

could lead to an acceleration of warming, while changes in others could lead to cooling. It is, thus, important to understand the factors controlling trace gas dynamics in the surface ocean.

## See also

**Air–Sea Gas Exchange. Air–Sea Transfer:  $\text{N}_2\text{O}$ , NO,  $\text{CH}_4$ , CO. Atmospheric Input of Pollutants. Carbon Cycle. Chlorinated Hydrocarbons. Nitrogen Cycle.**

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## $\text{N}_2\text{O}$ , NO, $\text{CH}_4$ , CO

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## Introduction

The atmospheric composition is maintained by abiotic and biotic processes in the terrestrial and marine ecosystems. The biogenic trace gases nitrous oxide ( $\text{N}_2\text{O}$ ), nitric oxide (NO), methane ( $\text{CH}_4$ ) and carbon monoxide (CO) are present in the surface mixed layer over most of the ocean, at concentrations which exceed those expected from equilibration with the atmosphere. As the oceans occupy 70% of the global surface area, exchange of these trace gases across the air–sea interface represents a source/sink for global atmospheric budgets and oceanic biogeochemical budgets, although marine emissions of NO are poorly characterized. These trace gases contribute to global change directly and indirectly, by influencing the atmospheric oxidation and radiative capacity (the ‘greenhouse effect’) and, together with their reaction products, impact

stratospheric ozone chemistry (Table 1). The resultant changes in atmospheric forcing subsequently influence ocean circulation and biogeochemistry via feedback processes on a range of timescales. This article describes the marine sources, sinks, and spatial distribution of each trace gas and identifies the marine contribution to total atmosphere budgets. There is also a brief examination of the approaches used for determination of marine trace gas fluxes and the variability in current estimates.

## Nitrous Oxide ( $\text{N}_2\text{O}$ )

The  $\text{N}_2\text{O}$  molecule is effective at retaining long-wave radiation with a relative radiative forcing 280 times that of a  $\text{CO}_2$  molecule. Despite this the relatively low atmospheric  $\text{N}_2\text{O}$  concentration results in a contribution of only 5–6% of the present day ‘greenhouse effect’ with a direct radiative forcing of about  $0.1 \text{ Wm}^{-2}$ . In the stratosphere  $\text{N}_2\text{O}$  reacts with oxygen to produce NO radicals, which contribute to ozone depletion.

$\text{N}_2\text{O}$  is a reduced gas which is produced in the ocean primarily by microbial nitrification and denitrification.  $\text{N}_2\text{O}$  is released during ammonium

**Table 1** The oceanic contribution and atmospheric increase and impact for methane, nitrous oxide, nitric oxide, and carbon monoxide<sup>a</sup>

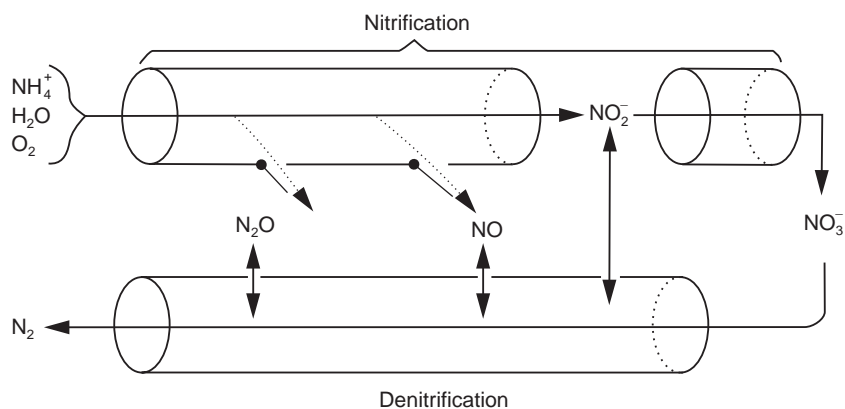
Trace gas	Atmospheric concentration (ppbv)	Atmospheric lifetime (years)	Major impact in atmosphere	Increase in atmosphere (1980-90)	Oceanic emission as % of total global emissions
Nitrous oxide (N <sub>2</sub> O)	315	110-180	Infrared active Ozone sink/source	0.25% (0.8 ppbv y <sup>-1</sup> )	7-34%
Nitric oxide (NO)	0.01	< 0.2	Ozone sink/source OH sink/oxidation capacity	Not known	Not known
Methane (CH <sub>4</sub> )	1760	10	Infrared active OH sink/oxidation capacity	0.8% (0.6 ppbv y <sup>-1</sup> )	1-10%
Carbon monoxide (CO)	120	0.2-0.8	Ozone sink/source OH sink/oxidation capacity Ozone sink/source Infrared active	- 13 to 0.6%	0.9-9%

<sup>a</sup>ppbv, parts per billion by volume. (Adapted from Houghton *et al.*, 1995.)

(NH<sub>4</sub><sup>+</sup>) oxidation to nitrite (NO<sub>2</sub><sup>-</sup>) (Figure 1), although the exact mechanism has yet to be confirmed. N<sub>2</sub>O may be an intermediate of nitrification, or a by-product of the decomposition of other intermediates, such as nitrite or hydroxylamine. Nitrification is an aerobic process, and the N<sub>2</sub>O yield under oxic conditions is low. However, as the nitrification rate decreases under low oxygen, the relative yield of N<sub>2</sub>O to nitrate production increases and reaches a maximum at 10-20 μmol dm<sup>3</sup> oxygen (μmol = 1 × 10<sup>-6</sup> mol). Conversely, denitrification is an anaerobic process in which soluble oxidized nitrogen compounds, such as nitrate and nitrite, are converted to volatile reduced compounds (N<sub>2</sub>O and N<sub>2</sub>) in the absence of oxygen. Oxygen availability inhibits denitrification at ambient levels, and also determines the products of denitrification. An enzymatic gradient of sensitivity to oxygen results

in the accumulation of N<sub>2</sub>O under sub-oxia (3-10 μmol dm<sup>3</sup>) due to the inhibition of the enzyme nitrous oxide reductase. At lower oxygen (< 3 μmol dm<sup>3</sup>) the reaction continues through to N<sub>2</sub> and so anoxic environments are sinks for N<sub>2</sub>O. N<sub>2</sub>O yields from nitrification are 0.2-0.5%, whereas denitrification yields may be as high as 5% at optimal levels of sub-oxia.

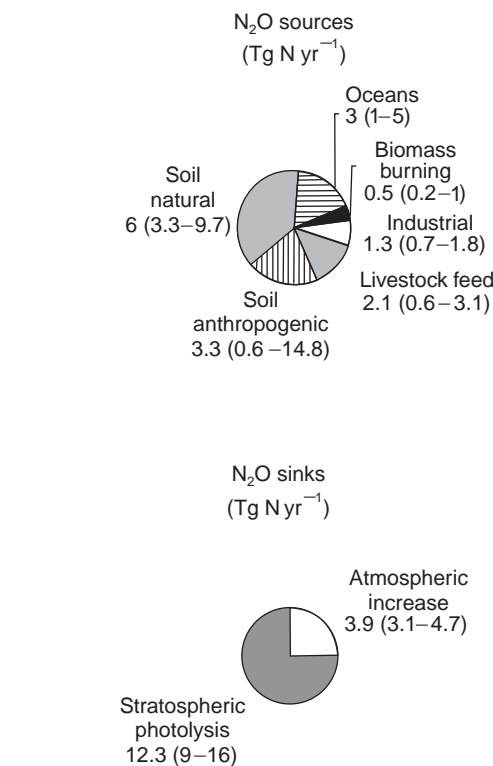
An inverse correlation between N<sub>2</sub>O and oxygen, and associated linear relationship between nitrate and N<sub>2</sub>O, suggest that N<sub>2</sub>O in the ocean originates primarily from nitrification. This may not be the case for sediments, in which denitrification is the dominant source of N<sub>2</sub>O under variable oxygen tension, with nitrification only contributing in a narrow sub-oxic band. Attribution of source is difficult as nitrification and denitrification may occur simultaneously and interact, with exchange of products



**Figure 1** 'Leaky Pipe' flow diagram of nitrification and denitrification indicating the potential exchange and intermediate role of NO and N<sub>2</sub>O (Reprinted by permission from *Nature* copyright (1990), Macmillan Magazines Ltd.)

and intermediates (Figure 1). This is further complicated, as denitrification will be limited to some extent by nitrate supply from nitrification. Isotopic data from the surface ocean in oligotrophic regions imply that N<sub>2</sub>O originates primarily from nitrification. However, recent evidence from waters overlying oxygen-deficient intermediate layers suggests that the elevated surface mixed-layer N<sub>2</sub>O arises from coupling between the two processes, as the observed isotope signatures cannot be explained by nitrification or denitrification alone. An additional N<sub>2</sub>O source from the dissimilatory reduction of nitrate to ammonium is restricted to highly anoxic environments such as sediments.

The oceanic N<sub>2</sub>O distribution is determined primarily by the oxygen and nutrient status of the water column. Estuaries and coastal waters show elevated supersaturation in response to high carbon and nitrogen loading, and the proximity of sub-oxic zones in sediment and the water column. As a result the total marine N<sub>2</sub>O source tends to be dominated by the coastal region. The N<sub>2</sub>O flux from shelf sea sediments is generally an order of magnitude lower than estuarine sediments, although the former have a greater spatial extent. A N<sub>2</sub>O maximum at the base of the euphotic zone is apparent in shelf seas and the open ocean, and is attributed to production in sub-oxic microzones within detrital material. Oceanic surface waters generally exhibit low supersaturations (< 105%), although N<sub>2</sub>O supersaturations may exceed 300% in surface waters overlying low oxygen intermediate waters and upwelling regions, such as the Arabian Sea and eastern tropical North Pacific. These 'natural chimney' regions dominate the open ocean N<sub>2</sub>O source, despite their limited surface area (Table 2). The surface N<sub>2</sub>O in upwelling regions such as the Arabian Sea originates in part from the underlying low-oxygen water column at 100–1000m, where favorable conditions result in the accumulation of N<sub>2</sub>O to supersaturations exceeding 1200%. N<sub>2</sub>O transfer into the surface mixed layer will be limited by vertical transport processes and a significant proportion of N<sub>2</sub>O



**Figure 2** Atmospheric nitrous oxide sources and sinks (adapted from Houghton *et al.*, 1995). Units: Tg =  $1 \times 10^{12}$ g.

produced at these depths will be further reduced to N<sub>2</sub>.

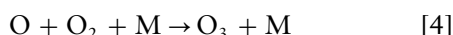
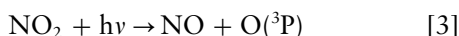
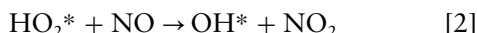
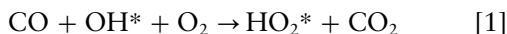
The oceans account for 1–5 Tg N-N<sub>2</sub>O per annum (Tg =  $1 \times 10^{12}$ g) or 6–30% of total global N<sub>2</sub>O emissions, although there is considerable uncertainty attached to this estimate (Figure 2). A recent estimate with greater representation of coastal sources has resulted in upward revision of the marine N<sub>2</sub>O source to 7–10.8 Tg N-N<sub>2</sub>O per annum; although this may represent an upper limit due to some bias from inclusion of estuaries with high N<sub>2</sub>O supersaturation. However, this estimate is in agreement with a total oceanic production rate of 11 Tg N-N<sub>2</sub>O per annum calculated from new production and nitrification.

**Table 2** N<sub>2</sub>O and CH<sub>4</sub> regional surface water supersaturations (from Bange *et al.*, 1996; 1998) (supersaturation is > 100%, undersaturation is < 100% with equilibrium between atmosphere and water at 100%)

	Surface % N <sub>2</sub> O saturation mean (range)	Surface % CH <sub>4</sub> saturation mean (range)
Estuaries	607 (101–2500)	1230 (146–29000)
Coastal/shelf	109 (102–118)	395 (85–42000)
Oligotrophic/transitional ocean	102.5 (102–104)	120 (80–200)
Upwelling ocean	176 (108–442)	200 (86–440)

## Nitric Oxide (NO)

Nitric oxide (NO) plays a central role in atmospheric chemistry, influencing both ozone cycling and the tropospheric oxidation capacity through reactions with hydroperoxy- and organic peroxy-radicals. When the NO concentration exceeds ~ 40 pptv (pptv = parts per trillion by volume) it catalyzes the production of ozone (O<sub>3</sub>):

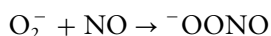


At high concentrations (> 50 ppbv; ppbv = parts per billion by volume), O<sub>3</sub> in the atmospheric boundary layer becomes a toxic pollutant that also has important radiative transfer properties. The production of nitric acid from NO influences atmospheric pH, and contributes to acid rain formation. In addition, the oxidation of NO to the nitrate (NO<sub>3</sub>) radical at night influences the oxidizing capacity of the lower troposphere. Determination of the magnitude and location of NO sources is critical to modeling boundary layer and free tropospheric chemistry.

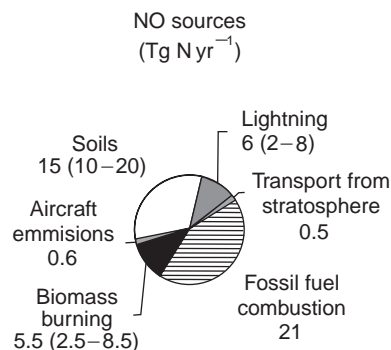
NO cycling in the ocean has received limited attention, as a result of its thermodynamic instability and high reactivity. Photolysis of nitrite in surface waters occurs via the formation of a nitrite radical with the production of NO:



This reaction may account for 10% of nitrite loss in surface waters of the Central Equatorial Pacific, resulting in a 1000-fold increase in dissolved NO at a steady-state surface concentration of 5 pmol dm<sup>-3</sup> during light periods (pmol = 1 × 10<sup>-12</sup> mol). This photolytic production is balanced by a sink reaction with the superoxide radical (O<sub>2</sub><sup>-</sup>) to produce peroxynitrite:



This reaction will be dependent upon steady-state concentration of the superoxide radical; however, as the reaction has a high rate constant, NO is rapidly turned over with a half-life on the order of 10–100 seconds.



**Figure 3** Atmospheric nitric oxide sources (from Graedel and Crutzen, 1992). Units: Tg = 1 × 10<sup>12</sup> g.

As with N<sub>2</sub>O, NO may also be produced as a by-product or intermediate of denitrification and nitrification (Figure 1). NO production by soils is better characterized than in marine systems, and is significant both in terms of nitrogen loss and the global NO budget (Figure 3). The greater oxygen availability in soils limits reduction of NO via denitrification and so enhances NO efflux. Sediment pore water NO maxima have been attributed to denitrification, although, as this process also represents a sink for NO (Figure 1), this may reflect poisoning at an optimal redox potential for NO production. Conversely, the NO maximum in low oxygen intermediate waters in the east tropical North Pacific derives from nitrification.

Current understanding of the oceanic NO distribution is that it is limited to the surface ocean and intermediate low oxygen water column. There is potential for higher NO concentrations in coastal and estuarine waters from sediment and photolytic sources, and nitrite photolysis to NO may also be significant in upwelling regions. Despite the short half-life of NO in surface waters, the maintenance of steady-state NO concentration suggests that photolytic production may support an, as yet unquantified, source of atmospheric NO. Surface concentrations in the Central Equatorial Pacific suggest that the oceanic NO source would not exceed 0.5 Tg N per annum, which is relatively insignificant when compared with other sources (Figure 3).

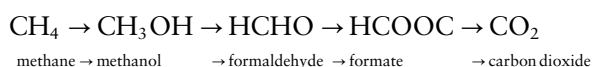
## Methane (CH<sub>4</sub>)

CH<sub>4</sub> is the most abundant organic volatile in the atmosphere and, next to CO<sub>2</sub>, is responsible for 15% of the current greenhouse radiative forcing, with a direct radiative forcing of 0.5 Wm<sup>-2</sup>. CH<sub>4</sub> reacts with OH and so limits the tropospheric oxidation capacity and influences ozone and other greenhouse gases. The reaction with OH generates

a feedback that leads to a reduction in the rate of CH<sub>4</sub> removal.

CH<sub>4</sub> is a reduced gas which, paradoxically, is supersaturated in the oxidized surface waters of the ocean (see Table 2). CH<sub>4</sub> is produced biotically and abiotically, although its oceanic distribution is controlled primarily by biological processes. Methanogenesis is classically defined as the formation of CH<sub>4</sub> from the fermentation and remineralization of organic carbon under anoxic conditions. Methanogens require a very low reducing potential and are generally obligate anaerobes, although there is evidence that they can tolerate some exposure to oxygen. However, methanogens cannot utilize complex organic molecules and often coexist with aerobic consortia to ensure a supply of simple C<sub>1</sub> substrates. Methanogens utilize formate, acetic acid, CO<sub>2</sub>, and hydrogen in sulfate-rich anoxic environments, although they are generally out-competed by sulfate-reducing bacteria which have a greater substrate affinity. However, the methanogens can also utilize other noncompetitive substrates such as methanol, methylamines, and reduced methylated compounds, when out-competed for the C<sub>1</sub> compounds.

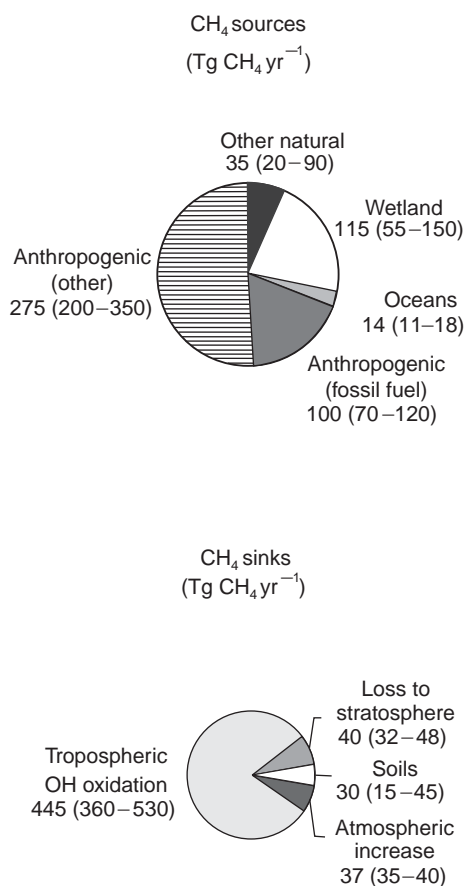
A significant fraction of CH<sub>4</sub> is oxidized before exiting the marine system and so the oxidation rate is critical in determining the air-sea flux. This is accomplished by methanotrophs that obtain their carbon and energy requirements from CH<sub>4</sub> oxidation under aerobic conditions via the following reactions:



Methanotrophs are found in greater numbers in sediments than in oxic sea water, and consequently the oceanic water column CH<sub>4</sub> oxidation is an order of magnitude lower than in sediments. Methanotrophs have a high inorganic nitrogen requirement and so methanotrophy is highest at the oxic-anoxic interface where ammonium is available. Anaerobic CH<sub>4</sub> oxidation also occurs but is less well characterized. It is generally restricted to anaerobic marine sediments, utilizing sulfate as the only oxidant available, and is absent from anaerobic freshwater sediments which lack sulfate. A significant proportion of CH<sub>4</sub> produced in anaerobic subsurface layers in sediments is oxidized during diffusive transport through the sulfate-CH<sub>4</sub> transition zone by anaerobic oxidation and subsequently by aerobic oxidation in the overlying oxic layers. Anaerobic oxidation represents the main sink for CH<sub>4</sub> in marine sediments, where it may account for 97% of CH<sub>4</sub> production.

CH<sub>4</sub> production is characteristic of regions with high input of labile organic carbon such as wetlands and sediments, but is usually restricted to below the zone of sulfate depletion. The oceanic CH<sub>4</sub> source is dominated by coastal regions, which exhibit high CH<sub>4</sub> fluxes as a result of bubble ebullition from anoxic carbon-rich sediments, and also riverine and estuarine input. Some seasonality may result in temperate regions due to increased methanogenesis at higher temperatures. The predominant water column source in shelf seas and the open ocean is CH<sub>4</sub> production at the base of the euphotic zone. This may arise from lateral advection from sedimentary sources, and *in situ* CH<sub>4</sub> production. The latter is accomplished by oxygen-tolerant methanogens that utilize methylamines or methylated sulfur compounds in anoxic microsites within detrital particles and the guts of zooplankton and fish. Lateral advection and *in situ* production may be greater in upwelling regions, as suggested by the increased CH<sub>4</sub> supersaturation in surface waters in these regions. Oceanic CH<sub>4</sub> concentration profiles generally exhibit a decrease below 250 m due to oxidation. Methanogenesis is elevated in anoxic water columns, although these are not significant sources of atmospheric CH<sub>4</sub> due to limited ventilation and high oxidation rates. Other sources include CH<sub>4</sub> seeps in shelf regions from which CH<sub>4</sub> is transferred directly to the atmosphere by bubble ebullition, although their contribution is difficult to quantify. Abiotic CH<sub>4</sub> originating from high-temperature fluids at hydrothermal vents also elevates CH<sub>4</sub> in the deep and intermediate waters in the locality of oceanic ridges. A significant proportion is oxidized and although the contribution to the atmospheric CH<sub>4</sub> pool may be significant in localized regions this has yet to be constrained. Hydrates are crystalline solids in which methane gas is trapped within a cage of water molecules. These form at high pressures and low temperatures in seafloor sediments generally at depths below 500 m. Although CH<sub>4</sub> release from hydrates is only considered from anthropogenic activities in current budgets, there is evidence of catastrophic releases in the geological past due to temperature-induced hydrate dissociation. Although oceanic hydrate reservoirs contain 14 000 Gt CH<sub>4</sub>, there is currently no evidence of significant warming of deep waters which would pre-empt release.

Other aquatic systems such as rivers and wetlands are more important sources than the marine environment. Shelf regions are the dominant source of CH<sub>4</sub> from the ocean (14(11–18) Tg CH<sub>4</sub> per annum), accounting for 75% of the ocean flux (Table 2). The ocean is not a major contributor



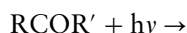
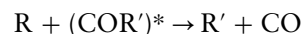
**Figure 4** Atmospheric methane sources and sinks (adapted from Houghton *et al.* (1995)). Units: Tg =  $1 \times 10^{12}$  g.

to the atmospheric CH<sub>4</sub> budget, as confirmed by estimates of the oceanic CH<sub>4</sub> source (Figure 4).

## Carbon Monoxide (CO)

The oxidation of CO provides the major control of hydroxyl radical content in the troposphere and limits the atmospheric oxidation capacity. This results in an increase in the atmospheric lifetime of species such as CH<sub>4</sub>, N<sub>2</sub>O, and halocarbons, and enhances their transfer to the stratosphere and the potential for subsequent ozone destruction. It has been suggested that decreasing stratospheric ozone and the resultant increase in incident ultraviolet (UV) radiation may increase marine production and efflux of CO, thereby generating a positive feedback loop. However, this may be compensated by a negative feedback in which increased UV reduces biological production and dissolved organic matter, so reducing the CO source. CO also influences tropospheric ozone by its interaction with NO<sub>x</sub>, and is a minor greenhouse gas with a radiative forcing of  $0.06 \text{ W m}^{-2}$  at current atmospheric concentrations.

The principal source of dissolved CO is the abiotic photodegradation of dissolved organic matter (DOM) by UV-R, and CO represents one of the major photoproducts of DOM in the ocean. Quantum yields for CO are highest in the UV-B range (280–315 nm) and decrease with increasing wavelengths. However, the UV-A (315–390 nm) and blue portion of the visible spectrum contribute to marine CO production as a greater proportion of radiation at these wavelengths reaches the Earth's surface. Humics represent approximately half of the DOM and account for the majority of the chromophoric dissolved organic matter (CDOM), the colored portion of dissolved organic matter that absorbs light energy. The CO photoproduction potential of humics is dependent upon the degree of aromaticity. Terrestrial humics are characterized by an increased prevalence of phenolic groups, and addition of precursor compounds containing phenolic moieties to natural samples stimulates CO production. Direct photo-oxidation of humics and compounds containing carbonyl groups, such as aldehydes, ketones, and quinones, occurs via the production of a carbonyl radical during  $\alpha$ -cleavage of an adjacent bond:-



CO production may also occur indirectly by a photosensitized reaction in which light energy is transferred via an excited oxygen atom to a carbonyl compound. This may occur with ketonic groups via the photosensitized production of an acetyl radical. Whereas light and CDOM are the primary factors controlling CO production there may also be additional influence from secondary factors. For example, organo-metal complexes have increased light absorption coefficients and their photo-decomposition will enhance radical formation and CO production at higher levels of dissolved metals such as iron. There is also minor biotic production of CO by methanogens, but this does not appear to be significant.

CO can be oxidized to carbon dioxide by selected microbial groups including ammonia oxidizers and methylotrophs that have a broad substrate specificity and high affinity for CO. However, only the carboxidotrophs obtain energy from this reaction, and these may be unable to assimilate CO efficiently at *in situ* concentrations. CO turnover times of 4 hours are typical for coastal waters, whereas this varies between 1 and 17 days in the open ocean. The lower oxidation rate in the open ocean may be

due to light inhibition of CO oxidation. Extrapolation from laboratory measurements suggests that only 10% of photochemically produced CO is microbially oxidized.

Dissolved CO exhibits diurnal variability in the surface ocean in response to its photolytic source, although this is also indicative of a strong sink term. The decline in the surface mixed-layer CO concentration in the dark results from a combination of CO oxidation, vertical mixing, and air-sea exchange. As the equilibration time between atmosphere and oceanic surface mixed layer is on the order of a month, this suggests that the former two processes dominate. Superimposed upon the diurnal cycle of CO in the surface ocean are spatial and seasonal gradients that result from the interaction of photo-production and the sink processes. Below the euphotic zone CO is uniformly low throughout the intermediate water column.

CO production potential is highest in wetland regions, which are characterized by high CDOM and enhanced light attenuation. Photochemical production of CO represents a potential sink for terrestrial dissolved organic carbon (DOC) in estuaries and coastal waters. This pathway may account for some of the discrepancy between the total terrestrial DOC exported and the low proportion of terrestrial DOC observed in the marine pool. Although a strong lateral gradient in CDOM exists between rivers and the open ocean, estuarine CO production may be limited by reduced UV light penetration. CO photoproduction may occur down to 80 m in the open ocean, and 20 m in the coastal zone, but is restricted to the upper 1 m in wetlands and estuaries. In addition, estuarine and coastal CO flux may also be restricted by the higher CO oxidation rates. There is evidence that upwelling regions may support enhanced CO production, in response to upwelled CDOM that is biologically refractory but photo-labile.

The presence of a CO gradient in the 10 m overlying the surface ocean suggests that the photolytic source of CO may influence the marine boundary layer. The marine source of CO is poorly constrained, with estimates varying from 10 to 220 Tg CO per annum. A flux of 1200 Tg CO per annum was estimated on the assumption that low rates of oceanic CO oxidation would only remove a small proportion of photoproduced CO, and that the residual would be ventilated to the atmosphere. The discrepancy between this and other flux estimates implies that a significant CO sink has been overlooked, although this may reflect shortcomings of different techniques. The oceanic contribution to the global source is between 1 and 20%, although Extrapolation of photochemical production rates from wetlands, estuaries, and coasts suggests that these alone may account for 20% of the total global CO flux. Although the marine source is responsible for < 10% of the total global flux (Table 3), it may still dominate atmospheric oxidation conditions in remote regions at distance from land.

### Air-Sea Exchange of Trace Gases

The flux of these trace gases across the air-sea interface is driven by physical transfer processes and the surface concentration anomaly, which represents the difference between the partial pressure observed in surface water and that expected from equilibrium with the atmosphere. Direct determination of the oceanic emission of a trace gas is difficult under field conditions. Atmospheric gradient measurements above the ocean surface require enhanced analytical resolution, whereas more advanced micrometeorological techniques have yet to be applied to these trace gases. Determination of the accumulation rate in a floating surface flux chamber is a simpler approach, but may generate artefactual results from the damping of wave- and wind-driven exchange,

**Table 3** Atmospheric CO sources and sinks<sup>a</sup> (adapted from Zuo *et al.*, 1998)

CO sources (Tg CO y <sup>-1</sup> )		CO sinks (Tg CO y <sup>-1</sup> )	
Industrial/fuel combustion	400–1000	Tropospheric hydroxyl oxidation	1400–2600
Biomass burning	300–2200	Soils	250–530
Vegetation and soils	50–200	Flux to stratosphere	80–140
Methane oxidation	300–1300		
NMHC oxidation	200–1800		
Ocean	10–220		
(Coast/Shelf	300–400)		
Total sources	1260–6720	Total sinks	1730–3270

<sup>a</sup>Note that a separate estimate of the coastal/shelf CO source is shown for comparison, but does not contribute to the total source. Tg = 1 × 10<sup>12</sup> g.

and enhanced transfer on the inner chamber surfaces. Consequently the majority of flux estimates are calculated indirectly rather than measured. The surface anomaly is derived from the difference between the measured surface concentration ( $C_w$ ), and an equilibrium concentration calculated from the measured atmospheric concentration ( $C_g$ ) and solubility coefficient ( $\alpha$ ) at ambient temperature and salinity. This is then converted to a flux by the application of a dynamic term, the gas transfer velocity,  $k$ :

$$F = k(C_w - \alpha C_g)$$

The transfer velocity  $k$  is the net result of a variety of molecular and turbulent processes that operate at different time and space scales. Wind is the primary driving force for most of these turbulent processes, and it is also relatively straightforward to obtain accurate measurements of wind speed. Consequently,  $k$  is generally parameterized in terms of wind speed, with the favored approaches assuming tri-linear and quadratic relationships between the two. These relationships are defined for CO<sub>2</sub> at 20°C in fresh water and sea water and referenced to other gases by a Schmidt number ( $Sc$ ) relationship:

$$k_{gas} = k_{ref}(Sc_{gas}/Sc_{ref})^n$$

where  $n$  is considered to be  $-1/2$  at most wind speeds. This dependency of  $k$  is a function of the molecular diffusivity ( $D$ ) of the gas and the kinematic viscosity of the water ( $\mu$ ), and is expressed in terms of the Schmidt number ( $Sc = \mu/D$ ).

Determination of marine trace gas fluxes using different wind speed-transfer velocity relationships introduces uncertainty, which increases at medium-high wind speeds to a factor of two. Furthermore, additional uncertainty is introduced by the extrapolation of surface concentration gradient measurements to long-term climatological wind speeds. Current estimates of oceanic fluxes are also subject to significant spatial and temporal bias resulting from the fact that most studies focus on more productive regions and seasons. This uncertainty is compounded by the extrapolation of observational

data sets to uncharted regions. With the exception of N<sub>2</sub>O, the ocean does not represent a major source for these atmospheric trace gases, although spatial variability in oceanic source strength may result in localized impact, particularly in remote regions. In the near future, advances in micrometeorological techniques, improved transfer velocity parameterizations and the development of algorithms for prediction of surface ocean concentrations by remote sensing should provide further constraint in determination of the oceanic source of N<sub>2</sub>O, NO, CH<sub>4</sub>, and CO.

## See also

**Air-Sea Gas Exchange. Air-Sea Transfer: Dimethyl Sulphide, COS, CS<sub>2</sub>, NH<sub>4</sub>, Non-methane Hydrocarbons, Organo-halogens. Carbon Dioxide (CO<sub>2</sub>) Cycle. Gas Exchange in Estuaries. Photochemical Processes. Plankton and Climate. Surface Films. Upwelling Ecosystems.**

## Further Reading

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# ALASKA CURRENT

See CALIFORNIA AND ALASKA CURRENTS