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Improved method for quantifying the air-sea flux of volatile and semi-volatile organic carbon

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Abstract

A method for quantifying the diffusive air-sea exchange of gaseous organic carbon (OC) was developed. OC compounds were separated into two operational pools—those that were kinetically air limited in diffusion across the air-sea interface and those that were water limited—during simultaneous air/water sampling. The method separates OC compounds into low Henry's law constant (low-H) semivolatile OC (SOC) and high Henry's law constant (high-H) volatile OC (VOC) pools that can be categorized by relating diffusion kinetic parameters to Henry's Law constant. Air limited (low-H; $H << ~0.1$ L atm mol^{-1}) compounds were collected in pure water traps and were quantified as dissolved OC, whereas water limited (high-H; $H >> ~0.1$ L atm mol^{-1}) compounds were collected on solid sorbent tubes downstream from the water traps and were analyzed by gas chromatography-flame ionization detection (GC-FID). Separating OC based on H, rather than measuring OC as one bulk pool, allows improved estimates of OC concentration gradients and fluxes. A 10-month field study in the York River Estuary in Gloucester Point, VA revealed an average VOC flux of 138 µg C m^{-2} d^{-1} and an average SOC flux of 832 mg C m^{-2} d^{-1} (positive fluxes denote sea to air transfer).

Understanding the global cycling of bioelements, such as carbon, requires linking their transport vectors and pools in atmospheric, aquatic, and terrestrial systems. Quantifying carbon movement through the oceanic system is critical for a complete picture of the global carbon budget. Given the variability in metabolic balance within and between marine and coastal aquatic ecosystems (Caffrey et al. 1998; del Giorgio and Duarte 2002; Gupta et al. 2009; Kemp et al. 1997; Raymond et al. 2000), lateral transport of carbon could be the key to reconciling gaps in carbon budgets. One possible transport vector that has not been thoroughly investigated is organic carbon transfer between surface waters and the atmosphere.

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There is currently no universally accepted method for quantifying the diffusive air-sea flux of OC. Previous studies have mainly measured only a few compounds and have used atmospheric gas phase OC (GOC) quantification techniques such as direct trapping followed by chromatographic analysis (Baker et al. 2000; Chuck et al. 2005; Singh et al. 2003), stripping airborne OC into water traps (Dachs et al. 2005; Ruiz-Halpern et al. 2010), and averaging of literature values (Beale et al. 2010). To quantify aqueous exchangeable dissolved OC (EDOC) concentrations, researchers have purged OC onto solid sorbents (Beale et al. 2010; Baker et al. 2000) or water traps (Dachs et al. 2005; Ruiz-Halpern et al. 2010), or assumed surface ocean-atmospheric steady state (Singh et al. 2003). Further discrepancies in handling of wind speed effects, average molecular weight of bulk OC, and most importantly, mass transfer coefficients make flux calculations nearly incomparable.

The few studies that have attempted to measure bulk OC (Dachs et al. 2005; Ruiz-Halpern et al. 2010) established the potential importance of air-sea volatile OC (VOC) and semivolatile OC (SOC) fluxes in the context of carbon cycles. The researchers present a method in which air OC concentration was measured by purging air through pure water traps, and in which water OC concentration was measured by purging pure air through seawater and then purging the outgassed products through pure water traps. The dissolved OC in the traps was

used to calculate atmospheric and seawater OC concentrations, respectively. However, these studies may not have sufficiently accounted for differences in partitioning behavior across the OC pool. In the current study, we present an improved method to measure concentration and flux of gaseous OC, and consider important differences in mass transfer coefficient in the experimental model, which were not taken into account in previous work (Dachs et al. 2005; Ruiz-Halpern et al. 2010). The current study also addresses the need to properly account for equilibration of airborne OC in the water traps. The method was developed in the laboratory and tested in the York River Estuary in Gloucester Point, Virginia, USA.

Materials and procedures

Theory

In quantifying the air-sea flux of OC compounds, a film model consisting of a two-layer bottleneck boundary at the air-sea interface (Whitman 1923) is adopted. This model is characterized by two stagnant zones comprising a film lying between two well-mixed bulk zones. Chemical transfer between the water and the atmosphere is limited by molecular diffusion across the film—a thin, stagnant water layer in contact with a thin, stagnant air layer (Fig. 1). From this model, equations for flux are derived using the air phase as a reference (Liss and Slater 1974):

$$F = -v_{tot}[GOC - (H \times EDOC)] \qquad (1)$$

where

$$1/v_{tot} = 1/v_A + H/v_W \qquad (2)$$

In Eq. 1, F is the total flux across the two films, v_{tot} is the mass transfer coefficient across both films for the total OC pool, and H (in L atm^{-1} mol^{-1}) is unique to each compound.
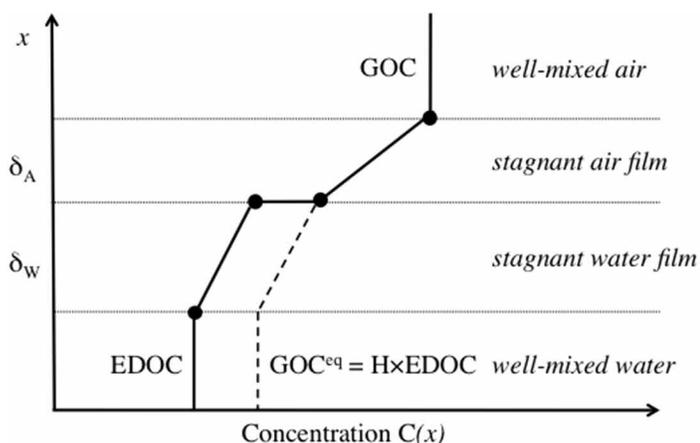
v_{tot} is dependent on the individual mass transfer coefficients across the air (v_A) and water (v_W) films as well as H (Eq. 2). If H for a compound is very large such that $H/v_W \gg 1/v_A$, then $v_{tot} \approx v_W/H$. In this case (very large H), the rate of diffusion across the air-sea interface is limited by diffusion across the water film, and is inversely proportional to H. If H is very small such that $H/v_W \ll 1/v_A$, then $v_{tot} \approx v_A$. In this case (very small H), the rate of diffusion across the air-sea interface is limited by diffusion across the air film and is essentially independent of H.

In the current study, bulk OC concentration gradients (GOC – [H × EDOC]) were determined experimentally and mass transfer coefficients (v_{tot}) were estimated using a combination of experimental results and theoretical calculations as described below. Air and water OC was experimentally separated into operationally defined SOC (low-H) and VOC (high-H) pools so the proper kinetic parameters could be applied. VOC (H $\gg$ 0.1 L atm mol^{-1}) was considered water-film limited and SOC (H $\ll$ 0.1 L atm mol^{-1}) was considered air-film limited in diffusion across the air-sea interface.

Air sampling

To measure GOC, a known volume (20-30 L for sufficient signal:noise) of marine air was pumped (50 mL min^{-1}) through a glass fiber filter (47 mm diameter) to remove particulate aerosols. The particulate-free air was sparged through two water traps consisting of Teflon impingers with 40 mL of ultrapure water (Milli-Q; 18.2 MΩ·cm) and a 10-μm stainless steel gas diffuser in each (Fig. 2A). The gas diffusers were used to create very small bubbles to establish equilibrium between the air and water in the traps. Finally, the air was passed through two sorbent tubes in series—one containing ~3 g Tenax GR

Fig. 1. Two-film model of diffusive air-sea exchange adapted from Liss and Slater (1974).
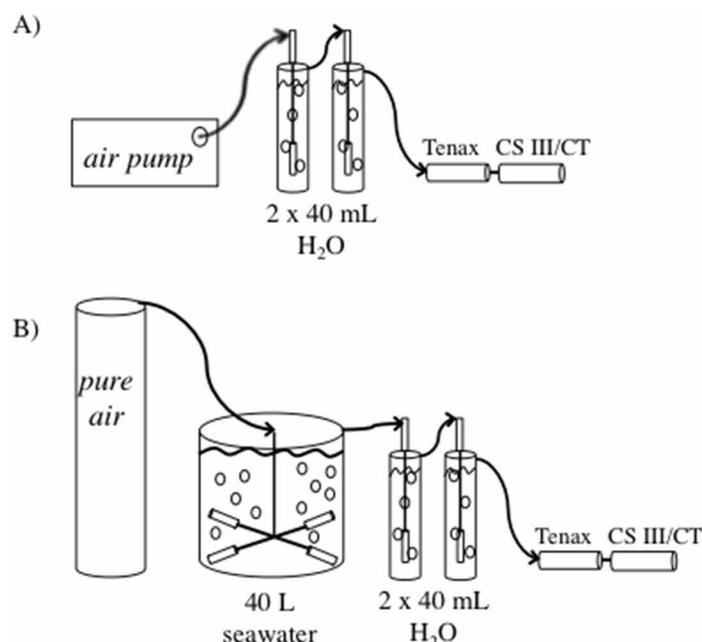
Fig. 2. A) Air-sampling apparatus and B) water-sampling apparatus.

(Markes/Agilent) and one containing ~3 g molecular sieve sorbent (Carboseive III [CSIII] or Carbotrap [CT] [Markes/Agilent])—that effectively trap a range of organic compounds, according to manufacturer specifications and experiments described below. The sorbent tubes were heated (Sidewinder LC column heater) to 15-20°C above ambient temperature during sampling to decrease water vapor adsorption and increase the amount of active sites available for OC capture (Gawrys et al. 2001). Three liters of ultrapure air were passed through the water traps following sampling to purge any residual VOC out of the water traps and onto the sorbent tubes.

Water sampling

For water sampling, approximately 41 L surface water were pumped from a depth of 1 m (stainless steel Mini-Monsoon groundwater pump) through Teflon tubing into a stainless steel tank with four ports and an airtight lid sealed with a Teflon-coated rubber O-ring and minimal headspace (≤0.5 L). Pumping the water into the bottom of the tank avoided splashing, and the water was analyzed immediately after careful transport to the lab. Water samples and air samples were collected simultaneously. To measure exchangeable OC in seawater (H × EDOC), 1 L clean air was pumped through a 1/4-inch Teflon line to the bottom of the tank and through an array of four 10-μm stainless steel gas diffusers that dispersed air into the water as small bubbles. The air passed through the water, collecting seawater dissolved OC, and through an outlet at the top of the tank. Upon exiting the tank, the air was bubbled through two Teflon impingers each containing 40 mL ultrapure water and a stainless steel diffuser, and then through heated sorbent tubes filled with Tenax and CSIII or CT as described for the air sampling (Fig. 2B). The air exiting the top of the tank contained OC in equilibrium with the seawater (H × EDOC) as shown by validation experiments (see below); airborne OC then either diffused into the water traps (SOC) or was retained on the sorbent tubes (VOC) as explained for the air sampling method.

EDOC samples (i.e., 1 L of air purged through seawater and through 1 set of water traps and Tenax/CSIII or CT sorbent tubes) were collected at four time points separated by 2-3 L of purged/vented air such that OC was stripped out of the seawater over time. Each sample was expected to show reduced OC concentration reflecting OC stripping out of the seawater into the bubbling air. Alternatively, an increase in OC concentration, which was occasionally observed, may reflect biological production of OC during purging. The initial OC concentration in water was estimated as the y-intercept of the linear regression of the natural log of the OC concentration in the 1 L of purged air versus purge time as described in Mackay et al. (1979). The resulting OC concentration is an estimate for the initial in situ seawater-equilibrated air OC concentration at the time of water sample collection.

OC quantification

VOC on the sorbent tubes was analyzed with a platform thermal desorber (TD) (Markes Unity 2) in line with a gas chromatograph (GC) (Agilent) with a flame ionization detector (FID), which is carbon specific. Tubes were sealed at room temperature after sampling and usually analyzed within 24 h, and within 2-3 d in isolated cases. Calibration curves using representative organic standards were constructed to relate FID signal to amount of carbon on the tube (S1). All compounds used for calibration had a similar concentration-signal relationship, so a calibration curve consisting of only the tridecane, tetradecane, and pentadecane standards was constructed before each analysis. Tenax tubes were desorbed at 300°C for 5 min, and CSIII and CT tubes were desorbed at 340°C for 5 min. GC column temperature was 35°C, held for 1 min, followed by a 10°C/min increase to 300°C (27.5 min total). Only the first 20 min of each chromatogram were integrated to exclude baseline irregularities due to column bleed at the end of the temperature ramps. All standards eluted in less than 17 min.

The water in the traps containing the SOC was transferred to Teflon bags, sealed and frozen immediately, and analyzed within 2 months. The SOC water samples for both the ambient air and seawater samples were analyzed with a Shimadzu DOC analyzer using high temperature (680°C) Pt-catalyzed oxidation coupled to non-dispersive infrared gas detection of CO_2. Samples were pre-acidified (20% HCl) and purged to remove inorganic carbon, though since purge times were short compared to sampling times, removal of SOC is expected to be minimal. Mean response areas for triplicate injections for each sample were calibrated to standard (potassium hydrogen phthalate or glycine) curves to calculate SOC concentrations.

For both GOC and EDOC, SOC concentrations were corrected for equilibration between the air and water traps according to the following mass balance:

$$m_{SOC} = SOC_{trap}V_W + SOC_{breakthrough}V_A \qquad (3)$$

In Eq. 3, m_{SOC} is the total mass of SOC in the air/water trap system, SOC_{trap} and $SOC_{breakthrough}$ are concentration of SOC that equilibrate into the water traps and air, respectively, and V_W and V_A are the water trap and air volumes, respectively. Although the assumption that most SOC remains in the water traps is inherent in the method, a rigorous treatment of equilibrium is required. Assuming the water traps equilibrate with the OC in the air:

$$m_{SOC} = SOC_{trap}V_W + SOC_{trap}K_{H,SOC}V_A \qquad (4)$$

where $K_{H,SOC}$ is the dimensionless Henry's Law constant for the bulk SOC pool. Then, the actual concentration of SOC in the air bubbling through the water traps is related to the concentration in the water traps as follows:

$$m_{SOC}/V_A = SOC_{trap}[(V_W + K_{H,SOC}V_A)/V_A] \qquad (5)$$

Therefore, concentrations measured in water traps must be

multiplied by the following correction factor: $(V_W + K_{H,SOC}/V_A)/V_A$. $K_{H,SOC}$ was assumed to be 4.1×10^{-5}, as it is likely that K_H values for the bulk of SOC compounds range from 10^{-6} to 10^{-4} (Schwarzenbach et al. 2003).

Quality assurance and method validation

Sorbents were tested for retention of VOC by placing a standard-spiked tube and a clean tube in series, flowing 30 L of ultra pure air through them, and comparing the amount of material remaining on each. Tenax sufficiently retained mid- to high-molecular weight VOC standards (tetradecane, pentadecane, hexadecane, heptadecane) while CSIII retained the lighter, more volatile compounds (acrylonitrile, 1,3-butadiene, vinyl chloride, benzene, methylene chloride, 1,2-dichloroethane, chloroform, tetrachloroethane). Retention efficiency was approximately 99% for Tenax and 92% for CSIII.

The water traps were shown by experiments with chemical standards to 1) retain water-soluble compounds with low H and 2) *not* retain volatile compounds with high H following a 3 L purge with clean air. When high-H VOC compounds—including xylenes (p-xylene, H = 7.1 L atm mol⁻¹; o-xylene, H = 4.5 L atm mol⁻¹) and esters (ethyl acetate, H = 6.7 L atm mol⁻¹; isopropyl acetate, H = 3.3 L atm mol⁻¹; butyl acetate, H = 0.32 L atm mol⁻¹; pentyl acetate, H = 0.37 L atm mol⁻¹)—were added to pure water in the traps and air was bubbled through at routine sampling rates, approximately 93% of the VOC compounds were recovered on Tenax tubes using an air volume of 3 L. Approximately 50% and 57% of the VOC compounds were recovered with 1 L and 2 L purges, respectively, so the 3 L purge volume was determined to be optimal. Some of these compounds (butyl acetate, pentyl acetate) are on the lower end of the high-H compound class suggesting that most airborne VOC compounds will break through water traps and adsorb to sorbent tubes during sampling. The method was also tested to ensure that SOC compounds remain in the water traps throughout sampling. When methanol (H = 4.6×10^{-3} L atm mol⁻¹) was added to the water traps, bubbling 3 L of pure air through the traps retained approximately 98% of the methanol in the water.

All sampling equipment was cleaned with 10% HCl solution (Teflon) and/or methanol (Teflon and stainless steel) and ultrapure water before each sample. The stainless steel tank was also cleaned with a handheld steam cleaner before and after each sample. The whole sampling apparatus was blank tested for VOC typically before each sample by running ultra pure air through the air sampling system (20 L) and water sampling system (1 L) and sorbent tubes to observe the level of intrinsic contamination. The GC-FID integration of the blanks (0-112 ng C for air sampler and 0-41.0 ng C for water sampler) was subtracted from sample integrations to make sure only in situ VOC was being measured. For blank-correcting the measurements of SOC in the water traps, a sealed Teflon impinger with the same water used for sampling was placed next to the sampling apparatus for the duration of sampling. DOC concentrations found in this field blank impinger

were averaged over all samples. Since field blanks varied considerably from sample to sample, the average field blank DOC value plus 2 standard deviations (8.8 μM) was subtracted from the concentrations measured in the sample impingers. All VOC and SOC concentrations in this study are reported after subtracting system blank chromatograms and field blank DOC concentrations, respectively.

Verifying equilibrium conditions between the sparged pure air and the 41 L seawater sample was necessary for measuring H × EDOC. Because separating DOC from gaseous OC is difficult, the air phase was used as a reference in deriving the flux equation, so that VOC and SOC concentration in air-equilibrated water (H × EDOC) rather than aqueous OC could be measured. Air and water gaseous OC concentrations at equilibrium are related by H. To determine if the system reaches equilibrium, a gas stripping method was used to estimate H of two chemical standards, 4-isopropyltoluene (H = 7.69 L atm mol⁻¹) and n-butylbenzene (H = 12.5 L atm mol⁻¹). The water tank was filled with 41 L ultrapure water and spiked with a small amount (~200 μmol) of each compound. Following complete stirring and headspace purging, four 1 L air samples were collected on a set of sorbent tubes (Tenax and CSIII) as air was continuously bubbled through the tank and vented in between samples. The rate at which the compounds were stripped from the water into the air is related to H as follows (Mackay et al. 1979):

$$\ln(C/C_0) = -(HG/VRT)t \qquad (6)$$

where C and C_0 are the substrate concentration and initial concentration, G is the gas flow rate (5.0×10^{-4} m³ min⁻¹), V is water volume, R is the gas constant, T is the system temperature (25°C), and t is time. H is calculated using the slope of a plot of the amount of compound collected on the sorbent tubes versus purge time. Obtaining an estimate for H that is similar to values reported in the literature indicates the air and water in the sampling apparatus were able to come to equilibrium. In this experiment, estimated H for n-butylbenzene (13.7 L atm mol⁻¹) was within 10% of literature values, and estimated H for 4-isopropyltoluene (10.6 L atm mol⁻¹) was within 30% (Fig. 3).

Assessment

Field study

VOC and SOC samples were collected in York River, Gloucester Point, VA, off of the Virginia Institute of Marine Science pier (S2). The purpose of the field study was to validate the method for use in coastal systems and to obtain an order of magnitude estimate for air and water VOC and SOC concentrations and air-water diffusive OC flux. Samples were collected approximately monthly from July 2010 to May 2011. GOC and H × EDOC were measured for VOC and SOC for each date, with the exception of 1 July 2010 when no SOC measurements were made, and January, February, and March

2011, when no VOC measurements were made. VOC (Table 1) and/or SOC (Table 2) air and water concentrations and concentration gradients were calculated for each sampling date. Plots of VOC and SOC concentration versus purge time are included in the Supporting Information (S3).

The negative of the difference between air and water concentrations is used to reflect the model convention, such that
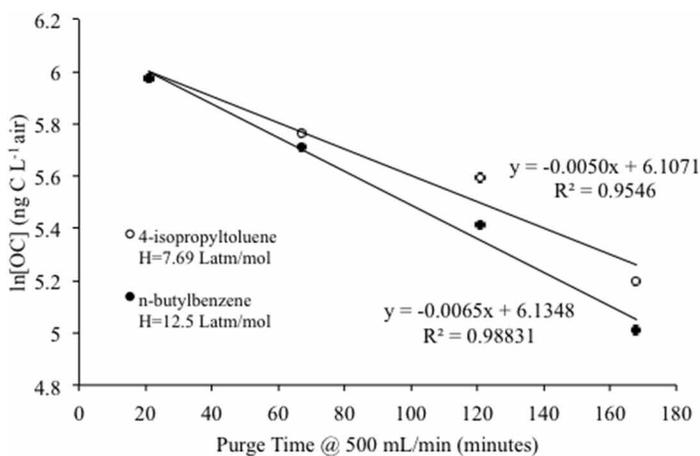
Fig. 3. Declining 4-isopropyltoluene and n-butylbenzene concentration on sorbent tubes that collected air continuously bubbled through 41-L water spiked with the two standards.
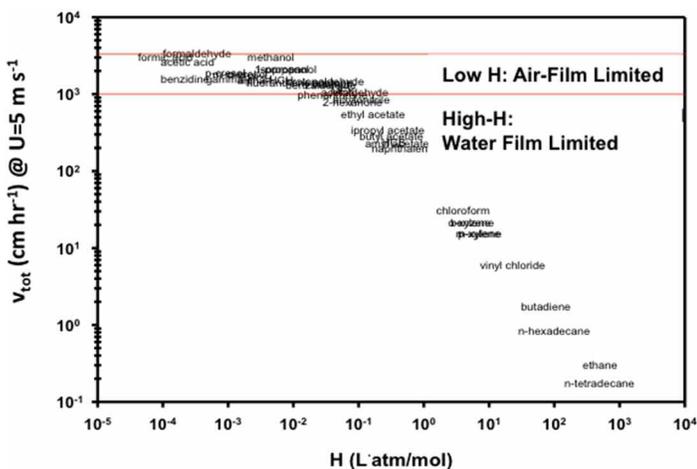
a positive concentration gradient indicates a flux from the surface water to the atmosphere. For VOC, GOC concentration ranged from 17.5 ng C L^{-1} in July to 105 ng C L^{-1} in May and H × EDOC ranged from 131 ng C L^{-1} in October to 560 ng C L^{-1} in July. Concentration gradient ranged from 78.3 ng C L^{-1} in May to 542 ng C L^{-1} in July (Table 1). For SOC, GOC ranged from below detection in December to 3.82 ng C L^{-1} in April and H × EDOC ranged from 58 ng C L^{-1} in February to 2.45 µg C L^{-1} in May. Concentration gradient ranged from 56 ng C L^{-1} in February to 2.45 µg C L^{-1} in May (Table 2).
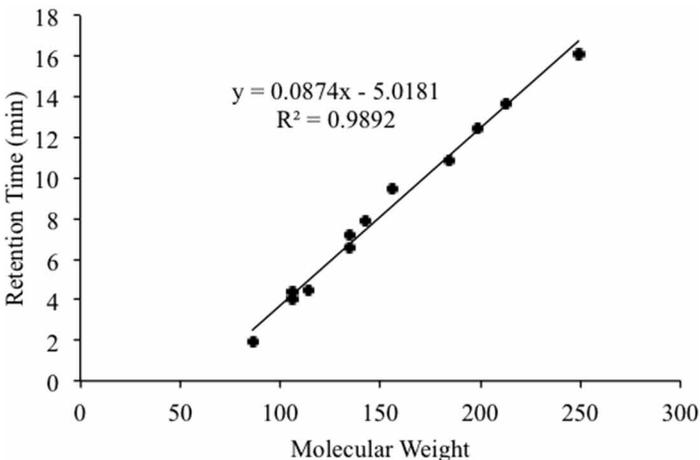
Calculating VOC flux

Gaseous OC flux is equal to the product of the OC concentration gradient and mass transfer coefficient (Eq. 1), so an estimate of v_{tot} precludes flux calculation. Mass transfer coefficients vary widely across compounds of varying Henry's Law constant, as is shown for a range of chemical standards (Fig. 4). Therefore, mass transfer coefficients were calculated separately for VOC and SOC—to our knowledge, this is the first experiment that does so.

Estimation of mass transfer coefficients of VOC compounds is crucial since v_{tot} varies exponentially with H (Fig. 4). The method presented here includes a way to constrain v_{tot} for the VOC fraction. Since no attempt was made to rigorously identify VOC compounds, an observed linear relationship between retention time and molecular weight of calibration standards (Fig. 5) was used to estimate molecular weight from the GC

Table 1. VOC concentrations in air and water, and VOC concentration gradients across the air-sea interface.

Sample date	GOC ng C L^{-1}	Error	H×EDOC ng C L^{-1}	Error	–(GOC-H×EDOC) ng C L^{-1}	Error
1-Jul-2010	17.5	3.5	560	112	542	112
28-Jul-2010	97.2	19.4	496	99	399	101
15-Oct-2010	46.5	9.3	131	26	84.8	27.9
9-Nov-2010	37.1	7.4	158	32	121	33
3-Dec-2010	23.5	4.7	161	32	137	33
13-Apr-2011	52.2	10.4	155	31	102	33
2-May-2011	105	23	183	38	78.3	44.7

Table 2. SOC air and water concentrations, and SOC concentration gradient across the air-sea interface.

Sample date	GOC ng C L^{-1}	Error	H×EDOC ng C L^{-1}	Error	–(GOC-H×EDOC) ng C L^{-1}	Error
28-Jul-2010	1.71	0.34	980	196	978	196
15-Oct-2010	2.64	0.53	780	156	777	156
9-Nov-2010	1.50	0.30	786	157	785	157
3-Dec-2010	b.d.*	—	347	69	347	69
19-Jan-2011	1.95	0.39	955	191	953	191
31-Jan-2011	—	—	141	28	—	—
23-Feb-2011	1.89	0.38	58	12	56	12
14-Mar-2011	0.505	0.101	313	63	313	63
13-Apr-2011	3.82	0.77	2,000	400	2,000	400
2-May-2011	1.77	0.35	2,450	490	2,450	490

* b.d. = below detection

Fig. 4. H and mass transfer coefficient for representative compounds above and below the operational cutoff between VOC and SOC.

Fig. 6. Typical air sample with estimated molecular weights of major peaks and midpoint of retention time window.
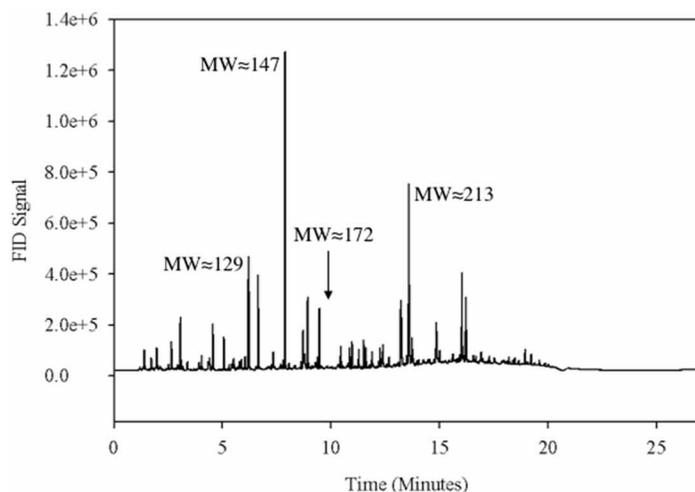

Fig. 5. Relationship between molecular weight and retention time of methanol-dissolved liquid chemical standards (propanal, pentanal, o-xylene, p-xylene, 4-isopropyltoluene, nonanal, n-butylbenzene, decanal, tridecane, tetradecane, pentadecane, 4-bromophenyl phenyl ether [gas]).

chromatograms of in situ VOC. The first 20 min of the 27-min chromatogram were integrated and ranged in molecular weight from an estimated 57 to 286, with a molecular weight of 172 corresponding to the midpoint retention time (Fig. 6).

With an estimate of the average molecular weight of VOC, average water phase diffusivities (D_W) were estimated by using an empirical relationship derived from a suite of organic compounds such as aromatics, ketones, acids, and low molecular weight organohalogens (Schwarzenbach et al. 2003):

$$D_{W,sample} = (2.7 \times 10^{-4})/(MW_i^{0.71}) \qquad (7)$$

Water phase diffusivities are used because for high-H compounds, $v_{tot} \approx v_W/H$. Using this relationship and the average molecular weight of 172, sampled compounds have an aver-

age diffusivity of 6.98×10^{-6} cm^2 s^{-1} (Table 3). Since the chemical composition of the sampled material is not known, temperature effects on D_W were not taken into account.

The next step toward estimating a mass transfer coefficient for the sampled compounds is determining their Schmidt numbers (Sc, ratio of viscosity to diffusivity). The ratio of the Schmidt number of the unknown compound and that of a known reference compound is found by its relationship to the ratio of water phase diffusivities (Schwarzenbach et al. 2003). Carbon dioxide is used as a reference since it has high H and is water limited in diffusion:

$$Sc_{W,sample}/Sc_{W,CO2} = D_{W,CO2}/D_{W,sample} \qquad (8)$$

The values used for $D_{W,CO2}$ were those corresponding to the closest 5° incremental temperature to the in situ water temperature at the time the sample was taken (Himmelblau 1964; Jahne et al. 1987; Oelkers 1991; Schwarzenbach et al. 2003) (S4). Values used for $Sc_{W,CO2}$ were those corresponding to saltwater at the closest 1° incremental temperature to the in situ water temperature (Matson and Harriss 1995). These values as well as the date-specific sample diffusivities ($D_{W,sample}$; Eq. 7) were used to solve for date-specific sample Schmidt numbers ($Sc_{W,sample}$; Eq. 8). $Sc_{W,sample}$ ranged from 1300 in July to 1910 in November and April (Table 3).

From the $Sc_{W,sample}$ estimates, water phase mass transfer coefficients of the sampled material were calculated using the following relationship (Schwarzenbach et al. 2003):

$$v_{tot,sample}/v_{tot,CO2} = (Sc_{W,sample}/Sc_{W,CO2})^{-a} \qquad (9)$$

where $a = 0.67$ for wind speeds (U_{10}) less than 5.0 m s^{-1} and a = 0.5 for wind speeds of greater than or equal to 5.0 m s^{-1} (Wanninkhof et al. 2009) (S4). Mass transfer coefficients of

Table 3. Calculation of VOC flux from concentration gradients and physical parameters estimated as described in the text.

Sample date	$-(GOC-H \times EDOC)$ ng C L^{-1}	$D_{W,sample}$ cm^2 s^{-1}	$Sc_{W,CO2}$	$D_{W,CO2}$ cm^2 s^{-1}	$Sc_{W,sample}$	U_{10} m s^{-1}	$v_{tot,CO2}$ cm s^{-1}	$v_{tot,sample}$ cm s^{-1}	Flux µg C m^{-2} d^{-1}	Error
1-Jul-2010	542	6.98×10^{-6}	472	1.92×10^{-5}	1300	4.8	1.54×10^{-3}	7.80×10^{-4}	365	90
28-Jul-2010	399	6.98×10^{-6}	451	2.18×10^{-5}	1410	3.7	9.13×10^{-4}	4.26×10^{-4}	147	37
15-Oct-2010	84.8	6.98×10^{-6}	666	1.68×10^{-5}	1600	4.3	1.23×10^{-3}	6.84×10^{-4}	50.1	19.2
9-Nov-2010	121	6.98×10^{-6}	912	1.46×10^{-5}	1910	6.1	2.48×10^{-3}	1.72×10^{-3}	179	48
3-Dec-2010	137	6.98×10^{-6}	1017	1.26×10^{-5}	1840	5.0	1.67×10^{-3}	1.24×10^{-3}	147	35
13-Apr-2011	102	6.98×10^{-6}	912	1.46×10^{-5}	1910	3.8	9.63×10^{-4}	5.87×10^{-4}	51.9	16.8
2-May-2011	78.3	6.98×10^{-6}	701	1.68×10^{-5}	1690	3.1	6.41×10^{-4}	3.56×10^{-4}	24.0	13.7

CO_2 were calculated using the relationship with wind speed for saltwater $v_{660} = 0.24U_{10}^2$ (Wanninkhof et al. 2009). Calculated mass transfer coefficients for the unknown sampled VOC were 0.356-1.72×10^{-3} cm s^{-1} (Table 3). With $v_{tot,sample}$ estimated for each sample date, flux calculations (Eq. 1) were made by multiplying by the concentration gradient (Table 1) for that sample date. VOC flux averaged 138 µg C m^{-2} d^{-1} in Gloucester Point (Table 3). No strong seasonal patterns were observed in VOC flux, possibly due to the lack of sampling frequency (Fig. 7).

Molecular weight for the SOC fraction cannot be used to estimate diffusivity because carbon is quantified nonspecifically. However, compounds with H << 0.1 L atm mol^{-1} tend to have high values of v_{tot} ($\approx v_A$); and, more importantly, v_{tot} does not vary greatly enough with H to change the order of magnitude of the flux estimate. v_A also only varies by about a factor of 2 across the wind speeds encountered (Schwarzenbach et al. 2003; S4)—calm days were chosen preferentially. Therefore, a typical (for air phase reference system) v_{tot} value of 1.0 cm s^{-1} for SOC compounds is used for flux calculation (Schwarzenbach et al. 2003). Fluxes were calculated by multiplying the concentration gradient (Table 2) and the mass transfer coefficient (Table 4). Average SOC
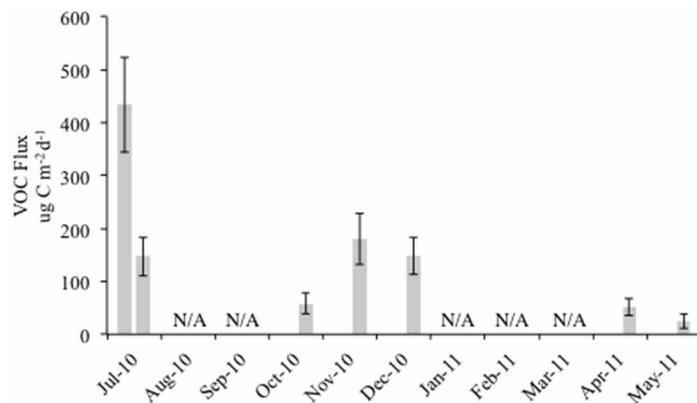
Fig. 7. VOC flux in Gloucester Point, VA for dates sampled.

flux was 832 mg C m^{-2} d^{-1}. Springtime samples showed higher SOC fluxes than the rest of the year, due to higher concentration gradients driven by very high H × EDOC observed in the spring months (Fig. 8). The reported errors in VOC and SOC fluxes reflect an estimated 20% error due to drift in air flow rate as well as the error associated with estimating H × EDOC by linear regression and extrapolation. Errors in mass transfer coefficients are not well defined and are not included in compounded errors.
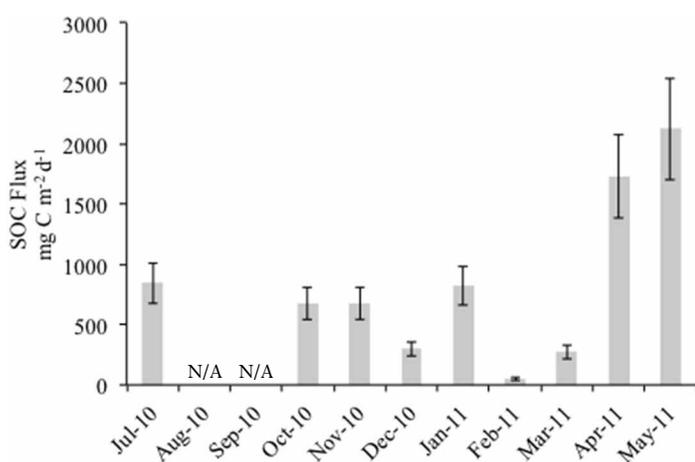
Discussion

Anthropogenic and biogenic gaseous OC emissions are estimated to be 19-100 and 1100-1500 Tg C y^{-1}, respectively (Bond et al. 2004; Fuentes et al. 2000; Larsen et al. 2001; Schauer et al. 2002). By comparison, biogenic organic primary aerosol emissions have been estimated to total 78 Tg C y^{-1} (Heald and Spracklen 2009; Penner 1995). Fossil fuel/biomass burning related emissions of aerosol OC and black carbon are estimated to be 33.9-73.1 and 8.0 Tg C y^{-1}, respectively (Bond et al. 2004; Liousse et al. 1996). Gaseous OC is being emitted at a higher rate than aerosol and black carbon emissions combined, and the atmospheric reservoir has the potential to drive a significant flux of material into surface waters. Additionally, biological activity and anthropogenic contaminants in surface waters have been shown to emit OC into the atmosphere (Harman-Fetcho et al. 2000; Liss et al. 1997; Ratte et al. 1998; Riemer et al. 2000; Sartin et al. 2001). There is evidence that gaseous OC flux could be greater than global wet and dry deposition (Jurado et al. 2008). With such large potential for carbon movement across and between reservoirs, advancement in methodology to quantify diffusive OC flux is necessary.

As the current study shows, mass transfer coefficients vary widely across compounds of different H, and high-H and low-H compounds behave differently. This is not only important when measuring flux across the air-sea interface, but also when experimental methods depend on diffusion processes to capture gaseous OC. For example, attempting to measure the

Table 4. Calculation of SOC flux from concentration gradients and physical parameters estimated as described in the text.

Sample date	$-(GOC-H \times EDOC)$ ng C L^{-1}	$v_{tot,sample}$ cm s^{-1}	Flux mg C m^{-2} d^{-1}	Error
28-Jul-2010	978	1.0	845	169
15-Oct-2010	777	1.0	671	135
9-Nov-2010	785	1.0	678	135
3-Dec-2010	347	1.0	300	60
19-Jan-2011	953	1.0	823	165
23-Feb-2011	56	1.0	48.4	10.4
14-Mar-2011	313	1.0	270	54
13-Apr-2011	2,000	1.0	1730	346
2-May-2011	2,450	1.0	2120	423

Fig. 8. SOC flux in Gloucester Point, VA for dates sampled.

surface water concentration of low-H (SOC) compounds by purging and stripping OC with a gas likely leads to an underestimation unless equilibrium is explicitly established, because low-H OC is air-film limited and largely partitions into water. If, by extension, airborne SOC is quantified by direct collection from the atmosphere, flux calculations will be erroneous since the SOC would be extracted from the water and air with very different efficiencies. In addition, the current study shows that OC concentrations and flux vary temporally (and likely spatially) on small scales. This suggests simultaneous air and water measurements are critical for accurate flux estimates.

Whereas the results of the current study cannot be directly compared with the few previous gaseous OC flux studies, which use a host of different methods at different locations, a discussion of the appropriateness of methods is useful. Attempts to quantify the air-sea diffusive flux of OC have been primarily limited to studies of biogeochemically significant compounds (e.g., methanol [Jacob et al. 2005; Singh et al. 2003]; dimethylsulfide [Simo and Dachs 2002]; acetaldehyde, propanal, acetone [Singh et al. 2003]; ethanol, 1- and 2-propanol [Beale et al. 2010]), halocarbons (Quack and Wallace

2004), or pollutants (i.e., polychlorinated biphenyls and polychlorinated dibenzo-p-dioxins/furans) (Jurado et al. 2004, 2005). Singh and colleagues (2003), who conducted their study in the Pacific Ocean, used atmospheric VOC concentrations, VOC precursor concentrations, hydroxyl radical concentrations, and photolytic loss to infer overall atmospheric VOC loss. They then assumed that atmospheric VOC was in steady state with the surface ocean concentrations to deduce air-sea fluxes of –64.3 µg C m^{-2} d^{-1} for acetone to 518 µg C m^{-2} d^{-1} for acetaldehyde. No equilibration step was used in the VOC collection procedure, and flux estimates do not take H or mass transfer coefficient into account and could vary in accuracy across compounds of different H. Beale and colleagues (2010), working in the Atlantic Ocean, used published atmospheric OC (ethanol and propanol) concentrations and an air stripping/solid sorbent technique to sample OC from surface seawater. They found fluxes of –7.21 to 96.1 µg C m^{-2} d^{-1} for 1-propanol and ethanol, respectively. Extraction efficiencies were estimated and both air and water phase resistances were considered, but no proof of equilibrium in the extraction was established, which could have been important since the compounds of interest have low H.

Baker and colleagues (2000) studied air-sea fluxes of methyl iodide, isoprene, and ethane, calculated by collecting Eastern Atlantic marine boundary layer air and cryogenically trapping the compounds of interest, purging seawater with nitrogen and trapping the outgassed products, and analyzing both chromatographically. This method, since only outgassed air is sampled, only effectively captures high-H VOC; however, all compounds of interest have H >> 0.1 L atm mol^{-1} so the method is appropriate. Average flux estimates for the three compounds were up to approximately 52, 5600, and 5880 ng C m^{-2} d^{-1}, respectively. Another study, conducted in the Atlantic and Southern Oceans, examined air and seawater measurements of five high-H halocarbons (CH_3I, CH_2ClI, $CHBr_3$, $CHBrCl_2$, $CHBr_2Cl_2$) and found average fluxes of –480 to 288 ng C m^{-2} d^{-1} (Chuck et al. 2005). This study also used seawater purging methods, appropriate for high-H VOC. Both studies accounted for differences in purging efficiencies

between compounds and differences in mass transfer coefficient, but did not verify equilibrium in the purging process.

Overall, studies aiming to quantify specific compounds can easily be adapted to consider differences in partitioning behavior based on H; however, as this study illustrates, this is more difficult when measuring a pool of many unknown organic compounds. A complete determination of total bulk VOC gas flux in the northeast Atlantic was attempted by Dachs and coworkers (2005) and in a Greenland fjord by Ruiz-Halpern and coworkers (2010). These researchers calculated OC flux using measured surface ocean and marine boundary layer OC concentrations and an average mass transfer coefficient based on wind speed. Gaseous OC in air was measured by bubbling it through pure water, and OC in seawater by bubbling air through the seawater, and then bubbling the outgassed products through pure water. Total gaseous OC in air and seawater was quantified as the DOC in the water traps, where DOC was equated to EDOC and GOC/K_H (dimensionless Henry's Law constant) for the seawater and air measurements, respectively. Diffusive OC fluxes in Dachs et al. (2005) ranged on average from –372 to –300 mg C m^{-2} d^{-1}. It is possible that the methods used by Dachs and colleagues (2005) did not adequately achieve equilibrium between pure water and air samples, or between pure air and water samples, as seawater stripping was conducted over 30 min, rather than a few hours, as was determined to be necessary in the current study. In the Ruiz-Halpern et al. (2010) study, equilibrium was verified and observed fluxes were –264 to 24 mg C m^{-2} d^{-1}. In the flux calculation, these studies treated all OC as a bulk pool without addressing differences in mass transfer coefficient across compounds of different H, which could influence flux estimates. By using only water traps for quantifying VOC, they could have been underestimating concentrations of these high-H compounds. Last, these researchers simply quantified the OC in the water traps as GOC/K_H and did not explicitly account for air and water volumes involved in separation in the sampling system.

The studies of individual compounds reviewed here found concentrations in the range of picograms to nanograms of carbon per liter of air and water. Measured fluxes of the high-H halocarbons are 1-2 orders of magnitude lower than total VOC flux estimates from the current study. When fluxes of individual compounds are added, previous estimates of VOC flux could be equal in magnitude and direction to those observed in the current study. Previous studies measuring SOC and/or total gaseous OC found concentrations in the range of nanograms to micrograms of carbon per liter. This parallels the current study, where SOC was found in much higher concentrations in air and water and also had a higher flux. The previous SOC flux estimates are much lower than those reported for Gloucester Point; however, these researchers were farther from land and were only measuring a few compounds (Singh et al. 2003; Beale et al. 2010). Total OC flux estimates are, with the exception of a couple very high fluxes (April and May measurements), comparable in magnitude to what was observed in Gloucester Point for SOC, but in the opposite direction. This could be a result of the shallow estuarine site chosen for the current study, differences in OC extraction efficiencies between water and air in the methods used by other researchers, or differences in treatment of equilibration steps during sampling.

Comments and recommendations

Gaseous OC flux has the potential to be significant in the context of the global carbon cycle (Jurado et al. 2008). A recent study (Wozniak et al. 2011) estimates that wet and dry carbon deposition in the same region as the current study totals 1.6 mg C m^{-2} d^{-1}, two orders of magnitude below the average gaseous OC flux calculated here. Greater spatial and temporal variability in sampling is required, especially in estuaries, where small scale variation in physical and biological phenomena cause high variability in biogeochemistry. Gaseous OC sampling needs to be conducted in environments of different productivities, salinities, and at different times throughout the day to determine an estuarine and eventually global, diffusive OC flux estimate.

More importantly, this study demonstrates the need in air-sea gaseous OC flux investigation for 1) optimization of experimental techniques to match compounds of interest and 2) differentiation of high-H (VOC) and low-H (SOC) material when using mass transfer coefficients to calculate total OC flux. In previous studies attempting to measure OC flux of a few chemicals or the entire pool, methods were often not optimal for capturing target compounds. Unless equilibrium is explicitly established, using a trapping method that relies on VOC diffusion from air to water is likely to underestimate high-H VOC concentrations, and using a method that relies on diffusion from water to air is likely to underestimate SOC. If a water trap is used, a correction factor like the one described (Eq. 5) is required to relate measured water trap OC concentrations with airborne OC concentrations of interest. Further, mass transfer coefficients for OC vary over 4 orders of magnitude H—compounds with H >> 0.1 L atm mol^{-1} have especially variable H. The use of one average mass transfer coefficient for the entire OC pool is insufficient and could cause erroneous flux estimates. Although SOC dominated in this study, this might not be true for all sites and more effort should be made to sample the entire range of OC, even if this means using multiple sampling methods.

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