

**Gas Exchange Rates in the Parker River Estuary, Massachusetts**

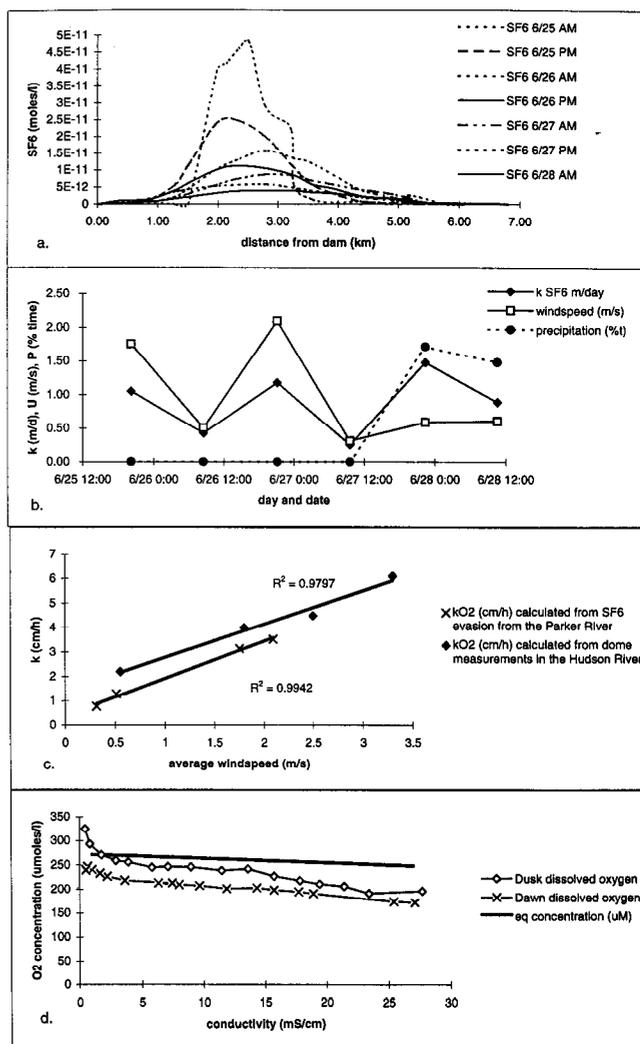
*Stephen Carini (University of Colorado), Nathaniel Weston<sup>1</sup>, Charles Hopkinson<sup>2</sup>, Jane Tucker<sup>2</sup>, Anne Giblin<sup>2</sup>, and Joseph Vallino<sup>2</sup>*

Gas exchange rates between natural waters and the atmosphere are an important component of our understanding of the dynamics of biologically active gases. For example, estimates of whole system metabolism must account for the transfer of gas (O<sub>2</sub>) between the atmosphere and water. Previous studies in estuaries have relied on dome measurements to estimate O<sub>2</sub> exchange rates (1, 2). In this study we measured gas exchange rates using sulfur hexafluoride (SF<sub>6</sub>) as a tracer. SF<sub>6</sub> is well suited for this application because it is chemically and biologically nonreactive, occurs at low background levels, and extremely low concentrations are readily detectable (3). The gas exchange coefficient, *k*, calculated for SF<sub>6</sub> can be related to the exchange coefficient for other gases (4).

We injected ~0.004 moles of SF<sub>6</sub> into the Parker River estuary, Newbury Massachusetts, and monitored the evasion of the gas over time by the decrease in its total mass. The tracer was allowed to mix for one tidal cycle and we then sampled SF<sub>6</sub> concentration in the water at each of seven successive high tides. Surface water samples were drawn into 100-ml glass syringes, transported, submerged in river water, to a field laboratory, and analyzed within 6 h using gas chromatography with electron capture detection. Windspeed and precipitation data were recorded continuously. Several previous surveys were used to determine cross-sectional areas along a 10-km stretch of the estuary. The total mass of SF<sub>6</sub> in the estuary was calculated by integrating concentration and water volume by estuarine distance.

The distribution of the tracer changed over time in relation to processes controlling mixing and loss to the atmosphere (Fig. 1a). After the initial tidal cycle the tracer plume measured 5.2 km in length, and the distribution was gaussian. The exchange coefficient, *k*, and mass are related by the function  $k = \ln(M/M_0)h/t$  where *M* is the measured mass of SF<sub>6</sub> in the estuary, *M*<sub>0</sub> is the previously measured mass of SF<sub>6</sub>, *h* is the depth, and *t* is the time between samplings. Calculated values for *k*<sub>SF6</sub> range from 1.1–6.2 cm·h<sup>-1</sup>. Fluctuations in *k* are well correlated with wind velocity [in agreement with previous studies (4, 5)] and with precipitation (Fig. 1b). These values are lower than those predicted from wind relations established from dome studies (Fig. 1c). For estuarine systems with complicated geometry (e.g., channel longitudinal direction, marsh grass, and high tidal range), direct measurement of SF<sub>6</sub> evasion may be a more accurate determination of gas exchange rates.

The importance of gas exchange as a process influencing the determination of system metabolism was determined by applying our measured gas exchange coefficient for SF<sub>6</sub> to the calculation of O<sub>2</sub> gas exchange. System respiration was calculated by mass loss of dissolved oxygen between dusk and dawn (Fig. 1d) and corrected for gas exchange with the atmosphere. The gas transfer velocities of O<sub>2</sub> and SF<sub>6</sub> are related by the function  $k_{O_2}$



**Figure 1.** (a) Concentration and distribution of SF<sub>6</sub> measured from the Parker Dam. (b) *k* as a function of windspeed (*U*) and precipitation (*P*).  $k = 2.15547U + 8.099P + 0.04785$  with a total model  $R^2$  of 88.7 ( $P = .037$ ). (c) *k*<sub>O<sub>2</sub></sub> measured by the dome method in the Hudson River (1) and by measurement of SF<sub>6</sub> evasion from the Parker River Estuary. (d) Dawn and dusk dissolved oxygen concentrations plotted against conductivity.

$= k_{SF_6} (Sc_{SF_6})^n / (Sc_{O_2})^n$  where *Sc* is the Schmidt number and *n* is assumed to be -2/3 (4). The resulting *k* for O<sub>2</sub> was 1.28 cm·h<sup>-1</sup> and a net influx of O<sub>2</sub> was added to the total mass loss of oxygen. This resulted in a calculated respiration rate of 208 mmoles O<sub>2</sub>·m<sup>-2</sup>·d<sup>-1</sup>. Although the correction for gas exchange during the period of this study was less than 0.15%, under different environmental conditions, such as higher concentration gradients or windspeeds, corrections would be substantially greater.

<sup>1</sup> Hampshire College School of Natural Science.  
<sup>2</sup> Ecosystems Center, Marine Biological Laboratory.

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## Estimating Denitrification in Sediments of the Parker River Estuary, Massachusetts

Nathaniel Weston (Hampshire College), Stephen Carini<sup>1</sup>, Anne Giblin<sup>2</sup>, Gary Banta<sup>3</sup>, Charles Hopkinson<sup>2</sup>, and Jane Tucker<sup>2</sup>

Nitrogen cycling plays a major role in determining the level and pattern of estuarine productivity, because most coastal ecosystems are nitrogen limited (1, 2). The fate of inorganic nitrogen entering an estuary is key to understanding estuarine nitrogen dynamics. Denitrification, an anaerobic respiration process in which nitrate is reduced to N<sub>2</sub> gas by bacteria (1, 2, 3), is an important nitrogen sink in estuarine systems. Nitrate

for denitrification in the sediments comes from two sources: diffusion of NO<sub>3</sub><sup>-</sup> into the sediment from the water column (direct denitrification), or NO<sub>3</sub><sup>-</sup> produced from the oxidation of ammonium (NH<sub>4</sub><sup>+</sup>) released by the degradation of organic matter (coupled denitrification) (1, 4, 5).

The purpose of this study was to investigate sediment denitrification at an oligohaline site in the Parker River Estuary, Massachusetts. Our objectives were to compare (1) three methods of estimating coupled denitrification, (2) rates of denitrification with several NO<sub>3</sub><sup>-</sup> concentrations in the overlying water, and (3) denitrification rates in intertidal and subtidal sediments.

<sup>1</sup> University of Colorado, Boulder.

<sup>2</sup> Ecosystems Center, Marine Biological Laboratory.

<sup>3</sup> Dept. Life Science and Chemistry, Roskilde University, Denmark.

Table I

Sediment-water fluxes of DIC, O<sub>2</sub>, NH<sub>4</sub><sup>+</sup>, and NO<sub>3</sub><sup>-</sup>, sediment NH<sub>4</sub><sup>+</sup> production, and estimates of denitrification for the Parker River Estuary (mean ± standard error). Fluxes are in mmol·m<sup>-2</sup>·d<sup>-1</sup>, and denitrification estimates are in mmol N·m<sup>-2</sup>·d<sup>-1</sup>. Negative fluxes are directed into the sediment. Ambient nitrate concentrations were ~9 μM.

Treatment: Site:	+0 μM NO <sub>3</sub> <sup>-a</sup>	+0 μM NO <sub>3</sub> <sup>-a</sup>	+5 μM NO <sub>3</sub> <sup>-a</sup>	+25 μM NO <sub>3</sub> <sup>-b</sup>
	Intertidal Flux ± SE	Subtidal Flux ± SE	Subtidal Flux ± SE	Subtidal Flux ± SE
NH <sub>4</sub> <sup>+</sup> flux	2.64 ± 0.41	2.02 ± 0.10	3.69 ± 1.35	2.32 ± 0.37
O <sub>2</sub> flux	-35.53 ± 1.01	-27.01 ± 0.54	-44.47 ± 10.41	-38.47 ± 4.90
O <sub>2</sub> :N ratio	13.86 ± 6.01	13.40 ± 0.74	12.74 ± 2.40	17.30 ± 4.92
Coupled denitrification	2.73 ± 0.56	2.05 ± 0.18	3.03 ± 0.22	3.49 ± 1.03
DIC flux	65.71 ± 5.30	18.62 ± 0.55	32.14 ± 4.11	23.55 ± 6.98
C:N ratio	25.85 ± 6.01	9.24 ± 0.74	9.59 ± 2.40	9.92 ± 1.53
Coupled denitrification	7.28 ± 1.21	0.79 ± 0.19	1.16 ± 0.73	1.24 ± 0.68
NH <sub>4</sub> <sup>+</sup> production <sup>c</sup>	8.48 ± 1.94	5.37 ± 1.95	5.37 ± 1.95	5.37 ± 1.95
Coupled denitrification	5.84 ± 1.98	3.35 ± 1.95	1.69 ± 2.37	3.05 ± 1.99
NO <sub>3</sub> <sup>-</sup> flux	-0.48 ± 0.14	0.00 ± 0.04	-0.87 ± 0.49	-2.38 ± 0.40
Direct denitrification	0.48 ± 0.14	0.00 ± 0.04	0.87 ± 0.49	2.38 ± 0.40
Total denitrification <sup>d</sup>	3.20–7.76	0.79–3.35	2.03–3.89	3.62–5.87
% direct denitrification <sup>e</sup>	6–15%	0%	22–43%	41–66%
% N denitrified <sup>f</sup>	50–73%	50–62%	26–47%	32–59%

Notes: <sup>a</sup>n = 2; <sup>b</sup>n = 3; <sup>c</sup>n = 9; <sup>d</sup>calculated as a range for coupled + direct; <sup>e</sup>calculated as a range of percent of total denitrification; <sup>f</sup>calculated as a range of percent remineralized N denitrified.