# **GAS EXCHANGE IN ESTUARIES**

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# Introduction

Many atmospherically important gases are present in estuarine waters in excess over levels that would be predicted from simple equilibrium between the atmosphere and surface waters. Since estuaries are defined as semi-enclosed coastal bodies of water that have free connections with the open sea and within which sea water is measurably diluted with fresh water derived from land drainage, they tend to be supplied with much larger amounts of organic matter and other compounds than other coastal areas. Thus, production of many gases is enhanced in estuaries relative to the rest of the ocean. The geometry of estuaries, which typically have relatively large surface areas compared to their depths, is such that flux of material (including gases) from the sediments, and fluxes of gases across the air/water interface, can have a much greater impact on the water composition than would be the case in the open ocean. Riverine and tidal currents are often quite marked, which also can greatly affect concentrations of biogenic gases.

## Gas Solubility

The direction and magnitude of the exchange of gases across an air/water interface are determined by the difference between the surface-water concentration of a given gas and its equilibrium concentration or gas solubility with respect to the atmosphere. The concentration of a specific gas in equilibrium with the atmosphere ( $C_{eq}$ ) is given by Henry's Law:

$$C_{eq} = p_{gas}/K_{H}$$
 [1]

where  $p_{gas}$  is the partial pressure of the gas in the atmosphere, and  $K_{H}$  is the Henry's Law constant for the gas. Typically as temperature and salinity increase, gas solubility decreases. (Note that Henry's Law and the Henry's Law constant also may be commonly expressed in terms of the mole fraction

of the gas in either the gas or liquid phase.) For gases that make up a large fraction of the atmosphere (O<sub>2</sub>, N<sub>2</sub>, Ar),  $p_{gas}$  does not vary temporally or spatially. For trace atmospheric gases (carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), hydrogen (H<sub>2</sub>), nitrous oxide (N<sub>2</sub>O), and others),  $p_{gas}$  may vary considerably geographically or seasonally, and may be affected by anthropogenic activity or local natural sources.

# Gas Exchange (Flux) Across the Air/Water Interface

The rate of gas exchange across the air/water interface for a specific gas is determined by the degree of disequilibrium between the actual surface concentration of a gas ( $C_{surf}$ ) and its equilibrium concentration ( $C_{eq}$ ), commonly expressed as R:

$$R = C_{surf} / C_{eq}$$
 [2]

If R = 1, the dissolved gas is in equilibrium with the atmosphere and no net flux or exchange with the atmosphere occurs. For gases with R < 1, the dissolved gas is undersaturated with respect to the atmosphere and there is a net flux of the gas from the atmosphere to the water. For gases with R > 1, a net flux of the gas from the water to the atmosphere occurs.

## Models of Gas Exchange

The magnitude of the flux (F) in units of mass of gas per unit area per unit time across the air/water interface is a function of the magnitude of the difference between the dissolved gas concentration and its equilibrium concentration as given by Fick's First Law of Diffusion:

$$F = k(C_{surf} - C_{eq})$$
[3]

where k is a first order rate constant, which is a function of the specific gas and surface water conditions. The rate constant, k, also known as the transfer coefficient, has units of velocity and is frequently given as

$$k = D/z$$
 [4]

where D is the molecular diffusivity (in units of  $cm^2 s^{-1}$ ), and z is the thickness of the laminar layer

at the air/water interface, which limits the diffusion of gas across the interface.

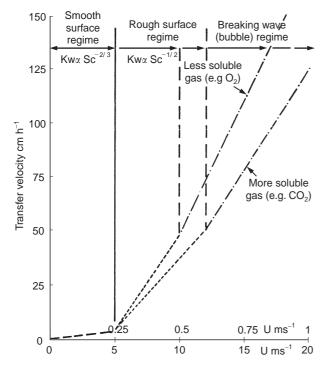
In aquatic systems,  $C_{surf}$  is easily measured by gas chromatographic analysis, and  $C_{eq}$  may be calculated readily if the temperature and salinity of the water are known. In order to determine the flux of gas (F) in or out of the water, the transfer coefficient (k) needs to be determined. The value of k is a function of the surface roughness of the water. In open bodies of water, wind speed is the main determinant of surface roughness. A number of studies have established a relationship between wind speed and either the transfer coefficient, k, or the liquid laminar layer thickness, z (Figure 1). The transfer coefficient is also related to the Schmidt number, Sc, defined as:

$$Sc = v/D$$
 [5]

where v is the kinematic viscosity of the water. In calmer waters, corresponding to wind speeds of  $<5 \text{ m s}^{-1}$ , k is proportional to  $\text{Sc}^{-2/3}$ . At higher wind speeds, but where breaking waves are rare, k is proportional to  $\text{S}^{-1/2}$ . Therefore, if the transfer coefficient of one gas is known, the k value for any other gas can be determined as:

$$k_1/k_2 = 5c_1/5c_2$$
 [6]

۲<u>/</u>1



**Figure 1** Idealized plot of transfer coefficient (Kw) as a function of wind speed (u) and friction velocity (u\*). (Adapted with permission from Liss PS and Merlivat L (1985) Air-sea gas exchange rates. In: Buat-Menard P (ed.) The Role of Air-sea Exchange in Geochemical Cycling, p. 117. *NATO ASI Series C*, *vol. 185*. Dordrecht: Reidel.)

where n = the exponent. For short-term steady winds, the transfer coefficient for  $CO_2$  has been derived as

$$k_{CO_2} = 0.31 (U_{10})^2 (Sc/600)^{-0.5}$$
[7]

where  $U_{10}$  is the wind speed at a height of 10 m above the water surface. Eqns [6] and [7] can be used to estimate k for gases other than CO<sub>2</sub>. In most estuarine studies wind speeds are measured closer to the water surface. In such cases, the wind speed measured at 2 cm above the water surface can be approximated as  $0.5U_{10}$ .

In restricted estuaries and tidally influenced rivers, wind speed may not be a good predictor of wind speed due to limited fetch or blockage of prevailing winds by shore vegetation. Instead, streambedgenerated turbulence is likely to be more important than wind stress in determining water surface roughness. In such circumstances, the large eddy model may be used to approximate k as:

$$\mathbf{k} = 1.46(\mathbf{D} * \mathbf{u} * \mathbf{l}^{-1})^{1/2}$$
 [8]

where u is the current velocity, and l is equivalent to the mean depth in shallow turbulent systems. Much of the reported uncertainty (and study to study variability in fluxes) is caused by differences in assumptions related to the transfer coefficient rather than to large changes in concentration of the gas in the estuary.

# **Direct Gas Exchange Measurements**

Gas exchange with the atmosphere for gases for which water column consumption and production processes are known can be estimated using a dissolved gas budget. Through time-series measurements of biological and chemical cycling, gas loss or gain across the air/water interface can be determined by difference. For example, in the case of dissolved O2, the total change in dissolved O2 concentration over time can be attributed to air/water exchange and biological processes. The contribution of biological processes to temporal changes in dissolved  $O_2$  may be estimated from concurrent measurements of phosphate and an assumed Redfield stoichiometry, and subtracted from the total change to yield an estimate of air/water  $O_2$ exchange.

Gas fluxes also may be measured directly using a flux chamber that floats on the water surface. The headspace of the chamber is collected and analyzed over several time points to obtain an estimate of the net amount of gas crossing the air/water interface enclosed by the chamber. If the surface area enclosed by the chamber is known, a net gas flux can be determined. Some flux chambers are equipped with small fans that simulate ambient wind conditions. However, most chambers do not use fans and so do not take account of the effects of windinduced turbulence on gas exchange. Despite this limitation, flux chambers are important tools for measuring gas exchange in environments (such as estuaries or streams) where limited fetch or wind breaks produced by shoreline vegetation make wind less important than current-induced turbulence in shallow systems. While flux chambers may alter the surface roughness and, hence, gas/exchange rates via diffusion, flux chambers or other enclosed gas capturing devices also are the best method for determining loss of gases across the air/water interface due to ebullition of gas bubbles from the sediment.

Measurement of radon (Rn) deficiencies in the upper water column can be used to determine gas exchange coefficients and laminar layer thickness, which can then be applied to other gases using eqn [3]. In this method, gaseous <sup>222</sup>Rn, produced by radioactive decay of <sup>226</sup>Ra, is assumed to be in secular equilibrium within the water column. <sup>222</sup>Rn is relatively short-lived and has an atmospheric concentration of essentially zero. Therefore, in nearsurface waters, a <sup>222</sup>Rn deficiency is observed, due to flux of <sup>222</sup>Rn across the air/water interface. The flux of <sup>222</sup>Rn across the air/water interface can be determined by the depth-integrated difference in measured <sup>222</sup>Rn and that which should occur based on the <sup>226</sup>Ra inventory. From this flux, the liquid laminar layer thickness, z, can be calculated.

Other volatile tracers have been used in estuaries to determine gas exchange coefficients. These tracers, such as chlorofluorocarbons (CFCs) or sulfur hexafluoride (SF<sub>6</sub>), are synthetic compounds with no known natural source. Unlike <sup>222</sup>Rn, these gases are stable in solution. These tracers may be added to the aquatic system and the decrease of the gas due to flux across the air/water interface monitored over time. In some estuaries, point sources of these compounds may exist and the decrease of the tracer with distance downstream may be used to determine k or z values for the estuary.

## **Individual Gases**

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

Atmospheric methane plays an important role in the Earth's radiative budget as a potent greenhouse gas, which is 3.7 times more effective than carbon dioxide in absorbing infrared radiation. Despite being

present in trace quantities, atmospheric methane plays an important role controlling atmospheric chemistry, including serving as a regulator of tropospheric ozone concentrations and a major sink for hydroxyl radicals in the stratosphere. Methane concentrations have been increasing annually at the rate of approximately 1–2% over the last two centuries. While the contribution of estuaries to the global atmospheric methane budget is small because of the relatively small estuarine global surface area, estuaries have been identified as sources of methane to the atmosphere and coastal ocean and contribute a significant fraction of the marine methane emissions to the atmosphere.

Surface methane concentrations reported primarily from estuaries in North America and Europe range from 1 to > 2000 nM throughout the tidal portion of the estuaries. Methane in estuarine surface waters is generally observed to be supersaturated (100% saturation  $\sim 2-3$  nM CH<sub>4</sub>) with R-values ranging from 0.7 to 1600 (Table 1). In general, estuarine methane concentrations are highest at the freshwater end of the estuary and decrease with salinity. This trend reflects riverine input as the major source of methane to most estuaries, with reported riverine methane concentrations ranging from 5 to 10 000 nM. Estuaries with large plumes have been observed to cause elevated methane concentrations in adjacent coastal oceans. In addition to riverine input, sources of methane to estuaries include intertidal flats and marshes, ground-water

 Table 1
 Methane saturation values (R) and estimated fluxes to the atmosphere for US and European estuaries

Geographical region <sup>a</sup>	R⁵	Flux $CH_4$ (µmol $m^{-2} h^{-1}$ )
North Pacific coast, USA North Pacific coast, USA Columbia River, USA Hudson River, USA Tomales Bay, CA, USA Baltic Sea, Germany European Atlantic coast Atlantic coast, USA Pettaguamscutt Estuary,	3-290 1-550 78 18-376 2-37 10.5-1550 0.7-1580 n.a. 81-111	6.2-41.7° 3.6-8.3° 26.0° 4.7-40.4° 17.4-26.3° 9.4-15.6° 5.5° 102-1107° 0.8-14.2°
USA		541-3375 <sup>d</sup>

<sup>a</sup>For studies that report values for a single estuary, the major river feeding the estuary is provided. For studies that report values for more than one estuary, the oceanic area being fed by the estuaries is given.

 ${}^{b}R$  = degree of saturation = measured concentration/atmospheric equilibrium concentration. n.a. indicates values not available in reference.

<sup>c</sup>Diffusive flux.

<sup>d</sup>Ebullition (gas bubble) flux.

input, runoff from agricultural and pasture land, petroleum pollution, lateral input from exposed bank soils, wastewater discharge and emission from organic-rich anaerobic sediments, either diffusively or via ebullition (transport of gas from sediments as bubbles) and subsequent dissolution within the water column. Anthropogenically impacted estuaries or estuaries supplied from impacted rivers tend to be characterized by higher water-column methane concentrations relative to pristine estuarine systems. Seasonally, methane levels in estuaries are higher in summer compared with winter, primarily due to increased bacterial methane production (methanogenesis) in estuarine and riverine sediments.

Methane can be removed from estuarine waters by microbial methane oxidation and emission to the atmosphere. Methane oxidation within estuaries can be quite rapid, with methane turnover times of <2 h to several days. Methane oxidation appears to be most rapid at salinities of less than about 6 (on the practical salinity units scale) and is strongly dependent on temperature, with highest oxidation rates occurring during the summer, when water temperatures are highest. Methane oxidation rates decrease rapidly with higher salinities.

Methane diffusive fluxes to the atmosphere reported for estuaries (Table 1) fall within a narrow range of 3.6–41.7 µmol m<sup>-2</sup> h<sup>-1</sup> (2–16 mg CH<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup>). Using a global surface area for estuaries of  $1.4 \times 10^6$  km<sup>2</sup> yields an annual emission of methane to the atmosphere from estuaries of 1–8 Tg y<sup>-1</sup>. Because the higher flux estimates given in Table 1 generally were obtained close to the freshwater end-member of the estuary, the global methane estuarine emission is most likely within the range of 1–3 Tg y<sup>-1</sup>, corresponding to approximately 10% of the total global oceanic methane flux to the atmosphere, despite the much smaller global surface area of estuaries relative to the open ocean.

Methane is also released to the atmosphere directly from anaerobic estuarine sediments via bubble formation and injection into the water column. Although small amounts of methane from bubbles may dissolve within the water column, the relatively shallow nature of the estuarine environment results in the majority of methane in bubbles reaching the atmosphere. The quantitative release of methane via this mechanism is difficult to evaluate due to the irregular and sporadic spatial and temporal extent of ebullition. Where ebullition occurs, the flux of methane to the atmosphere is considerably higher than diffusive flux (**Table 1**), but the areal extent of bubbling is relatively smaller than that of diffusive flux and, except in organic-rich stagnant areas such as tidal marshes, probably does not contribute significantly to estuarine methane emissions to the atmosphere. Methane emission via ebullition has been observed to be at least partially controlled by tidal changes in hydrostatic pressure, with release of methane occurring at or near low tide when hydrostatic pressure is at a minimum.

#### Nitrous Oxide (N<sub>2</sub>O)

Nitrous oxide is another important greenhouse gas that is present in elevated concentrations in estuarine environments. At present,  $N_2O$  is responsible for about 5–6% of the anthropogenic greenhouse effect and is increasing in the atmosphere at a rate of about 0.25% per year. However, the role of estuaries in the global budget of the gas has only been addressed recently.

Nitrous oxide is produced primarily as an intermediate during both nitrification (the oxidation of ammonium to nitrate) and denitrification (the reduction of nitrate, via nitrite and N<sub>2</sub>O, to nitrogen gas), although production by dissimilatory nitrate reduction to ammonium is also possible. In estuaries, nitrification and denitrification are both thought to be important sources. Factors such as the oxygen level in the estuary and the nitrate and ammonium concentrations of the water can influence which pathway is dominant, with denitrification dominating at very low, but non-zero, oxygen concentrations. Nitrous oxide concentrations are typically highest in the portions of the estuary closest to the rivers, and decrease with distance downstream. A number of workers have reported nitrous oxide maxima in estuarine waters at low salinities (< 5-10 on the PSU scale), but this is not always the case. The turbidity maximum has been reported to be the site of maximum nitrification (presumably because of increased residence time for bacteria attached to suspended particulate matter, combined with elevated substrate (oxygen and ammonium)).

Table 2 presents a summary of the data published for degree of saturation and air-estuary flux of nitrous oxide from a variety of estuaries, all of which are located in Europe and North America. Concentrations are commonly above that predicted from air-sea equilibrium, and estimates of fluxes range from 0.01 µmol m<sup>-2</sup> h<sup>-1</sup> to 5 µmol m<sup>-2</sup> h<sup>-1</sup>. Ebullition is not important for nitrous oxide because it is much more soluble than methane. Researchers have estimated the size of the global estuarine source for N<sub>2</sub>O based on fluxes from individual estuaries multiplied by the global area occupied by estuaries to range from 0.22 Tg N<sub>2</sub>O y<sup>-1</sup> to 5.7 Tg y<sup>-1</sup> depending on the characteristics of the

Estuary	R	Flux <sup>a</sup> N <sub>2</sub> O (μmol m <sup>-2</sup> h <sup>-1</sup> )
Europe		
Gironde River	1.1–1.6	n.a.
Gironde River	$\approx$ 1.0–3.2	n.a.
Oder River	0.9–3.1	0.014-0.165
Elbe	2.0-16	n.a.
Scheldt	≈ 1.0–31	1.27-4.77
Scheldt	1.2-30	3.56
UK Colne	0.9–13.6	1.3
Tamar	1-3.3	0.41
Humber	2-40	1.8
Tweed	0.96–1.1	≈ 0
Mediterranean		
Amvraikos Gulf	0.9–1.1	$0.043\pm0.0468$
North-west USA		
Yaquina Bay	1.0-4.0	0.165-0.699
Alsea River	0.9-2.4	0.047-0.72
East coast USA		
Chesapeake Bay	0.9–1.4	n.a.
Merrimack	1.2–4.5	n.a.

 $\label{eq:constraint} \begin{array}{c} \textbf{Table 2} & \text{Nitrous oxide saturation values (R) and estimated} \\ \text{fluxes to the atmosphere for US and European estuaries} \end{array}$ 

<sup>a</sup>All fluxes given are for diffusive flux to the atmosphere. n.a. indicates that insufficient data were given to permit calculation of flux.

rivers studied. Independent estimates based on budgets of nitrogen input to rivers, assumptions about the fraction of inorganic nitrogen species removed by nitrification or denitrification, and the fractional 'yield' of nitrous oxide production during these processes indicate that nitrous oxide fluxes to the atmosphere from estuaries is about 0.06–0.34 Tg N<sub>2</sub>O y<sup>-1</sup>.

## Carbon Dioxide (CO<sub>2</sub>) and Oxygen (O<sub>2</sub>)

Estuaries are typically heterotrophic systems, which means that the amount of organic matter respired within the estuary exceeds the amount of organic matter fixed by primary producers (phytoplankton and macrophytes). Since production of carbon dioxide then exceeds biological removal of carbon dioxide, it follows that estuaries are likely to be sources of the gas to the atmosphere. At the same time, since oxidation of organic matter to CO<sub>2</sub> requires oxygen, the heterotrophic nature of estuaries suggests that they represent sinks for atmospheric oxygen. In many estuaries, primary productivity is severely limited by the amount of light that penetrates into the water due to high particulate loadings in the water. In addition, large amounts of organic matter may be supplied to the estuary by runoff from agricultural and forested land, from

Table 3	Fluxes of	carbon	dioxide	from	estuaries	in Europe
and easte	rn USA					

Estuary	R	Flux <sup>a</sup> CO <sub>2</sub> (mmol m <sup>-2</sup> h <sup>-1</sup> )
European rivers		
Northern Europe	0.7-61.1	1.0-31.7
Scheldt estuary	0.35-26.2	4.2-50
Portugal	1.6–15.8	10–31.7
UK	1.1–14.4	4.4-10.4
Clyde estuary	≈ 0.7–1.8	n.a.
East coast USA		
Hudson River	1.2–5.4	0.67-1.54
(tidal freshwater)		
Georgia rivers	Slight supersaturation to 22.9	1.7–23

<sup>a</sup>n.a., insufficient data were available to permit calculation of this value.

ground water, from sewage effluent, and from organic matter in the river itself. There are many reports of estuarine systems with oxygen saturations below 1 (undersaturated with respect to the atmosphere), but few studies in which oxygen flux to the estuary has been reported. However, estuaries are often dramatically supersaturated with respect to saturation with  $CO_2$ , especially at low salinities, and a number of workers have reported estimates of carbon dioxide flux from these systems (Table 3).

#### **Dimethylsulfide (DMS)**

DMS is an atmospheric trace gas that plays important roles in tropospheric chemistry and climate regulation. In the estuarine environment, DMS is produced primarily from the breakdown of the phytoplankton osmoregulator 3-(dimethylsulfonium)propionate (DMSP). DMS concentrations reported in estuaries are generally supersaturated, ranging from 0.5 to 22 nM, and increase with increasing salinity. DMS levels in the water column represent a balance between tightly coupled production from DMSP and microbial consumption. Only 10% of DMS produced from DMSP in the estuarine water column is believed to escape to the atmosphere from estuarine surface water, since the biological turnover of DMS (turnover time of 3-7 days) is approximately 10 times faster than DMS exchange across the air/water interface. A large part of the estuarine DMS flux to the atmosphere may occur over short time periods on the order of weeks, corresponding to phytoplankton blooms. The DMS flux for an estuary in Florida, USA, was estimated to be on the order of < 1 nmoles m<sup>-2</sup> h<sup>-1</sup>. Insufficient

data are available to determine reliable global DMS air/water exchanges from estuaries.

## Hydrogen (H<sub>2</sub>)

Hydrogen is an important intermediate in many microbial catabolic reactions, and the efficiency of hydrogen transfer among microbial organisms within an environment helps determine the pathways of organic matter decomposition. Hydrogen is generally supersaturated in the surface waters of the few estuaries that have been analyzed for dissolved hydrogen with R-values of 1.5–67. Hydrogen flux to the atmosphere from estuaries has been reported to be on the order of 0.06–0.27 nmol m<sup>-2</sup> h<sup>-1</sup>. The contribution of estuaries to the global atmospheric H<sub>2</sub> flux cannot be determined from the few available data.

#### **Carbon Monoxide (CO)**

Carbon monoxide in surface waters is produced primarily from the photo-oxidation of dissolved organic matter by UV radiation. Since estuarine waters are characterized by high dissolved organic carbon levels, the surface waters of estuaries are highly supersaturated and are a strong source of CO to the atmosphere. Reported R-values for CO range from approximately 10 to  $> 10\ 000$ . Because of the highly variable distributions of dissolved CO within surface waters (primarily as the result of the highly variable production of CO), it is impossible to derive a meaningful value for CO emissions to the atmosphere from estuaries.

#### **Carbonyl Sulfide (OCS)**

Carbonyl sulfide makes up approximately 80% of the total sulfur content of the atmosphere and is the major source of stratospheric aerosols. Carbonyl sulfide is produced within surface waters by photolysis of dissolved organosulfur compounds. Therefore, surface water OCS levels within estuaries exhibit a strong diel trend. Carbonyl sulfide is also added to the water column by diffusion from anoxic sediments, where its production appears to be coupled to microbial sulfate reduction. Diffusion of OCS from the sediment to the water column accounts for  $\sim 75\%$  of the OCS supplied to the water column and is responsible for the higher OCS concentrations in estuaries relative to the open ocean. While supersaturations of OCS are observed throughout estuarine surface waters, no trends with salinity have been observed. Atmospheric OCS fluxes to the atmosphere from Chesapeake Bay have been reported to range from 10.4 to 56.2 nmol  $m^{-2}$   $h^{-1}$ . These areal fluxes are over 50 times greater than those determined for the open ocean.

#### Elemental Mercury (Hg<sup>o</sup>)

Elemental mercury is produced in estuarine environments by biologically mediated processes. Both algae and bacteria are able to convert dissolved inorganic mercury to volatile forms, which include organic species (monomethyl- and dimethyl-mercury) and Hg<sup>0</sup>. Under suboxic conditions, elemental mercury also may be the thermodynamically stable form of the metal. In the Scheldt River estuary, Hg<sup>0</sup> correlated well with phytoplankton pigments, suggesting that phytoplankton were the dominant factors, at least in that system. Factors that may affect elemental mercury concentrations include the type of phytoplankton present, photo-catalytic reduction of ionic Hg in surface waters, the extent of bacterial activity that removes oxygen from the estuary, and removal of mercury by particulate scavenging and sulfide precipitation. Fluxes of elemental mercury to the atmosphere have been estimated for the Pettaquamscutt estuary in Rhode Island, USA, and for the Scheldt, and range from 4.2–29 pmol  $m^{-2} h^{-1}$ , although the values are strongly dependent on the model used to estimate gas exchange coefficients.

#### Volatile Organic Compounds (VOCs)

In addition to gases produced naturally in the environment, estuaries tend to be enriched in by-products of industry and other human activity. A few studies have investigated volatile organic pollutants such as chlorinated hydrocarbons (chloroform, tetrachloromethane, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene) and monocyclic aromatic hydrocarbons (benzene, toluene, ethylbenzene, o-xylene and m- and p-xylene). Concentrations of VOCs are controlled primarily by the location of the sources, dilution of river water with clean marine water within the estuary, gas exchange, and in some cases, adsorption onto suspended or settling solids. In some cases (for example, chloroform) there also may be natural biotic sources of the gas. Volatilization to the atmosphere can be an important 'cleansing' mechanism for the estuary system. Since the only estuaries studied to date are heavily impacted by human activity (the Elbe and the Scheldt), it is not possible to make generalizations about the importance of these systems on a global scale.

# Conclusions

Many estuaries are supersaturated with a variety of gases, making them locally, and occasionally regionally, important sources to the atmosphere. However, estuarine systems are also highly variable in the amount of gases they contain. Since most estuaries studied to date are in Europe or the North American continent, more data are needed before global budgets can be reliably prepared.

Air-water interface: The boundary between the gaseous phase (the atmosphere) and the liquid phase (the water).

Catabolic: Biochemical process resulting in breakdown of organic molecules into smaller molecules yielding energy.

Denitrification: Reduction of nitrate via nitrite to gaseous endproducts (nitrous oxide and dinitrogen gas).

**Ebullition**: Gas transport by bubbles, usually from sediments.

Estuary: Semi-enclosed coastal body of water with free connection to the open sea and within which sea water is measurably diluted with fresh water derived from land drainage.

Gas solubility: The amount of gas that will dissolve in a liquid when the liquid is in equilibrium with the overlying gas phase.

Henry's Law Constant: Proportionality constant relating the vapor pressure of a solute to its mole fraction in solution.

Liquid laminar thickness: The thickness of a layer at the air/water interface where transport of a dissolved species is controlled by molecular (rather than turbulent) diffusion.

Molecular diffusivity (D): The molecular diffusion coefficient.

Nitrification: Oxidation of ammonium to nitrite and nitrate.

**Practical salinity scale:** A dimensionless scale for salinity.

**Redfield stoichiometry:** Redfield and colleagues noted that organisms in the sea consistently removed nutrient elements from the water in a fixed ratio (C : N : P = 106 : 16 : 1). Subsequent workers have found that nutrient concentrations in the sea typically are present in those same ratios.

**Transfer coefficient:** The rate constant which determines the rate of transfer of gas from liquid to gas phase.

# 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. Air–Sea Transfer: N<sub>2</sub>O, NO, CH<sub>4</sub>, CO.

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