.
Typical Surface Nitrate Concentrations in the East Central Pacific

(Derived from numerous references)

High nutrient, low chlorophyll regions (HNLC regions)

In HNLC regions iron, not nitrogen, is the likely limiting nutrient.
Iron in Mineral Dust

Average mineral matter contains \(~3.5\%\) iron, but only a small fraction of that iron is soluble and available to organisms.

The iron in mineral matter undergoes significant chemical changes in the atmosphere, primarily involving aqueous photochemical processes that include organic matter.
Mineral dust and iron transport to the ocean

Marine Phytoplankton Used as a micronutrient

Fe(II) & Fe(III) released
What nutrient really limits primary productivity in the ocean?

There has been considerable controversy about what the limiting nutrient is in the ocean. Many biologists have said that it is N, since the nitrogen in surface waters is often depleted while there is still P available. Others state that it is P, because nitrogen fixation can always take place in the ocean to replenish available N, but there is no similar source for P. Still others point out that in many HNLC regions there is plenty of both N and P, and it is Fe that is limiting.
Part of the problem relates to the time scale of interest. There are two definitions of importance in this regard:

• A “proximate limiting nutrient” is the local limiting nutrient on a short time scale.

• An “ultimate limiting nutrient” is the nutrient which controls system productivity over long time scales.
With this idea in mind, it might appear that the proximate limiting nutrient in the ocean is usually either N or Fe. However, others suggest that the ultimate limiting nutrient on very long time scales is P, i.e. when N gets low, cyanobacteria can fix N\textsubscript{2} for biological use, but when P runs out there is no similar atmospheric source for P (it is very minor in most regions).

How can we be sure where the iron is coming from?
Sources of New Nutrients
(Simple Model)

- Dry Deposition
- Wet Deposition
- Photic Zone
- Nitrogen Fixation
- Advection (Upwelling)
- Eddy Diffusion
## Comparison of Iron Source Strengths in the Sargasso Sea and the North Pacific Gyre

<table>
<thead>
<tr>
<th>Source</th>
<th>Sargasso Sea</th>
<th>North Pacific Gyre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertical advection</td>
<td>0 - 1.5</td>
<td>0.3 - 0.6</td>
</tr>
<tr>
<td>Eddy diffusion</td>
<td>1.2 - 7.3</td>
<td>1.2 - 7.3</td>
</tr>
<tr>
<td>Atmospheric deposition</td>
<td>70 - 300</td>
<td>30 - 60</td>
</tr>
<tr>
<td>TOTAL</td>
<td>71 - 310</td>
<td>32 - 68</td>
</tr>
<tr>
<td>ATMOSPHERIC INPUT</td>
<td>88 - 99%</td>
<td>79 - 98%</td>
</tr>
</tbody>
</table>

Modified from Duce (1987)
To evaluate the importance of iron from dust, we needed to have some sense of the rate and geographical distribution of the deposition of dust to the oceans.
Estimate of Dust Flux to the Oceans
(Duce et al., 1991 from GESAMP R&S No. 38)

This was significantly improved on by models by Tegen et al., Ginoux et al. and others, with the latest being:
Estimate of Dust Flux to the Oceans
(Jickells et al. (2005))

Average dust deposition (g/m²/year)

GESAMP 36
Geneva, Switzerland
27-30 April 2009
Atmospheric Fe Flux

Fe fluxes, mg/m²/month

From Gao et al. (2001)
Dust particles observed in the atmosphere just north of Oahu, Hawaii.

From Betzer et al. (1988)
But really how good are our estimates of dust deposition to the ocean or to the land surface?
Large discrepancies were found between modeled and measured dust deposition in a study by Prospero and others in Florida.
Conclusions about those model comparisons

• Models yielded widely varying results.
• Most models seriously underestimated dust deposition rates.
• Most models yielded strong latitudinal gradients not observed in FAMS.
• Model wet-to-dry ratios varied widely, reflecting large difference in deposition schemes.

They concluded that a proper comparison was needed:

• To better understand how the models perform,
• To identify the factors most important to improved performance.
Iron Perturbation Studies

This interest in dust and iron has lead to a series of iron perturbation studies in a number of ocean regions to determine whether the addition of iron in iron-limited regions has a significant impact on ocean biogeochemistry, and in particular on the sequestration of carbon.

These studies have been primarily in high nutrient, low chlorophyll (HNLC) regions, where iron has been artificially added to surface seawater and the impact of this addition on the biology and chemistry of the artificial patch has been followed.

One particularly interesting such study, SOIREE, took place in the Southern Ocean south of New Zealand.
Location of the SOIREE experiment

From Boyd et al. (2000)
Some SOIGREE results

From Boyd et al. (2000); Turner et al. (2002)
The SOIREE patch about 30 days after formation

From Abraham et al. (2000)
Surface water fCO$_2$ during SOIREE
From Watson et al. (2000)

Days since addition of iron
SEEDS 1 and 2 were similar experiments carried out by the Japanese and the Canadians in the Northwest Pacific.
SEEDS 1 Results

Plankton net samples (100mm, 0-20m) in the patch on day 2 and day 11

Slide courtesy of Peter Liss
But the results for SEEDS 2 the next year were very different.
7-day backward trajectories during July, 2003 - SEEDS I

Longitude, °E

2003

Slide courtesy of Peter Liss
The climatic implications may be significant as well.

Note the positive correlation between iron and MSA as well as the negative correlation with CO$_2$ in this Antarctic ice core.

From Turner et al. (1996)
Atmospheric Anthropogenic Nitrogen

Let’s take a look at atmospheric anthropogenic nitrogen deposition to the ocean. Nitrogen is also a critical, and in many areas, limiting nutrient. Thus there is the potential for additional input of anthropogenic nitrogen to have an impact on primary productivity.

Humans have been injecting increasing amounts of nitrogen species into the atmosphere, particularly from the combustion of fossil fuels and the formation and use of fertilizers.

But the geographical distribution of these injections are expected to change significantly in the future.
Increase in Fertilizer N Production, 1990-2020

Asia, 87%
Africa, 6%
US/Canada, 2%
C/So America, 5%

Courtesy of James Galloway
Increase in NOx Emissions, 1990 to 202

- Asia: 40%
- C/So America: 18%
- Africa: 15%
- FSU: 15%
- US/Canada: 10%
- Europe: 1%
- Australia: 1%

Courtesy of James Galloway
A workshop was held in late 2006 at the University of East Anglia in Norwich, UK that addressed the impacts of the deposition of atmospheric anthropogenic nitrogen on the open ocean. A paper from this workshop was subsequently published in Science in May, 2008.
Total Atmospheric Reactive Nitrogen Deposition in 1860 in mg m$^{-2}$ yr$^{-1}$

Total Atmospheric Reactive Nitrogen Deposition in 2000 in mg m$^{-2}$ yr$^{-1}$

(From Duce et al., 2008)
Ratio of the projected nitrogen flux in 2030 to that in 2000

(From Duce et al., 2008)
Early estimates of the deposition of atmospheric nitrogen did not consider organic forms of atmospheric nitrogen, only inorganic forms.

<table>
<thead>
<tr>
<th>Location</th>
<th>DON as a % of Total N in Rain</th>
</tr>
</thead>
<tbody>
<tr>
<td>NE Atlantic</td>
<td>65</td>
</tr>
<tr>
<td>NW Atlantic</td>
<td>59</td>
</tr>
<tr>
<td>Central Pacific</td>
<td>63</td>
</tr>
<tr>
<td>Hawaii</td>
<td>19</td>
</tr>
</tbody>
</table>

From Cornell et al. (2001)
## Atmospheric Nitrogen Emissions and Deposition to the Ocean (Tg N yr\(^{-1}\))

<table>
<thead>
<tr>
<th></th>
<th>1860</th>
<th>2000</th>
<th>2030</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Emission to the Atmosphere:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total NO(_x)</td>
<td>13</td>
<td>52</td>
<td>54</td>
</tr>
<tr>
<td>Anthropogenic NO(_x)</td>
<td>2.6</td>
<td>38</td>
<td>43</td>
</tr>
<tr>
<td>Total NH(_3)</td>
<td>21</td>
<td>64</td>
<td>78</td>
</tr>
<tr>
<td>Anthropogenic NH(_3)</td>
<td>7.4</td>
<td>53</td>
<td>70</td>
</tr>
<tr>
<td>Total Atmospheric N Emissions</td>
<td>34</td>
<td>116</td>
<td>132</td>
</tr>
<tr>
<td>Total Anthropogenic N(_r) (AAN)</td>
<td>10</td>
<td>91</td>
<td>113</td>
</tr>
<tr>
<td><strong>Deposition to the Ocean:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total NO(_y)</td>
<td>6.2</td>
<td>23</td>
<td>25</td>
</tr>
<tr>
<td>Anthropogenic NO(_y)</td>
<td>1.2</td>
<td>17</td>
<td>18</td>
</tr>
<tr>
<td>Total NH(_x)</td>
<td>8</td>
<td>24</td>
<td>29</td>
</tr>
<tr>
<td>Anthropogenic NH(_x)</td>
<td>2.4</td>
<td>21</td>
<td>25</td>
</tr>
<tr>
<td>Total organic N(_r)</td>
<td>6.1</td>
<td>20</td>
<td>23</td>
</tr>
<tr>
<td>Anthropogenic organic N(_r)</td>
<td>2.1</td>
<td>16</td>
<td>19</td>
</tr>
<tr>
<td>Total N(_r) Deposition</td>
<td>20</td>
<td>67</td>
<td>77</td>
</tr>
<tr>
<td>Total Anthropogenic N(_r) (AAN)</td>
<td>5.7</td>
<td>54</td>
<td>62</td>
</tr>
</tbody>
</table>
Atmospheric Nitrogen Deposition to the Ocean in 2000 and its Impact on Productivity

<table>
<thead>
<tr>
<th>Global Ocean Anthropogenic Nitrogen (Tg N yr(^{-1}))</th>
<th>Resultant Global Ocean Productivity (Pg C yr(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>~54</td>
<td>~0.31</td>
</tr>
</tbody>
</table>
Impacts

Atmospheric anthropogenic nitrogen (AAN) input to the ocean accounts for up to ~3% of the annual new oceanic primary productivity (which is about 11 Pg C yr⁻¹) and about 1/3 of that generated from all external sources (which is about 0.95 Pg C yr⁻¹).

Atmospheric inputs approach N₂-fixation as a source of reactive nitrogen in the open ocean.

Present day anthropogenic carbon uptake by the ocean is ~2.2 ± 0.5 Pg C yr⁻¹ (IPCC, 2007). Thus the 0.3 Pg C yr⁻¹ from nitrogen fertilization may account for ~10% of the anthropogenic CO₂ uptake by the ocean from the atmosphere, thus helping to reduce radiative forcing.
Impacts (Continued)

The input of AAN also likely stimulates N<sub>2</sub>O emissions (~1.6 Tg N yr<sup>-1</sup>) and could account for ~1/3 of its emission from the ocean and ~1/4 of the total anthropogenic flux of N<sub>2</sub>O.

~2/3 of the decrease in radiative forcing resulting from increased CO<sub>2</sub> drawdown by nitrogen fertilization may be offset by increased radiative forcing by the additional N<sub>2</sub>O.

Clearly human-derived nitrogen entering the ocean from the atmosphere cannot be ignored.
Lead deposition to the ocean, early 1980s
Atmospheric and Marine Lead Near Bermuda

From Duce (2008)
## Global Input of Metals to the World Ocean

<table>
<thead>
<tr>
<th>Form</th>
<th>Pb (10^9 g/y)</th>
<th>Cd (10^9 g/y)</th>
<th>Cu (10^9 g/yr)</th>
<th>Ni (10^9 g/yr)</th>
<th>Zn (10^9 g/yr)</th>
<th>As (10^9 g/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric Input</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dissolved</td>
<td>50 - 100</td>
<td>1.9 - 3.3</td>
<td>14 - 45</td>
<td>8 - 11</td>
<td>33-170</td>
<td>2.3 - 5</td>
</tr>
<tr>
<td>Particulate</td>
<td>6 - 12</td>
<td>0.4 - 0.7</td>
<td>2 - 7</td>
<td>14 - 17</td>
<td>11 - 55</td>
<td>1.3 - 3</td>
</tr>
<tr>
<td>Riverine Input</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dissolved</td>
<td>2</td>
<td>0.3</td>
<td>10</td>
<td>11</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>Particulate</td>
<td>1600</td>
<td>15</td>
<td>1500</td>
<td>1400</td>
<td>3900</td>
<td>80</td>
</tr>
</tbody>
</table>

(From GESAMP R&S No. 38)
### Global Input of Organochlorine Compounds to the World Ocean

<table>
<thead>
<tr>
<th>Compound</th>
<th>Atmospheric Input (10^6 g/yr)</th>
<th>Riverine Input (10^6 g/yr)</th>
<th>% Atmospheric</th>
</tr>
</thead>
<tbody>
<tr>
<td>∑ HCH</td>
<td>4800</td>
<td>60</td>
<td>99</td>
</tr>
<tr>
<td>∑ PCB</td>
<td>240</td>
<td>60</td>
<td>80</td>
</tr>
<tr>
<td>∑ DDT</td>
<td>170</td>
<td>4</td>
<td>98</td>
</tr>
<tr>
<td>Chlordane</td>
<td>22</td>
<td>4</td>
<td>85</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>43</td>
<td>4</td>
<td>91</td>
</tr>
<tr>
<td>HCB</td>
<td>77</td>
<td>4</td>
<td>95</td>
</tr>
</tbody>
</table>

(From GESAMP R&S No. 38)
Where do we go from here?

In the early 1990s, as part of the ICSU International Geosphere/Biosphere Program (IGBP) a new international research program was initiated: SOLAS - Surface Ocean/Lower Atmosphere Study

SOLAS was formed specifically to address the exchange of chemicals between the atmosphere and ocean and their impact on biogeochemical cycles and climate
The SOLAS Domain
GESAMP Working Group 38
The Atmospheric Input of Chemicals to the Ocean

First meeting at the University of Arizona, Tucson, AZ, from 10-14 December 2008.

Sponsors include the WMO, IMO, SCOR, SIDA, European Commission Joint Research Centre, and the University of Arizona

Co-Chairs are: Robert Duce, USA, and Peter Liss, United Kingdom.
Members of the Working Group are:
- Alex Baker - United Kingdom
- Frank Dentener - Italy
- Keith Hunter - New Zealand
- Maria Kanakidou - Greece
- Nilgun Kubilay - Turkey*
- Natalie Mahowald - United States
- Greg Okin - United States
- Joseph Prospero - United States
- Manmohan Sarin - India*
- Vanisa Surapipith - Thailand
- Ina Tegen - Germany*
- Mitsuo Uematsu - Japan
- Tong Zhu - China

* Unable to attend the first meeting
The charge for WG 38 is as follows:

I. Assess the need for the development of new model and measurement products for improving our understanding of the impacts of the atmospheric deposition of nitrogen species and dust (iron) to the ocean.

II. Review the present information on the atmospheric deposition of phosphorus species to both the marine and terrestrial environments, considering both natural and anthropogenic sources, and evaluate the impact of atmospheric phosphorus deposition on marine and terrestrial ecosystems. Consider whether such a review of any other substances would be useful.

III. Work with the WMO Sand and Dust Storm Warning and Assessment System and with the WMO Precipitation Chemistry Data Synthesis and Community Project to evaluate the needs of the marine community and assist in clearly articulating them in the development of these WMO efforts.
Thank you!
From Boyd et al. (2000); Turner et al. (2002)
AEROCE air sampling tower in Bermuda

AEROCE air sampling tower at Mace Head, Ireland
In particular there have been a number of iron perturbation studies undertaken, primarily in high nutrient, low chlorophyll regions, where iron has been artificially added to surface seawater and the impact of this addition on the biology and chemistry of the artificial patch was followed. One particularly interesting such study, SOIREE, took place in the Southern Ocean south of New Zealand.