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Development of a Method for Quantifying the Air-Sea Flux of Volatile Organic Carbon

Emily A. Jayne
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Development of a Method for Quantifying the Air-Sea Flux of Volatile Organic Carbon

A Thesis

Presented to

The Faculty of the School of Marine Science
The College of William and Mary in Virginia

In Partial Fulfillment

of the Requirements for the Degree of

Master of Science

by

Emily A. Jayne

2011
APPRAVAL SHEET

This thesis is submitted in partial fulfillment of
the requirements for the degree of

Master of Science

Emily A. Jayne

Approved, by the Committee, August 2011

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ABSTRACT

A method for quantifying the diffusive air-sea exchange of volatile organic carbon (VOC) is developed. Differences in Henry’s Law constant (H) and a novel experimental apparatus are utilized to separate VOC compounds into two operational pools during simultaneous air/water sampling, based on whether they are air or water limited in diffusion across the air-sea interface. High-H (water limited) compounds are collected on solid sorbent tubes and analyzed by gas chromatography/flame ionization detection, and low-H (air limited) compounds are collected in pure water traps and quantified on a dissolved organic carbon analyzer. A 10-month long field study was used to validate the method and to obtain an order of magnitude estimate of VOC flux in the lower York River Estuary, VA, USA. Average high-H VOC flux is calculated to be 1.85 ± 0.05 ng C m⁻² s⁻¹. Average low-H VOC flux is 115,000 ± 2410 ng C m⁻² s⁻¹. The method was also utilized on a research cruise in the northwest Atlantic Ocean, to validate its shipboard use and obtain a first estimate of open ocean VOC flux.
Quantifying the Air-Sea Flux of Volatile Organic Carbon
INTRODUCTION

Understanding the global cycling of bioelements, such as carbon, requires linking their chemical, biological, and physical transport vectors and pools in atmospheric, aquatic, and terrestrial systems. The oceans comprise the largest active reservoir of carbon on the planet by far, containing approximately 40,000 Pg C that actively exchanges with the continents, atmosphere, and sediments [Emerson and Hedges, 2008]. Oceanic gross primary production (P), currently estimated to be 84-108 Pg C yr\(^{-1}\), accounts for approximately half of the total global primary production [delGiorgio and Williams, 2005]. Coastal systems, such as estuaries and continental margins, add another 23 Pg C yr\(^{-1}\) of fixed carbon [delGiorgio and Williams, 2005]. Oceanic and terrestrial respiration (R) are also approximately equal—current estimates are that 108-144 Pg C yr\(^{-1}\) (126-201 Pg C yr\(^{-1}\) including estuaries and continental margins) are remineralized in oceanic systems, compared to terrestrial respiration rates of 114-126 Pg C yr\(^{-1}\) [delGiorgio and Williams, 2005]. Oceanic carbon fixation, remineralization, and transport are major components of the global carbon cycle, and understanding carbon movement through the oceanic system is critical in completing the global carbon loop.

The direction of net movement of reduced (organic) carbon into or out of a system—an estuary, a forest, or an entire continent—defines it as either an organic carbon sink or source, respectively. An alternative definition describes systems as either
net heterotrophic, in which more organic carbon is respired than produced, or net autotrophic, in which more organic carbon is produced than respired [Odum, 1956]. Historically, it has been assumed that most marine systems are net autotrophic—displaying an excess P over R—as a result of both a research emphasis on primary production and the tendency to study individual systems in isolation [Duarte and Prairie, 2005]. However, the aforementioned P and R estimates suggest that many systems, if not the marine system as a whole, undergo more respiration than production. Mounting evidence in the form of individual studies of aquatic systems that have observed net heterotrophy supports this claim [Agusti et al., 2004; Caffrey, 2004; Chen et al., 2003; delGiorgio and Peters, 1994; Duarte and Agusti, 1998; Gonzalez et al., 2001; Hoppe et al., 2002; Prairie et al., 2002]. This shifting paradigm has implications for how carbon movement throughout the entire global carbon cycle is understood, and is driving more detailed study of carbon transport and reservoirs.

Carbon Balance in Aquatic Systems

Open Ocean

Open ocean systems have received much attention in the exploration of production-respiration relationships [delGiorgio and Duarte, 2002]. It has been postulated that some areas of the oceans, specifically unproductive oligotrophic open-ocean systems, receive terrestrially-derived organic matter that has been chemically, biologically, and photolytically broken down, thus providing an allochthonous source of
labile organic matter and resulting in net heterotrophy \cite{delGiorgio et al., 1997; Duarte and Agusti, 1998; Duarte et al., 2001}. Other investigators, however, have failed to find a relative imbalance \cite{Williams, 1998}, and some have observed an ecosystem dependence on P:R, or production-respiration decoupling on small spatial scales \cite{Aristegui and Harrison, 2002; Duarte and Agusti, 1998; Robinson et al., 2002; Serret et al., 2001}. Respiration is typically the least constrained of the processes measured in these unproductive regions because of the poor suitability of methods used \cite{Karl et al., 1998; Suess, 1980}, the tendency for bias toward highly productive systems \cite{Duarte et al., 1999}, and because often only surface respiration, which may account for a modest portion of total respiration, is taken into account \cite{Biddanda and Benner, 1997; Moriarty and Odonohue, 1995}. More rigorous estimates of atmospheric, coastal, and ancient fixed carbon source inputs, as well as open ocean carbon export and deep water respiration are required for a more constrained carbon balance in the open ocean \cite{Bauer and Druffel, 1998; delGiorgio and Duarte, 2002}.

**Coastal Ocean**

Carbon imbalance has also been suggested in the coastal ocean, defined as the area comprising the continental shelf and estuaries, as well as in rivers and most lakes \cite{Duarte and Prairie, 2005}. Understanding carbon movement in the coastal ocean, a dynamic ecosystem with a high density of chemical and metabolic activity, is critical in understanding the global carbon cycle. According to one study, coastal ocean respiration accounts for 30\% of total marine organic matter oxidation; however, because of its small
surface area relative to the open ocean, coastal organic matter oxidation rates are about 5 times open ocean rates [Smith and Hollibaugh, 1993]. A number of estuarine and continental shelf systems studied exhibit excess organic matter oxidation [Chen and Borges, 2009; Gupta et al., 2009; Smith and Hollibaugh, 1993; Z A Wang et al., 2005]. One study that measured P:R in 22 estuaries along both coasts of the US found that all but 3 were net heterotrophic [Caffrey, 2004]. Conversely, some coastal lagoons and nutrient-rich lakes have been observed to be net autotrophic [Duarte and Prairie, 2005].

Production to respiration ratios in coastal areas are spatially and seasonally variable, complicating efforts to balance carbon budgets and to determine what is fueling the purported excess respiration [del Giorgio and Duarte, 2002]. Seasonality has been shown to affect the degree of CO$_2$ supersaturation (one possible indicator of net heterotrophy) in one tropical estuary, which shows a much higher degree of net heterotrophy during the height of the monsoon season [Gupta et al., 2009], and in the York River estuary, where degree of heterotrophy seems to be highest in the summer and fall [Raymond et al., 2000]. Other studies cite a shift from net heterotrophy to net autotrophy along the California coast with the onset of El Niño [Friederich et al., 2002] and the height of the algal bloom cycle [Caffrey et al., 1998]. A shift from net heterotrophy to autotrophy has also been observed moving downstream in coastal rivers and estuaries [Howarth et al., 1996; Raymond et al., 2000] and from estuarine channels to shoals [Caffrey et al., 1998; Kemp et al., 1997]. Vegetation type and adjacent habitats also impact P:R [Caffrey, 2004]. Seasonal and spatial variability in estuarine metabolic balance means that ecosystems could be regularly switching between being carbon
sources and sinks, and deciphering these patterns precludes an understanding of carbon transport on a larger scale.

Coastal areas are increasingly important in elemental cycling because they are highly susceptible to alteration by human activities, given their proximity to direct anthropogenic perturbations such as agriculture, sources of combustion, sewage release, etc. Relationships between organic and inorganic inputs, which are altered as land uses change, and degree of autotrophy or heterotrophy in coastal systems are poorly understood [Smith and Hollibaugh, 1993]. And, like all aquatic systems, coastal regions are subject to elevated atmospheric CO$_2$ concentrations that force diffusive uptake of anthropogenic CO$_2$ [Sabine et al., 2004].

The ocean as a whole is estimated to take up 2.2 Pg of anthropogenic carbon in the form of CO$_2$ per year [Fletcher et al., 2006]. However, the net heterotrophy of estuaries implies CO$_2$ disequilibrium with the atmosphere as respiration products accumulate, effectively decreasing or eliminating their anthropogenic CO$_2$ capacity. Some studies estimate that estuaries supply 0.43-0.50 Pg C yr$^{-1}$ to the atmosphere in the form of outgassed CO$_2$ [Borges et al., 2005; Chen and Borges, 2009]. Direct relationships between net ecosystem function and CO$_2$ exchange are not well constrained [Duarte and Prairie, 2005], and relationships between anthropogenic CO$_2$ perturbations and the organic C balance are poorly understood [delGiorgio and Duarte, 2002]. Because of the spatial and temporal variability of biological activity and pCO$_2$ gradient, the marine system as a whole could simultaneously be net heterotrophic and still be a net sink of anthropogenic CO$_2$ [Ducklow and McCallister, 2004]. Without a better
understanding of variability in ecosystem function, and how it relates to increased
organic/nutrient inputs, anthropogenic CO₂ loading, and CO₂ release, quantifying
relationships and predicting responses to perturbation is next to impossible.

Given the variability in metabolic balance between ecosystems, lateral transport
between aquatic systems as well as carbon transfer between terrestrial and aquatic
systems seems to be key in reconciling incidences of net heterotrophy. One possible
input fueling areas of presumed net heterotrophy, one that has not been thoroughly
explored, is organic carbon deposited from the atmosphere. The atmospheric organic
carbon input to the ocean could be quite large and is at present poorly quantified even
though carbon balancing attempts indicate missing sources of reduced organic material
[delGiorgio and Duarte, 2002]. In most models attempting to balance coastal production
and respiration, atmospheric transfer is either not included, or only accounts for
particulates or specific compounds like methane [Bauer and Druffel, 1998; Chen and
Borges, 2009; Gupta et al., 2009; Lucea et al., 2005]. Further, the carbon budget of
coastal regions have in many cases been less thoroughly studied because of their small
surface area and hence presumed lesser importance. The atmosphere may serve as a
source of organic carbon (OC) to the ocean which may fuel excess respiration.
Moreover, releases of OC from the oceans to the atmosphere have not been quantified in
global emissions inventories. Both directions of transfer need to be considered if the
global carbon cycle is to be balanced, and high spatial coverage is necessary given the
variability found in coastal ecosystems. A thorough understanding of the marine
system’s role in carbon sequestration, storage, and release requires narrowing the
uncertainties associated with the different pools, and identifying and accounting for all carbon transport processes.

Atmospheric OC

OC enters the atmosphere in the form of aerosols or gases from a variety of biogenic sources—e.g. sea spray, dust, biological debris, biogenic gases, forest fires, pollen, and spores—and anthropogenic sources—e.g. fossil fuel combustion, direct industrial release, and cooking operations [Castro et al., 1999; Fraser et al., 2003; Rogge et al., 1991; 1993a; 1993b; 1997; 1998; Schauer et al., 2002]. Biogenic organic primary aerosol emissions, from plants, microorganisms, fungi, etc. have been estimated to total 78 Tg C yr\(^{-1}\) [Heald and Spracklen, 2009; Penner, 1995]. Global annual fossil fuel and biomass related emissions of aerosol OC and black carbon, the soot-like substance that is produced by incomplete combustion, are estimated to be 33.9-73.1 and 8.0 Tg C yr\(^{-1}\), respectively [Bond et al., 2004; Liousse et al., 1996]. Anthropogenic and biogenic chemicals that are emitted into the atmosphere in the gas form—volatile organic carbon (VOC) emissions—are estimated at 19-100 and 1100-1500 Tg C yr\(^{-1}\), respectively [Bond et al., 2004; Fuentes et al., 2000; Larsen et al., 2001; Schauer et al., 2002]. At present, the two dominant VOC sources are thought to be contemporary terrestrial plant biomass emission, which is estimated to comprise up to 5% of plant net primary production, and incomplete combustion of fossil fuels [Chapin III et al., 2002; Lewis et al., 2004; Reddy and Eglinton, 2002]. In fact, two separate studies found that approximately 50% and 80% of the VOC in the atmosphere in Atlanta, Georgia, [Klouda et al., 1996] and Ispra,
Italy, [Larsen et al., 1998] respectively, was derived from fossil fuel combustion. VOC and aerosol OC are chemically diverse pools, and further diversify into a range of secondary products while undergoing reactions with sunlight and radicals in the atmosphere [Fuentes et al., 2000]. The fate of much of this material is at present unknown; as such, exchanges are generally not included in regional or global carbon cycle models [Jurado et al., 2008]. However, wet and dry aerosol transfers of OC have been more thoroughly studied than gaseous fluxes; so any estimates of diffusive VOC transfer should therefore be looked at in the context of these other fluxes.

Wet Deposition

Through molecular diffusion and particle scavenging, rainwater acquires aerosol and volatile organic matter, of which both biogenic [Andreae et al., 1990; Kawamura and Kaplan, 1986; Keene and Galloway, 1988; Talbot et al., 1988] and anthropogenic [Fraser et al., 1998; Kawamura and Kaplan, 1985; 1986; Talbot et al., 1988] OC are major components. Wet deposition, the addition of material to the earth’s surface through precipitation, is a significant source of dissolved OC (DOC) to both terrestrial and marine environments [Willey et al., 2000]. It adds an estimated 90 Tg C yr\(^{-1}\) to the surface ocean, which is equal to about half of the amount of OC that is removed and buried from the deep ocean [Willey et al., 2000]. Organic matter has been observed in marine, coastal, and continental rainwater in the eastern USA in concentrations of 22-56 \(\mu M\), 52-114 \(\mu M\), and 68-620 \(\mu M\), respectively [Willey et al., 2000]. Rainwater DOC is chemically diverse, and includes bioavailable components like organic acids (formic acid,
acetic acid, amino acids), aldehydes (formaldehyde, acetaldehyde) and a large fraction of uncharacterizable material (humic substances) [Tang and Willey, 1998]. Seasonal variability has also been observed in some cases, with continental rain generally showing higher DOC content in the summer than in the winter, and marine rain showing less significant temporal variation on an annual scale [Willey et al., 2000].

Organic matter found in rainwater has been shown to have a refractory component; therefore, it has the potential to transfer OC from one ecosystem to another as weather systems move. For example, 7 particular coastal rain samples from North Carolina (which overall had a 3 year, volume-weighted average of 116 $\mu$M DOC) showed a decrease in DOC concentration from approximately 36 $\mu$M after three months of refrigerated dark storage to approximately 14 $\mu$M after an additional month of dark storage at room temperature [Willey et al., 2000]. This suggests that about half of the DOC in the rain is resistant to microbial degradation, and has the potential to persist for at least several months, whereas the other half could be readily available to microbes and may contribute to net heterotrophy in some systems. Atmospheric OC could therefore be transported long distances and deposited in locations far from its origin—moving between land, the coast, and the open ocean. In fact, $^{13}$C/$^{12}$C measurements of rainwater DOC at remote oceanic locations—Enewetak Atoll, Sargasso Sea, Peru upwelling area, American Samoa, and New Zealand—indicate that it is about 80% terrestrially derived [Cachier, 1989]. By extension, carbon derived from ancient, fossil sources has been found in rainwater in both continental and marine environments [Ducret and Cachier, 1992; Reddy and Eglinton, 2002; Takase et al., 2003]. Current estimates yielded by examination of $\delta^{13}$C and $\Delta^{14}$C signatures of northeast US rainwater are that approximately
20-30% of rain OC is fossil carbon; and, when extrapolated to total northeastern US rainfall, yields a fossil carbon input proximate to the amount of fossil carbon transported to oceans by rivers, or about 0.5 g C m$^{-2}$ yr$^{-1}$ [Raymond, 2005].

Indeed, wet deposition has also been shown to be a source of marine-derived organic matter to coastal systems, as well as marine systems remote from the organic matter’s origin [O’Dowd et al., 2004; Raymond, 2005]. Marine biota produce VOC such as dimethyl sulfide and isoprene, substances that then diffuse out of the surface ocean and into the atmosphere where they condense and undergo photochemical transformations [Gantt et al., 2009; Simo and Dachs, 2002]. Breaking waves are also a physical producer of marine-derived VOC and aerosols, which can condense and undergo further reactions [Middlebrook et al., 1998; O’Dowd et al., 2004]. Hurricanes and storms that originate over the ocean can be a major vector transporting marine-derived OC to the continents. In a study conducted by Raymond and colleagues (2005), rainwater from storms that formed in the Gulf of Mexico still contained an appreciable amount of marine OC when it was deposited in New England. Presumably, this marine-derived OC was deposited over the entire east coast storm track [Raymond, 2005]. A separate study observed coastal precipitation containing DOC with isotopic signatures of both terrestrial and marine material [Avery et al., 2006]. This argues for significant transfer of OC between oceans and continents and between marine ecosystems—these vectors could be especially important in bringing chemically diverse OC to coastal regions because of their proximity to sources of both land and marine derived atmospheric OC [Avery et al., 2006].
Dry Deposition

Dry deposition is estimated to have regional importance, or to be a significant vector of specific compounds such as pollutants, but seems to represent only a small fraction of overall marine organic matter deposition [Gigliotti et al., 2002; Jurado et al., 2005]. Dry aerosol deposition of organic carbon has been regarded as relatively insignificant when compared to the other atmospheric vectors for bulk OC transport, and is generally assumed to be negligible or is not quantified in the literature, especially in the open ocean [Dachs et al., 2002; Simo and Dachs, 2002]. A major portion of marine aerosol is actually terrestrially derived material, much of which has been transported long distances—higher plant biomarkers (fatty alcohols, acids, and alkanes) from Asia, Indonesia, and the Americas have been found in even remote marine areas at concentrations of nearly 10 ng m$^{-3}$ [Chester et al., 1993; G Wang et al., 2009]. A study conducted at Chichi Jima, a remote island in the western North Pacific, found aerosol concentrations of 53 ng m$^{-3}$ with a Carbon Preference Index (CPI) of approximately 4, indicating a strong terrestrial signal [Bendale et al., 2006]. Fossil-fuel combustion byproducts are also ubiquitously associated with aerosols; compounds such as dicarboxylic acids have been observed as a dominant component of aerosols in virtually all environments [Mochida et al., 2003].

Dry deposition of organic carbon is more substantial in coastal areas closer to aerosol sources [Dachs et al., 2002]—in fact, aerosol deposition rates have been measured to be 3-10 times higher in coastal areas than in the open ocean [Duarte et al., 2006]. There seems to be an appreciable organic component of coastal marine aerosol
that could be important in fueling both local autotrophic and heterotrophic activity in
marine ecosystems [Conte and Weber, 2002; Kawamura et al., 2003; Sicre and Peltzer,
2004]. In a study conducted in the Yellow Sea to assess the influence of pollution from
China, organic matter was actually more abundant than the combined sum of K-
containing, Fe-containing, and ash material in airborne particulates [Geng et al., 2009].
One current estimate for dry depositional OC fluxes into the ocean, which combines field
measurements and model results, is a range from essentially no deposition in some mid-
ocean areas to up to 0.3 mg C m\(^{-2}\) d\(^{-1}\) in coastal and high-aerosol locations, yielding an
integrated global ocean total of approximately 11 Tg C yr\(^{-1}\) [Jurado et al., 2008].
However, deposition rates in the northeast Atlantic off the coast of the African continent
have been measured to be 11.8 mg C m\(^{-2}\) d\(^{-1}\) [Duarte et al., 2006], so global flux could be
even higher.

Gaseous OC Flux

The third type of chemical transfer between the atmosphere and the ocean is
gaseous diffusive air-sea flux. Biogenic and anthropogenic atmospheric emissions
produce a host of gaseous species that can diffuse across the air-sea interface. For
example, plants emit VOC compounds to deter pathogens from wounds and to attract
pollinators [European Science Foundation, 2005]. Emitted volatile species consist of
mostly hydrocarbons, like \(n\)-alkanes, hexane derivatives, isoprene, mono- and
sesquiterpenes, and some oxidized compounds like aromatic and aliphatic alcohols,
aldehydes, and ketones, and vary with season and plant species [European Science
Foundation, 2005; Atkinson and Arey, 2003; Fuentes et al., 2000]. Emission rates have been estimated to be approximately 11 mg C m$^{-2}$ h$^{-1}$ in forested areas [Guenther et al., 1994]. In urban areas where plant life is scarce, chemicals from vehicle emissions and chemical evaporative processes—such as aromatic hydrocarbons, short and long chain alkanes, and alkenes—tend to dominate anthropogenic VOC flux into the atmosphere, which has been measured to be approximately 1 mg m$^{-2}$ h$^{-1}$ [Kansal, 2009; Larsen et al., 2001; Muller, 1992; Na et al., 2005].

The marine atmosphere is an important reservoir for VOC and receives VOC from a variety of sources, even in areas far from terrestrial inputs. For example, a study at Mauna Loa identified over 80 organic compounds in the marine troposphere that had both local and very remote sources, indicating long range atmospheric transport of chemicals [Helmig et al., 1996]. However, spatial and temporal patterns indicative of short scale source-sink coupling have also been observed in both abundance and composition of airborne VOC: concentrations tend to be higher at night and decrease throughout the day, likely due to photochemistry and dilution through atmospheric entrainment and transport [Sartin et al., 2002]. In a study conducted by Sartin and colleagues (2001), airborne VOC was dependent on wind trajectories—oxygenated compounds were found in higher concentrations when the wind had a continental origin, but n-alkanes were more abundant when the wind trajectory indicated marine origins. A collection of routinely observed VOC compounds (10 compounds including alkanes, alcohols, and ketones) in this study were found to total, on average, approximately 518 pptv in areas where wind had continental origin, and 439 pptv where wind had an oceanic origin [Sartin et al., 2001]. Even in the southern hemisphere, where terrestrial influence
is weak, atmospheric VOC compounds have been measured to be up to 1000 pptv, although these compounds are mainly low molecular weight species such as methanol, acetone, and methyl hydroperoxide [Singh et al., 2001]. Current atmospheric chemistry models are unable to account for these high marine VOC concentrations; clearly there are contributing sources and/or sinks of VOC that are not well quantified [Singh et al., 2001].

One of the possible sources of marine VOC, in addition to transport from terrestrial emissions, is the surface ocean itself. It has long been recognized that marine phytoplankton are the major producer of atmospheric dimethylsulfide (DMS) after fossil fuel burning [Liss et al., 1997]; however, several marine species have been observed to produce other volatile organics. CH₃I, CH₃Br, multiple chlorinated species, low molecular weight hydrocarbons, and isoprene have been produced by laboratory cultures of a few phytoplankton species during growth and autolysis [Colomb et al., 2008; Happell and Wallace, 1996; Manley and de la Cuesta, 1997; Moore and Zafiriou, 1994; Moore et al., 1994]. Sartin and colleagues (2001) did a seaweed incubation experiment, in which they found an enrichment of gaseous long-chain n-alkanes in the air inside the seaweed enclosures. It should be noted too that phytoplankton and bacterioplankton have also been shown to be sinks for low molecular weight organic compounds—while large organic molecules are likely poor substrates for planktonic metabolism, smaller organics, that are often products of reactions involving larger molecules, might be more easily taken up [Kieber and Mopper, 1990]. Volatile short chain alkenes (C₂-C₄) are also formed from photolysis of dissolved organic matter in the surface ocean [Ratte et al., 1998; Riemer et al., 2000].
As would be expected given that phytoplankton has been shown to produce VOC compounds, a substantial plankton-dependent sea to air VOC flux has indeed been observed. Atmospheric concentrations of low molecular weight halocarbons such as CH$_3$I and CH$_3$Cl, proposed to function as antimicrobial or antigrazing agents, have been observed to be elevated in areas where phytoplankton biomass is high [Carpenter and Liss, 2000; Chuck et al., 2005; Kato et al., 2009]. Additionally, isoprene has shown strong correlations with phytoplankton biomass and chlorophyll-a concentration in both cultures and surface seawater, and atmospheric VOC studies have observed high levels of gaseous isoprene, even in remote marine locations, presumably from planktonic production and outgassing [Milne et al., 1995; Moore et al., 1994; Sinha et al., 2007]. While isoprene has considerable terrestrial plant and bacterial sources, its lifetime in the atmosphere is relatively short (hours); thus, it is not likely to survive long-distance transport to the open ocean. C$_2$-C$_4$ alkenes have been shown to be produced at estimated rates of up to 881 pg C L$^{-1}$ hr$^{-1}$ in highly colored coastal surface waters, likely because of high production and photochemical activity in these areas [Ratte et al., 1998; Riemer et al., 2000]. The oceanic emission of low molecular weight non-methane hydrocarbons such as isoprene, acetaldehyde, and acetone were light and/or biology dependent when measured in fjord mesocosms [Sinha et al., 2007]. The oceanic emission of anthropogenic compounds has been observed as well; for example, a study assessing the fate of pesticides used around the Chesapeake Bay found that the pesticide chlorpyrifos is emitted from estuarine waters at rates as high as 68 ng m$^{-2}$ d$^{-1}$ [Harman-Fetcho et al., 2000]. While global ocean emissions of VOC compounds are preliminarily estimated to be quite small (only about 5 Tg C yr$^{-1}$), they have been reported for some compounds in
certain conditions to match or exceed other modes of organic matter exchange at the air-
sea interface [Harman-Fetcho et al., 2000]. Moreover, in addition to its importance in
the balance of sources and sinks of the global carbon cycle, oceanic VOC emission is an
important factor in determining the overall oxidative capacity of the atmosphere
[Guenther et al., 1995].

Since the flux of VOC at the air-sea interface has been shown to occur in both
directions, with each vector of material having different chemical characteristics, a
holistic VOC flux with simultaneous air and water measurements is essential. Attempts
to quantify gaseous air-sea flux of VOC have thus far been mainly limited to studies
involving specific compounds, such as particular biogeochemically significant chemicals
[Jacob et al., 2005; Simo and Dachs, 2002] or pollutants [Jurado et al., 2004; 2005].
Methanol, for example, is thought to have an oceanic sink, and is deposited into the
surface ocean at rates of 10-15 Tg yr⁻¹ [Jacob et al., 2005; Singh et al., 2004]. In the case
of acetone, flux direction and magnitude are poorly quantified and have been measured to
range from -48 Tg yr⁻¹ to 27 Tg yr⁻¹ (a negative quantity denotes flux into the ocean)
[Jacob et al., 2002; Marandino et al., 2005]. Studies have found that the world’s oceans
are significant sinks for airborne persistent organic pollutants (POPs). In some areas,
gaseous POP diffusion can be of the same order of magnitude as wet and dry aerosol
deposition; however, during periods of little to no precipitation, diffusive flux tends to be
the most important source of POPs to the ocean [Eitzer and Hites, 1989; Gustafson and
Dickhut, 1997a; Harman-Fetcho et al., 2000]. Air-sea pollutant gas fluxes are spatially
and temporally variable (both seasonally and on longer timescales)—in one study
conducted in the Mediterranean, polycyclic aromatic hydrocarbon (PAH) fluxes between

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the air and the sea surface microlayer ranged from approximately -400 to -12,000 ng m\(^{-2}\) d\(^{-1}\) influx and from 500 to 14,000 ng m\(^{-2}\) d\(^{-1}\) efflux over the course of a year [Guitart et al., 2010]. Gas fluxes are influenced by the physical properties of individual organic compounds—those PAHs with a low Henry’s Law constant (H, air/water partition coefficient) tend to exhibit net fluxes into the water, whereas high-H compounds generally show a net efflux, the rate of which decreases with increasing molecular weight [Dickhut and Gustafson, 1995]. Other studies further indicate that water temperature and gas phase concentrations are the most important factors in determining flux [Gustafson and Dickhut, 1997b]. Generally, studies investigating individual compounds reveal that air-sea diffusive flux is higher than their wet and dry deposition [Jurado et al., 2005], and preliminary evidence suggests that this might be true for OC in general [Dachs et al., 2005].

Quantifying Gaseous Air-Sea Flux of OC

Since gaseous organic matter is chemically variable in both marine atmospheres and surface waters, considerable effort is required to quantify an overall carbon flux across the air-sea interface. Different VOC compounds have different partitioning behavior at the air-sea interface, which needs to be taken into account when developing a sampling methodology if truly all of the VOC is to be quantified. Singh and colleagues (2003) conducted a study combining air concentration measurements and a global 3-D model to measure net oxygenated VOC flux in the Pacific Ocean. Air-sea VOC flux was deduced based on concentrations of VOC precursors, hydroxyl radicals, and solar
irradiance. Globally extrapolated fluxes of acetaldehyde, propanal, methanol, and acetone were, in order, 125, 45, -8, and -14 Tg C\(^{-1}\) yr\(^{-1}\). A similar study, using measured surface ocean concentrations and averaged atmospheric concentrations from the literature, measured the flux of ethanol, 1-propanol and 2-propanol [Beale et al., 2010]. All three compounds showed diel (24-hour) variability as well as variability across areas of different rates of primary production—ethanol and 1-propanol were sufficiently variable to actually change the direction of flux. Both of these studies indicate the potential significance of specific organic chemical fluxes across the air-sea interface, but are limited in that they only measure a handful of compounds. Both also lack simultaneous air and water VOC measurements; indeed, only a few studies employ methods in which VOC is measured in both phases [Baker et al., 2000]. This may be crucial in measuring flux, since VOC seems to be spatially and temporally variable on small scales.

While some studies have tackled air-sea flux quantification of a subset of specific organic gases, a complete determination of total VOC gas flux has only recently been attempted. Dachs and coworkers [Dachs et al., 2005] employed a method where total VOC concentrations were measured both in the surface ocean and the marine boundary layer; no attempt was made to identify particular compounds. VOC flux was then calculated from estimated physical parameters and measured concentration gradients. With the Dachs et al. method, ambient air is sparged through pure water to capture airborne organics, and seawater is sparged with pure air, which is in turn sparged through pure water. It is assumed that the VOC in the air will in both cases diffuse into and equilibrate with the pure water traps. The water is then analyzed for total DOC and is
assumed to represent gaseous organic carbon found in the marine air and surface water.

Dachs and coworkers estimated that gaseous OC flux into the northeast Atlantic is -28 mmol C m$^{-2}$ d$^{-1}$ on average, but they measured a range from -140 to 40 mmol C m$^{-2}$ d$^{-1}$. This net OC diffusive flux exceeds measured dry aerosol deposition by more than a factor of ten, and flux of carbon dioxide by 3-4 times. While innovative, the method used by Dachs and coworkers is over-simplified and may lead to erroneous flux estimates since all VOC is assumed to have similar mass transfer coefficients, no attempt was made to determine breakthrough of VOC from the traps, and there was no effort to document whether equilibrium was actually achieved.

While the ocean is known to be a major sink for CO$_2$, studies attempting to holistically quantify a closed carbon loop have not taken into account diffusive VOC flux [Sabine et al., 2004; Takahashi et al., 2002]. Further, a ubiquitous assertion in studies attempting to quantify a partial or total OC flux is that high spatial variability in OC vectors requires spatial breadth in OC sampling and flux measurement [Dachs et al., 2005; Singh et al., 2003]. It is hypothesized here that gaseous organic carbon flux may be a significant input into, out of, or between oceanic environments, and on a global scale may be similar in magnitude to or even exceed wet and dry deposition and riverine input of OC. Therefore, air-sea gas exchange of OC may at least partially account for the proposed oceanic “missing carbon,” especially in remote open ocean systems. New development in methodology, including a way to quantify all VOC with various physical properties, is required to further constrain VOC fluxes. A description of a newly developed VOC flux measurement method and preliminary VOC flux measurements follows a discussion of the theory behind air-sea gas exchange.
THEORY

Two-film bottleneck boundary

In quantifying the air-sea flux of gaseous 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 the film, lying between two well-mixed bulk zones on either side. Chemical transfer between the ocean and the atmosphere is limited by molecular diffusion across two films—a very thin, stagnant water film in contact with a very thin, stagnant air film (Figure 1).

For a conservative substance, flux is given by Fick’s first law as:

\[ F(x) = -D(x) \frac{dC}{dx} \]

where \( F(x) \) is the flux along the coordinate \( x \), which is orthogonal to the boundary, \( C \) is compound concentration, and \( D(x) \) is the diffusivity, which is compound dependent.

Stated alternatively, since the film model allows the flux equation to be integrated normally,

\[ F = -D \frac{C_r - C_i}{\delta} \]
where $C_f$ and $C_i$ are the final and initial concentrations at either end of the film, and $\delta$ is the film thickness. To extend this model to the two-film case, we have, for the water and air films, respectively:

$$F_A = -D_A \frac{C_A - C_{AW}}{\delta_A} \quad F_W = -D_W \frac{C_{WA} - C_w}{\delta_W}$$

We can further simplify by use of the definition of the mass transfer coefficient $v$, which has units of velocity and is also referred to as the transport velocity:

$$v_A = \frac{D_A}{\delta_A} \quad v_W = \frac{D_W}{\delta_W}$$

This leads to the following flux equations:

$$F_A = -v_A (C_A - C_{AW}) \quad F_W = -v_W (C_{WA} - C_w)$$

Since it is assumed that at some point the entire air-water boundary system is at steady state, $F_W$ and $F_A$ must be equal and also must be equal to the overall air-sea flux. However, combining the two flux equations requires the assumption that the concentrations within the film directly on either side of the film interface are in equilibrium. Since the air and water films are of different media, it does not make sense to simply equate $C_{AW}$ and $C_{WA}$. Rather, the two concentrations are related by the Henry’s Law constant ($H$) such that:

$$H = \frac{C_{AW}}{C_{WA}}$$

$C_{AW}$ and $C_{WA}$ are practically immeasurable quantities; however, returning to the flux equations, we can eliminate these two variables and equate the air and water film fluxes.
using H. We are then left with the following flux equation that includes only parameters we can either measure or estimate:

\[ F_A = F_w = F = -v_{tot}(C_A - HC_w) ; \quad \frac{1}{v_{tot}} = \frac{1}{v_A} + \frac{H}{v_W} \]

This model can be further simplified in two limiting cases:

1) Henry’s Law constant is very large; \( \frac{H}{v_W} \gg \frac{1}{v_A} \)

In this case, \( v_{tot} = \frac{v_W}{H} \) and the rate of diffusion across the air-sea interface is essentially limited by diffusion across the water film only, and is inversely proportional to H.

2) Henry’s Law constant is very small; \( \frac{H}{v_W} \ll \frac{1}{v_A} \)

In this case, \( v_{tot} \approx v_A \) and the rate of diffusion across the air-sea interface is essentially limited by diffusion across the air film only, and is independent of H.

These simplifications will be useful in attempting to measure chemical fluxes using concentration gradient data.
METHODS

Calculating VOC flux from the aforementioned equations requires quantifying two parameters—air-sea concentration gradient and mass transfer velocity. Concentration gradients \((C_A\text{ and } HC_w)\) were determined experimentally, and the kinetic transfer coefficients were estimated using a combination of experimental results and theoretical calculations based on the physical/chemical parameters of the compounds of interest. The method utilized two limiting cases, where compounds with high \(H\ (> 0.1 \text{ L atm}^{-1} \text{ mol}^{-1})\) were water-film limited and compounds with low \(H\ (< 0.1 \text{ L atm}^{-1} \text{ mol}^{-1})\) were air-film limited in diffusion across the air-sea interface; organic compounds in the air and the water were separated into operational “high-H” and “low-H” groups, so the proper kinetic parameters could be applied when fluxes were calculated from observed concentration gradients.

Air Sampling

The concentration of VOC in air \((C_A)\) was measured by pumping a known volume (20-30 L) of marine air through a tube of solid sorbent. Air was pumped through a glass fiber filter (47 mm diameter) to remove particulate aerosols and through two sorbent tubes in series—one containing \(\sim 3\) g Tenax GR (Markes/Agilent) and then another
containing ~3 g molecular sieve sorbent (Carboseive III (CSIII) or Carbotrap (CT) (Markes/Agilent)) that effectively trap semi-volatile and highly volatile, low molecular weight organics, respectively. Before going through the sorbent tubes, the 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 (Figure 2). The gas diffusers ensured, through small bubble formation, that equilibrium was reached between the air and water in the traps. Calculations confirmed that with 20-30 L of air running through 80 mL of clean water at ambient temperatures, organic compounds in the air equilibrated such that compounds with $H << 0.1 \text{ L atm mol}^{-1}$, which have a higher affinity for water, effectively partitioned into the 80 mL water traps, whereas compounds with $H >> 0.1 \text{ L atm mol}^{-1}$, which tend to remain in air, broke through the water traps and adsorbed to the sorbent tubes down the line:

$$V_A = \frac{V_{\text{water traps}} \times R \times T}{H}$$

$$V_A = \frac{0.08 \text{ L} \times 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{0.1 \text{ L atm mol}^{-1}}$$

$$= 20 \text{ L}$$

where $V$ is volume, $R$ is the gas constant, and $T$ is temperature of the air. The minimum air volume used was 20 L so that signal:noise was sufficient.

After the air sample was complete, the water traps contained mostly low-$H$, water soluble VOC and the sorbent tubes contained mostly high-$H$ VOC. However, since even high-$H$ VOC to some extent equilibrates into water, the water traps also contained small concentrations of high-$H$ compounds. In order to remove these compounds and add them
to the sorbent tubes, initially a small volume of clean air (3 L) was bubbled through the water traps after sampling, purging the high-H VOC out of the water traps, into the air, and onto the sorbent tubes with the other highly volatile material. Additionally, the sorbent tubes were heated (Sidewinder LC column heater) to 15-20 °C above ambient temperature during sampling and purging to decrease water vapor adsorption and increase the amount of active sites available for VOC capture [Gawrys et al., 2001]. This procedure was required in order to keep the flame ionization detector (FID) flame from extinguishing due to water vapor during the analysis of molecular sieve sorbent tubes.

Water Sampling

To measure HC\textsubscript{w} and obtain a sufficient signal to noise ratio for VOC analysis in seawater, a large volume (approximately 41 L) of surface water was used for water sampling. The water was 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. Water samples and air samples were taken simultaneously in all but one case (December). Care was taken to avoid splashing and bubbling by pumping water into the bottom of the tank through a stainless steel tube. To remove and measure VOC, a Teflon line was run to the bottom of the tank where an array of 4, 10-μm stainless steel gas diffusers sparged pure air in small bubbles. Clean air bubbled up through the water and was pushed out of an outlet at the top of the tank; the smallest amount of headspace such that water would not be pushed out the top
of the tank (−0.5 L) was maintained. The air exiting the water tank was then bubbled through two Teflon impingers each with 40 mL ultrapure water and a stainless steel diffuser as described for the air sampling, and then again through heated sorbent tubes filled with Tenax and CSIII or CT (Figure 3). The air exiting the top of the tank contained VOC in equilibrium with the seawater ($H_{C_w}$) as shown by validation experiments (see below); airborne VOC then either diffused into the water traps (low-H) or broke through and was caught on the sorbent tubes (high-H) based on H as explained for the air sampling method.

One 1-L air sample (i.e. 1 set of water traps and Tenax/CSIII or CT sorbent tubes) was collected at four time points separated by 2-3 L of purged/vented air such that high-H compounds were stripped out of the water sample over time. Each successive 1 L sample taken should reflect VOC stripping out of the seawater into the air, but may also reflect particle stripping or biological production of VOC during purging. The initial VOC concentration in water was estimated by taking the y-intercept of linear regressions of the natural log of the VOC concentration in the 1 L of purged air versus purge time. This accounts for VOC equilibration from the seawater into the air, but may also reflect any small amount of biological production or particle stripping that did occur. Note that VOC concentration in the seawater was not measured directly; rather, VOC concentration in air in equilibrium with the seawater, $H_{C_w}$, was measured. By plotting the log of VOC concentration in the purged air versus time, an initial in situ seawater-equilibrated air VOC concentration upon water sample collection, could be determined. This was also thought to provide the most robust estimate of initial VOC concentration in the water, as
the highest possible number of data points were utilized. See the Appendix for all plots of purge time versus ln(VOC concentration).

System Calibration and Carbon Quantification

The high-H VOC on the sorbent tubes was analyzed with a platform thermal desorber (TD) for single tubes (Markes Unity 2) in line with a gas chromatograph (GC) (Agilent) with a flame ionization (FID) detector, which selectively detects carbon-containing molecules. Sorbent tubes were sealed at room temperature after sampling and analyzed mostly within 24 hours, but within 1 week at most in isolated cases. Calibration curves using a variety of representative organic standards (Table 1) were constructed to relate FID signal to amount of carbon (Figure 4). Once it was established that all the compounds used for calibration had similar concentration-FID signal relationships, a smaller calibration curve consisting of only the tridecane, tetradecane, pentadecane standards was made before each sample. Tenax tubes were desorbed at 300 °C for 5 minutes, and CSIII and CT tubes were desorbed at 340 °C for 5 minutes. For all calibration and sample GC analysis, starting GC column temperature was 35 °C, held for 1 minute, followed by a 10 °C/minute increase to 300 °C (27.5 minutes total run time). For integration for carbon quantification, only the first 20 minutes of each chromatogram were used to exclude baseline irregularities and peaks due to column bleed at the end of the temperature ramps.

The high purity water in the traps containing the low-H VOC was frozen immediately after sampling in sealed Teflon bags and analyzed within two months. The
water traps for both the air and water samples were analyzed with a Shimadzu DOC analyzer after acidification with 20% HCl to remove inorganic carbon. Calibration curves using potassium hydrogen phthalate (KHP) or glycine were compiled each time samples were analyzed.

Quality Assurance Protocols and Method Validation

VOC Retention

Sorbent tubes were tested for retention of VOC with 30 L of air flowing through the tube, the maximum volume used to sample atmospheric VOC, by placing 2 tubes in line and comparing the amount of material on each. Tenax sufficiently retained mid- to high-molecular weight VOC while CSIII retained the lighter, more volatile compounds. Various gas standards (acrylonitrile, 1,3-butadiene, vinyl chloride, benzene, methylene chloride, 1,2-dichloroethane, chloroform, tetrachloroethane) were used to monitor CSIII retention efficiency, while paraffin wax standards (n-tetradecane, n-pentadecane, n-hexadecane, n-heptadecane) in methanol were used for the Tenax experiments. Retention on the first of two sorbent tubes in line with 30 L of air was approximately 92% for the CSIII, and 99% with the Tenax. The fact that the two sorbents, when combined, show high retention efficiency and high breakthrough volume validates their use for ambient air sampling.

The water traps were shown, by experiments with a range of chemical standards, to 1) retain water-soluble compounds with low H values and 2) *not* retain volatile compounds with high H values following a 3 L purge with clean air. When various 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% recovery of these high-H compounds on Tenax tubes was observed with an air volume of 3 L (compared to approximately 50% and 57% with 1 L and 2 L purges, respectively). The fact that some of these compounds are on the lower end of the high-H compound class indicates that most airborne high-H compounds will effectively break through water traps and adsorb to sorbent tubes during sampling. However, the additional step of stripping the small amount of high-H VOC from the water traps after ambient air sampling requires that water soluble, low-H compounds remain in the water traps, to be analyzed as the overall low-H VOC fraction. When a methanol (H=4.6 \times 10^{-3} L atm mol\(^{-1}\)) solution was added to the water traps, bubbling 3 L of pure air through the traps retained approximately 98% of the methanol in the water.

During preliminary experiments conducted in the summer of 2009, a third water trap was placed in line during a 30 L air sampling and 3 L pure air purge. Upon completion of the experiment it contained little to no carbon, so it was determined that 80 mL (2 x 40 mL) was sufficient to trap water soluble VOC in air samples under these conditions. However, after completing January sampling in Gloucester Point it was observed that some of the second water traps in line contained fairly high amounts of DOC, and more experiments were conducted to validate the minimal water trap breakthrough observed in summer 2009. Sampling with both two and three water traps,
as well as both 1 and 3 L pure air purge volumes was tested for VOC retention efficiency (see Table 2 for experiment descriptions and retained VOC concentrations for each trap). The goal was for very little VOC to be remaining in the last trap in line, thereby indicating that essentially all possible VOC was trapped in the water traps. Experiment 5, where no clean air purge was used, was the only experiment that yielded sufficiently low breakthrough, including experiments where a third water trap was added. Although in preliminary experiments, methanol was retained in the water traps, the water soluble portion of VOC going through the water traps is likely a wide range of compounds. Based on these experiments, it was determined that the “smearing” of the VOC signal that resulted from doing the clean air purge was greater than the small amount of high-H VOC that likely remains in the water traps after air and water sampling. As such, the clean air purges were eliminated from the sampling procedure after the January sampling dates.

Cleaning

All sampling equipment—Teflon tubing, Teflon bags, Teflon water trap cells, stainless steel fittings, tank, and air diffusers—were cleaned with 10% HCl solution (Teflon) and/or methanol (Teflon and stainless steel) and deionized water before each sample. The stainless steel tank was also steam cleaned using a hand held household steam cleaner before and after each sample starting in October. Both the air and water sampling systems were blank tested typically before each sample by running about 20 L of pure air through the air sampling system and 1 L of pure air through the water
sampling system and collecting on the sorbent tubes (Tenax and molecular sieve) to observe the level of contamination. The average integration of all blanks taken were subtracted from each sample integration to make sure only in situ VOC was being measured. For blank-correcting the measurements of organic carbon in the water traps, a Teflon impinger with the same ultrapure water used for sampling was left outside with the air sampling equipment for the duration of the experiment. DOC concentration found in this field blank impinger was averaged over all samples. Since field blanks varied considerably from sample to sample, the average plus 2 standard deviations was then subtracted from the concentrations measured in the sample impingers. All high-H and low-H results in this study will be reported after subtracting system blank chromatograms and field blank DOC concentrations, respectively.

**Equilibrium**

Making sure equilibrium was reached between the sparged pure air and the 41 L seawater sample was a necessary validation step for measuring $HC_w$. The entire basis of the water sampling method is that rather than determining VOC concentration in water directly, we can use the VOC concentration in air-equilibrated water to determine the VOC air-sea concentration gradient. These two quantities are related by the equilibrium (Henry’s Law) constant H, but the system must be at equilibrium for this method to be valid. In order to determine if the system allows equilibrium to be reached, we used a gas stripping method to determine the Henry’s Law constant of two chemical standards, 4-isopropyltoluene ($H=7.69$ L atm mol$^{-1}$) and n-butylbenzene ($H=12.5$ L atm mol$^{-1}$). These
two standards in particular were chosen based on the convenient timescales with which they were purged out of the water tank; they were a practical balance between purging quickly enough to get the experiment done in a day and purging slowly enough to achieve sufficiently high signal:noise. The water tank was filled with 41 L of deionized water and then was spiked with a small amount (~200 μmol) of each compound. Following complete stirring and headspace purging, 4 successive 1 L air samples were taken on a set of sorbent tubes as air was continuously bubbled through the tank and vented in between samples. Essentially, the water sampling procedure was replicated. The rate at which the compounds were stripped from the water into the air is related to H as follows [Mackay et al., 1979].

\[
\ln \left( \frac{C}{C_0} \right) = -\left( \frac{HG}{VRT} \right) t
\]

Where \(C\) and \(C_0\) are the substrate concentration and initial concentration, \(G\) is the gas flow rate, \(V\) is water volume, \(R\) is the gas constant, \(T\) is the system temperature, and \(t\) is 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, \(H\) for n-butylbenzene was estimated to within 10% of literature values, and \(H\) for 4-isopropyltoluene was estimated to within 30%. It should be noted, though, that the latter \(H\) estimate was 30% higher than averaged literature values, which suggests that equilibrium was established. Figure 5 shows the relationship between the time the sample was taken during the stripping experiment, and the concentration of each compound in air.
For high-H and low-H VOC concentrations in air, a 20% relative error was assumed, estimated from the typical drift of the air sampling pump in between flow rate checks. For high-H and low-H VOC concentrations in seawater-equilibrated air, a 20% relative error was assumed in addition to the standard error associated with using linear regression to estimate initial HC\textsubscript{w}. The errors in C\textsubscript{A} and HC\textsubscript{w} were propagated through to describe the error in the concentration gradient estimates and fluxes. No additional error was added for estimating mass transfer coefficients.

**Sampling Locations**

Once the VOC sampling method was established, a field study was conducted lasting approximately ten months, with sampling at two different locations (Figures 6 and 7). The purpose of the study was to validate the method for use in estuarine and oceanic environments and to obtain an order of magnitude estimate for air and water VOC concentrations and air-sea VOC flux. The majority of the VOC sampling was conducted on the York River Estuary, a subestuary of Chesapeake Bay. Samples were taken in Gloucester Point, VA off of the end of the Virginia Institute of Marine Science pier (Figure 6). In total, seven high-H VOC air/water samples and eleven low-H VOC air/water samples were taken in Gloucester Point, VA from July 1, 2010 to May 2, 2011. To evaluate the use of the method for open ocean measurements, three high-H and three
low-H air/water VOC samples were taken on a Bermuda Atlantic Time-series study (BATS) cruise off the coast of Bermuda in the northwest Atlantic Ocean in August 2010. All samples were taken between the Hydrostation ‘S’ and Bermuda Atlantic Time Series (BATS) stations (Figure 8).
RESULTS

High-H VOC

Bermuda

The three samples off the coast of Bermuda were collected between August 19 and August 21, 2010; one sample was taken per day. High-H VOC in air ranged from 115 ± 23 to 212 ± 42 ng C L⁻¹ air (Table 3). High-H VOC in the air that was equilibrated with surface seawater was measured in concentrations of 1340 ± 268 and 3230 ± 645 ng C L⁻¹ on August 19 and 20 respectively (Table 3). High-H VOC in water-equilibrated air was 4420 ng C L⁻¹ air on August 21. A 1-way analysis of variance (ANOVA) by date of the three high-H samples reveals that the third water-equilibrated high-H VOC sample was significantly higher than samples 1 (p=0.003) and 2 (p=0.03). Field blanks taken on August 22 were higher than most of the samples, suggesting that organic/microbial material had built up in the water tank during the first two days of sampling. In collecting these samples, the water tank was simply rinsed with surface seawater prior to sampling. For all subsequent samples the tank was steam cleaned before and after each water sample, which lowered field blanks considerably. In order to analyze the Bermuda samples, however, a blank was necessary to correct the
chromatograms. Therefore, the field blanks conducted in Gloucester Point were used, since the only field blank taken in Bermuda was high enough to eliminate most of the samples taken. These blanks would seem more representative of the state of the sampling system upon starting sampling in Bermuda, before the three samples were taken.

**Gloucester Point**

Sampling in Gloucester Point began on July 1, 2010 and ended on May 2, 2011. Samples were taken approximately monthly to capture possible seasonal variation. High-H VOC concentrations in air ranged from 15.4 ± 3.1 to 101 ± 22 ng C L air. High-H VOC concentrations in air equilibrated with surface water ranged from 50.5 ± 14.8 to 507 ± 101 ng C L air (Table 3). For many samples in both Bermuda and Gloucester Point, the natural log of both high-H and low-H VOC in the sample air equilibrated with the water sample declined over sample purge time—this is presumably due to the VOC in the water equilibrating into the air as it was bubbled through the water and pushed out of the tank (Appendix). In some cases, however, the concentration of VOC in the air sample actually increased as samples were taken. This could be a result of biological production during the sampling period, or stripping of particulate material as VOC was stripped out of the water. In still other cases, there was really no clear increase or decrease. Although a regression line was fit to these datasets anyway, water VOC concentration estimates should be made with caution. For example, the October, November, April and May estimates of water VOC content could be dependent on just one point since only 3 time points were taken. In addition, the only high-H VOC sample that showed a significant
(α=0.05) change in VOC over purge time was the August 19 Bermuda sample which increased over the course of the experiment.

Low-H VOC

Bermuda

Low-H VOC in the air that was captured into the water traps was measured to be 546 ± 109 and 1670 ± 334 ng C L⁻¹ air on August 19 and 20, respectively (Table 4). Low-H VOC concentration of air equilibrated with surface seawater, HC₇w, was measured to be 9960 ± 1990 and 43,000 ± 8590 ng C L⁻¹ air on August 19 and 20, respectively (Table 4). Only two replicates were quantified for the low-H VOC because the glass vials containing the trap water only survived the trip back from Bermuda for samples 1 and 2. However, it is possible that many of the vials that were not badly broken and discarded also had cracks in them from expanding freezing water and transport. This could have resulted in contamination, so low-H VOC measurements should be interpreted with caution. For all subsequent concentration gradient and flux calculations, only the first two samples will be used since they were the only complete ones.

Gloucester Point

Low-H VOC concentrations in air ranged from below blank values (recorded as zero for subsequent calculations) to 1060 ± 213 ng C L⁻¹ air. Low-H concentrations in
the air equilibrated with surface water ranged from $726 \pm 145$ to $30,500 \pm 6110$ ng C L$^{-1}$ air (Table 4). As with the high-H case, some of the HC$_w$ extrapolations should be interpreted in the context of the purge time vs. ln(VOC) graph itself (See Appendix). For example, the November samples result in very high HC$_w$ estimates because of just one point. The December and January samples only have 3 points and would be drastically changed by variation in just one of them. The January 31 sample only had 2 time points that measured a nonzero VOC, so the extrapolation is entirely dependent on the line formed between these two points. The error on this estimate is also deceptively low, as the error associated with using linear regression to extrapolate cannot be calculated using only 2 data points. None of the low-H VOC samples showed a statistically significant ($\alpha=0.05$) change in ln(VOC) over the course of the purging.

Seasonal Trends in VOC Concentrations

Gloucester Point high-H VOC was measured to be highest in the July and August 2010 samples, in both the air and the water-equilibrated air (Figure 12). High-H VOC remained consistently low through the early May sample, where HC$_w$ actually dipped below CA. The air-sea concentration gradient of high-H VOC reflected the same patterns—high and positive (ocean > atmosphere) in July and August 2010 and low the rest of the sampling period, with a negative flux for May (Figure 14).

Low-H VOC concentrations in surface water showed slightly different patterns, remaining high from July through November, dropping significantly in the winter, with
the exception of the January 19, 2011 sample, and then reaching a maximum in April and May (Figure 13). Low-H VOC in air remained low throughout the sampling period (Figure 13). For both high-H (Figure 14) and low-H VOC (Figure 15), concentration gradients in all but one sample went from out of the ocean into the atmosphere or were near air-sea equilibrium. Low-H VOC concentration gradients were about 2 orders of magnitude higher than high-H VOC gradients and seem to be driving overall VOC fluxes at these sampling locations. Fluxes followed the same seasonal trends as concentration gradients since they were all multiplied by similar (high-H) or identical (low-H) values for $v_{\text{tot}}$ (Figures 16 and 17). Low-H VOC fluxes were orders of magnitude higher than high-H VOC fluxes because both low-H VOC (air-film limited) concentrations gradients and mass transfer coefficients were higher than that of high-H VOC (water-film limited).

For low-H VOC, a trend was observed between $C_A$ and $HC_W$ ($p=0.105$, adjusted $R^2=0.236$) (Figure 18). Although the correlation was not significant, this suggests a slight coupling between water-soluble, air-film limited VOC in the air and the water, which seems reasonable since the flux of the low-H VOC is out of the seawater into the marine boundary layer. Other researchers have observed a spatial coupling between air and water VOC concentrations [Dachs et al., 2005; Jaward et al., 2004], which suggests cycling of organic material through volatilization and deposition on relatively small spatial scales. The temporal variation observed in this data set suggests that seasonal factors are controlling $C_A$ and $HC_W$. No such relationship was observed for high-H VOC, perhaps because it was found in such low concentrations. Alternatively, high-H and low-H VOC might have had different sources. If, for example, the small amount of high-H
material, which has low water solubility, was mainly composed of pollutants, its sources could have been either airborne or aqueous and might have been inconsistent. Indeed, fluxes of PAHs in one study in Southern Chesapeake Bay were measured to be on the same order as the high-H VOC fluxes measured at the Gloucester Point sampling site in this study [Gustafson and Dickhut, 1997b]. This is also consistent with the fact that high-H VOC fluxes were highest in the hottest months, whereas low-H VOC fluxes were highest in the spring. Abiotic, allochthonous chemicals with high H are likely to be more controlled by temperature, whereas low-H material might be more biologically driven and coincide with the spring bloom.

Concentration Gradients and Fluxes

Using experimental estimates for air VOC concentration, \( C_A \), and air VOC concentration in equilibrium with measured surface water VOC concentration, \( H C_w \), VOC gradients can be calculated. Since \( F = -v_{tot}(C_A - HC_w) \), and \( v_{tot} \) is always positive because it is a rate constant, the direction of VOC transfer can then be observed before a \( v_{tot} \) estimate is even attempted. In Bermuda, high-H VOC concentration gradients were \( 1130 \pm 271 \) and \( 3020 \pm 646 \) ng C L\(^{-1}\) for August 19 and 20, respectively. High-H VOC concentration gradients in Gloucester Point ranged from \( -50.8 \pm 26.7 \) to \( 492 \pm 101 \) ng C L\(^{-1}\) (Table 5). For low-H VOC, concentration gradient was estimated to be \( 9420 \pm 2000 \) and \( 41,300 \pm 8600 \) ng C L\(^{-1}\) in Bermuda on August 19 and 20 respectively (Table 6). Low-H VOC concentration gradients in Gloucester Point ranged
from 235 ± 175 to 30,000 ± 6110 ng C L⁻¹ (Table 6). A positive concentration gradient implies a higher VOC concentration in the surface ocean than in the atmosphere, and an upward flux (i.e. out of surface water to air). The low-H VOC fraction was observed at higher concentrations and a much higher concentration gradient, and hence seems to be much more important to overall VOC flux in the regions sampled.

In addition to concentration gradient, an estimate of $v_{\text{tot}}$, the mass transfer coefficient, precludes any absolute flux calculations. Mass transfer coefficients vary widely across compounds of varying Henry’s Law constant, as was observed with a range of chemical standards (Figure 9). Therefore, mass transfer coefficients need to be calculated separately for high-H and low-H compounds—to our knowledge this is the first VOC measurement experiment that does so.

Estimation of mass transfer coefficients of high-H compounds is crucial since $v_{\text{tot}}$ varies exponentially with $H$ (Figure 9). Mass transfer coefficients for compounds with $H>>0.1$ L atm mol⁻¹ are on average approximately $1.0 \times 10^{-3}$ cm s⁻¹ [Schwarzenbach et al., 2003]; however, they can vary across orders of magnitude. Therefore, the method presented here includes a way to constrain $v_{\text{tot}}$ for the high-H fraction. Since no attempt was made to rigorously identify VOC compounds, an observed linear relationship between retention time of calibration standards (Figure 4) and molecular weight was utilized (Figure 10). Sampled compounds eluted over the first 20 minutes of the 27-minute chromatogram, ranging in molecular weight from an estimated 57 to 286, and the molecular weight corresponding to the mid-point retention time is 172 (Figure 11). In theory, chromatograms could be divided into retention time windows so molecular
weight could be further constrained and separate fluxes could be calculated for each window. However, because calibration curves were not conducted for each window, this was not possible in this experiment. Further, the observed range of retention times indicated that molecular weight varied by less than a factor of 2; using mass transfer coefficients corresponding to even the molecular weight end members would only change flux estimates by about 25%.

With some idea of the molecular weight of the VOC represented on the GC chromatograms, average water phase diffusivities could be estimated by using another empirical relationship derived from a suite of organic compounds such as aromatics, ketones, acids, and low molecular weight organohalogenes [Schwarzenbach et al., 2003]:

\[ D_{t,w} = \frac{2.7 \times 10^{-4}}{MW_i^{0.71}} \]

Water phase diffusivities are used because for high-H compounds, \( v_{tot} \approx v_{water} \). Using this relationship, sampled compounds have an average diffusivity of \( 6.98 \times 10^{-6} \) cm\(^2\) s\(^{-1}\). Although diffusivity is temperature-dependent, it generally seems to vary by less than a factor of two over the 30 degree temperature range observed [Schwarzenbach et al., 2003], and since diffusivity is already reported as an average and the chemical composition of the material is not known, temperature effects are not taken into account. The next step toward estimating a mass transfer coefficient for the sampled material is determining 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 typically used in the following relationship since it has a very
high H and is water-limited in diffusion:

\[
\frac{Sc_{sample,w}}{Sc_{CO_2,w}} = \frac{D_{sample,w}}{D_{CO_2,w}}
\]

For the reference Sc and D values for CO₂, it was possible to take temperature
into account. The values used were those corresponding to the closest 5-degree
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].

Calculated Sc for the sampled material ranged from 118 when the water was warmest to
576 when the water was coldest. From these sample Sc values, water phase mass transfer
coefficients of the sampled material were calculated using the following relationship
[Schwarzenbach et al., 2003]:

\[
\frac{v_{sample,w}}{v_{CO_2,w}} = \left( \frac{Sc_{sample,w}}{Sc_{CO_2,w}} \right)^{-a}
\]

Where Sc for CO₂ is again temperature-dependent and a value of \(0.65 \times 10^{-3}\) cm s⁻¹ was
used for the average mass transfer coefficient of CO₂, and a=0.67. These values are
chosen because they are appropriate for wind speeds of less than 4-5 m s⁻¹, which applied
to the large majority of the samples [Schwarzenbach et al., 2003; Wanninkhof et al.,
2009]. Temperature dependence was not available for mass transfer coefficients of CO₂.

Calculated mass transfer coefficients for the unknown sampled VOC were \(0.966-1.39 \times 10^{-3}\) cm s⁻¹, with the highest mass transfer coefficients observed for the warmest days.
The average value reported in Schwarzenbach, et al. [2003] is well within this range.
Once $v_{\text{tot}}$ was estimated for each sample date, flux calculation was simply a matter of multiplying $v_{\text{tot}}$ with the previously mentioned concentration gradients. VOC fluxes in Bermuda were $15.7 \pm 0.4$ and $42.0 \pm 0.9$ ng C cm$^{-2}$ s$^{-1}$ on August 19 and 20, respectively. In Gloucester Point, fluxes ranged from $-0.595 \pm 0.031$ to $6.29 \pm 0.13$ ng C cm$^{-2}$ s$^{-1}$ (Table 7).

While it would be ideal to estimate an average molecular weight for the low-H fraction, the method of analysis (total DOC) makes this impossible. It is not even reasonable to assume that the low-H and high-H fractions have a similar molecular weight ranges, because as discussed previously, low molecular weight compounds like methanol are produced in the surface ocean and may dominate the low-H pool. Alternatively, the low-H pool could be made up largely of high molecular weight compounds that do not readily volatilize. However, compounds with $H<0.1$ L atm mol$^{-1}$ tend to have high values of $v_{\text{tot}}$; and, more importantly, $v_{\text{tot}}$ only varies by a factor of 2 with $H$ (Figure 9). In contrast, $v_{\text{tot}}$ varies by a factor of 5 (approximately 0.52 to 2.71 cm$^2$ s$^{-1}$) over the range of molecular weights observed for the high-H material, but it is unlikely that the low-H molecular weights vary this much because this variability was not demonstrated with the representative compounds (Figure 9). Moreover, in both cases, this variability would never change the order of magnitude of the flux estimate. Another factor that needs to be taken into consideration is wind speed. Since low-H VOC is air-film limited in diffusion, its $v_{\text{tot}}$ linearly depends on wind speed [Schwarzenbach et al., 2003]. However, sampling days were preferentially chosen for clear, calm conditions. Over the range of wind speeds sampled, $v_{\text{tot}}$ estimates only vary by a factor of 1.6 for any
given molecular weight. Therefore, an accepted, typical \( v_{\text{tot}} \) value of 1.0 cm s\(^{-1}\) for air-film limited organic compounds is used for flux calculation [Schwarzenbach et al., 2003]. Flux was then calculated by multiplying the concentration gradient, determined experimentally, and the estimated mass transfer coefficient. Low-H VOC fluxes in Bermuda were 94,200 ± 6760 and 413,000 ± 13,400 ng C m\(^{-2}\) s\(^{-1}\) on August 19 and 20, respectively (Table 8). Gloucester Point fluxes ranged from 2350 ± 4150 ng C m\(^{-2}\) s\(^{-1}\) in February to 300,000 ± 5450 ng C m\(^{-2}\) s\(^{-1}\) in May (Table 8). Error in flux reflects an estimated 20\% error due to drift in air flow rate, as well as the error associated with estimating HC\(_{w}\) by linear regression and extrapolation. Error in mass transfer coefficient is not well defined so is not included in compounded errors.
DISCUSSION

This study provides almost a full year of air and water VOC concentrations in Gloucester Point, as well as flux estimates accompanied by environmental conditions (Table 9). Two complete samples from the northwest Atlantic Ocean do not comprise a complete enough data set for any rigorous statistical or long-term analysis, but serve as an interesting comparison to the more complete Gloucester Point data set. It was hypothesized that VOC flux could be equal to or exceed wet and dry atmospheric deposition or OC delivery to oceans by rivers. Since only one site was sampled long-term, it is impossible to extrapolate VOC fluxes to all estuaries or even the entire York River. However, even if the fluxes observed were the highest in all of the York River by far, diffusion has the potential to transport carbon in amounts comparable to these other vectors, although in the opposite direction as hypothesized. For example, wet deposition, which is generally much greater than dry deposition, has been postulated to be up to 29 ng C m$^{-2}$ s$^{-1}$ in coastal areas [Jurado et al., 2008]. This is 2 orders of magnitude greater than high-H VOC diffusive fluxes observed in this study, but 3-4 orders of magnitude less than the low-H VOC gas fluxes. In addition, riverine export of DOC has been estimated to be approximately 3-440 ng C m$^{-2}$ s$^{-1}$ in a survey of rivers around the world [Aitkenhead and McDowell, 2000], which is orders of magnitude lower than many fluxes.
observed here. Below, the reasonability of the results of this study are assessed by comparison with results obtained using other methods, VOC measurements are correlated with environmental conditions, discrepancies are reconciled and relationships are analyzed. Shortcomings and potential improvements are discussed.

Comparison With Other Studies

A comparison of my results with those of Dachs et al. [2005] is pertinent, since the method presented here is a re-working of the method used by those researchers. Dachs and coworkers measured VOC concentrations in the air and the water throughout the northeast subtropical Atlantic, in both coastal and open ocean sites. They measured VOC in air by bubbling air through pure water, and measured VOC in seawater by bubbling air through the seawater, and then bubbling the outgassed products through pure water. As such, Dachs et al. [2005] in effect only measured the low-H fraction of VOC, since this is the only VOC that would be effectively captured from the air by water traps. In the open ocean sites, they observed approximately 480 μg C L⁻¹ and 360 μg C L⁻¹ in the air and water fractions, respectively. This is higher than the analogous measurements made in the open ocean portion of my experiment—low-H C_A and HC_w—which were 1.1 μg C L⁻¹ and 26.5 μg C L⁻¹. However, even the open ocean sites visited by Dachs and colleagues were subject to continental winds and Saharan dust influence, and were relatively close to the African continent [Eglinton et al., 2002]. The air and water low-H VOC concentrations measured by Dachs in coastal areas were 1093 μg C L⁻¹ and 1273 μg C L⁻¹, respectively, compared to averages of 0.50 and 10.9 μg C L⁻¹ in Gloucester Point.
The authors addressed that they were likely in a very high-VOC area of the Atlantic due to upwind anthropogenic sources and productive marine areas as well as high wind speeds, which might have resulted in the VOC-enriched air and water. Also, blank corrections were not addressed in this paper so all samples might have been subject to background OC contamination. Other studies measuring VOC in air and seawater obtained concentrations within the range I observed [Williams et al., 2004].

Net VOC fluxes observed by Dachs and colleagues were lower (and in the opposite direction) than estimates in this study, despite the fact that the concentrations they measured were much higher. VOC fluxes in Dachs et al. (2005) ranged from an average of \(-0.876 \mu g \text{ C m}^{-2} \text{ s}^{-1}\) in the spring to \(-1.182 \mu g \text{ C m}^{-2} \text{ s}^{-1}\) in the fall. Net fluxes of low-H VOC observed in Bermuda and Gloucester Point were, on average, \(254 \mu g \text{ C m}^{-2} \text{ s}^{-1}\) and \(115 \mu g \text{ C m}^{-2} \text{ s}^{-1}\). The driver behind the discrepancy in fluxes is the much larger and opposite concentration gradients observed using the current method, as Dachs and colleagues used similar methods to estimate mass transfer coefficients, although exact values were not given. Perhaps one possible explanation is that the methods utilized by Dachs and colleagues did not adequately achieve equilibrium between pure water and air samples, or between pure air and water samples. The current study's seawater stripping experiments were carried out over the course of a few hours (as opposed to 30 minutes for the Dachs study) under verified equilibrium conditions and multiple air samples were analyzed. Further, in the water samples taken here, in many cases the VOC concentrations declined over the course of a few hours, but there was still substantial VOC present by the end, suggesting that Dachs, et al. are underestimating water VOC.
concentrations. If VOC recovery efficiency varied between the air and water sampling methods utilized by Dachs, or between the researchers’ and the current methods, this would cause discrepancies in both concentrations and resultant flux estimates.

The low-H flux estimates obtained from the current experiment were also much higher than other studies examining the flux of specific VOC compounds using different methods, although there is more agreement on flux direction. The results of studies involving the measurement of only individual compounds cannot be directly equated with this study, but rough comparisons can be made. The previously mentioned studies by Singh (2003) and Beale (2010) measured fluxes of low molecular weight, low-H oxygenated VOCs from -0.74 to 6.0 ng C m$^{-2}$ s$^{-1}$ for the individual compounds. All compounds measured in their studies had low H values, so are only comparable to the fluxes measured for the low-H VOC in the current study. Their fluxes are on the order of the high-H VOC fluxes measured in the current study but are up to 5 orders of magnitude lower than what was observed in Gloucester Point for low-H VOC; however, the study by Singh and colleagues was conducted in the open ocean at least 500 km away from land and only measured a relatively few compounds while the current study aimed to measure all organics. In addition, neither of these studies involved simultaneous air and water measurements. The study by Beale and colleagues did use an air stripping technique to sample VOC from surface seawater; however, no proof of equilibrium was established. The compounds of interest also had low Henry’s Law constants, so would tend to partition into a bubbling air stream very sparingly—these researchers could have been underestimating the amount of VOC in the seawater they sampled.
One of the few studies that did make simultaneous air and water measurements was that of Baker and colleagues (2000). Air-sea fluxes of methyl iodide, isoprene, and ethane were calculated by pumping marine boundary layer air through solid sorbent, and by purging seawater with nitrogen and trapping the outgassed products on solid sorbent. This method, since only outgassed air is sampled, only captures high-H VOC; however, all compounds measured have $H >> 0.1 \text{ L atm mol}^{-1}$ so the method is appropriate for the compounds of interest. Flux estimates for the three compounds were 0.0667, 0.0667, and $5.00 \times 10^{-4} \text{ ng C m}^{-2} \text{ s}^{-1}$, respectively. When added together, this is on the same order and direction as the current study’s estimates for high-H VOC flux. Another study examining air and seawater measurements of five low molecular weight halocarbons found an average sea to air flux of $3.34 \times 10^{-4}$ to $5.00 \times 10^{-2} \text{ ng C m}^{-2} \text{ s}^{-1}$ [Chuck et al., 2005]. All compounds fall into the high-H operational category, but their fluxes measured are 1-3 orders of magnitude lower than fluxes measured here for the same compound class.

However, again, these 5 compounds ($\text{CH}_3\text{I, CH}_2\text{ClI, CHBr}_3, \text{CHBrCl}_2, \text{CHBr}_2\text{Cl}_2$) likely comprise only a small fraction of total high-H VOC. Generally, studies quantifying the flux of high-H compounds are in good agreement with the results presented here. My low-H VOC fluxes are much higher than other low-H VOC fluxes observed; however, previous work in this area is limited, and in most cases the methods used and compounds measured are not directly comparable.
Environmental Factors and VOC

Regression analysis was performed in R, to examine relationships between Gloucester Point air VOC concentrations, water VOC concentrations, VOC gradients, and VOC fluxes with average air temperature throughout the air sampling period, average water temperature, sample water temperature, average wind speed, and average wind direction. Significant relationships are reported in Table 10 with p-values and adjusted R\(^2\). High-H VOC measurements seem to be the most closely correlated with environmental parameters, although high-H \(C_A\) only correlated (negatively) with wind speed while high-H \(HC_w\), gradient and flux correlated (positively) with the temperature parameters. The temperature correlations are likely due to VOC material becoming more soluble and/or volatile at higher temperatures or greater biological productivity of high-H VOC as temperature increases. Moreover, since the high-H VOC concentrations were always higher in the water, VOC gradients always increase as \(HC_w\) increases. Flux, also, is a scalar multiple of concentration gradient, and is multiplied by the mass transfer coefficient, which also increases with T for high-H material, so the consistent relationships between these three parameters with temperatures are expected. The only significant correlations observed for low-H VOC are \(HC_w\) and concentration gradient with average air temperature. If high-H VOC was driven by pollutant or other external sources, concentrations and fluxes would be more likely to be influenced by environmental parameters than low-H concentrations and fluxes if the latter are more biologically controlled.
Carbon Cycle

It was hypothesized that a net influx of VOC would be observed, fueling the aforementioned net heterotrophy (organic matter remineralization) that has been detected in the York and many estuaries worldwide. However, for both high-H and low-H VOC fractions, a sea-to-air flux was observed for each month sampled at Gloucester Point, VA. Using CO₂ evasion and DIC measurements, Raymond and colleagues (2000) measured net heterotrophy in the York River to be, on average, 100 g C m⁻² yr⁻¹. Although doing so is not statistically sound, extrapolating the average flux measured here would lead to a VOC evasion of approximately 3600 g C m⁻² yr⁻¹ in the York, over an order of magnitude greater than the amount of VOC that would have to flux into the York for metabolic balance. However, the hypothesis cannot conclusively be rejected since only one site was sampled. Pronounced spatial and temporal variability has been observed in estuarine metabolism, and in the York specifically [Raymond et al., 2000]. Net heterotrophy was lowest in the higher salinity regions of the York, which is where the current sampling site was located (salinity at this site was approximately 20-22 PSU). In addition, areas of net autotrophy have been observed in the southern York in the spring, when the sea to air VOC fluxes observed here reached their highest point. Further, net VOC emission and net heterotrophy are not necessarily mutually exclusive. Gross VOC fluxes in conjunction with CO₂ fluxes and/or water column DIC/DOC measurements would be more indicative of net metabolism, and it is possible that the area observed here was net heterotrophic, but metabolized organic material in other forms from other sources. Estuarine metabolism depends on both organic and inorganic inputs, two processes that
are rarely at steady state and are subject to rapid changes [Magnien et al., 1992]. Therefore, higher spatial and temporal breadth are required to decisively address whether atmospheric inputs could be fueling the heterotrophic activity in the York River Estuary.

All measurements were made during the day in this study and no attempt was made to quantify solar radiation parameters or phytoplankton abundance. Diel variability, including a complete reversal of flux direction with changes in photosynthetically active radiation, as well as dependence of phytoplankton species and abundance on flux, have been observed [Beale et al., 2010; Sinha et al., 2007]. Sampling over the entire diel period might have revealed a much smaller positive flux, or perhaps even a net negative flux, as VOC dynamics have been shown to change dramatically over a 24-hour period. Many VOC compounds are both produced and consumed by phytoplankton and can also be produced during organic matter decomposition [Beale et al., 2010; Zhou and Mopper, 1997], so total VOC dynamics would likely fluctuate even throughout the life span of a bloom. Concentrations and fluxes measured in this experiment should not be extrapolated to entire days or months—monitoring experiments have shown that methanol, acetaldehyde, and isoprene all reach air concentration maxima in early afternoon, right in the middle of all of the air samples taken in this experiment [Sinha et al., 2007]. In addition, since the sampling apparatus was not equipped for operation in heavy rain, samples were taken preferentially on calm, clear days, when solar radiation could have been destroying organic material and/or producing low molecular weight organics, which could be either decreasing or increasing VOC measured in both fractions, respectively.
It was not possible to identify the VOC compounds observed in this study. However, retention times can be used to estimate the molecular weight of some of the most prominent compounds. Peaks at three retention times, in particular, were present in nearly all the air and water samples from Gloucester Point—they correspond to molecular weights of 128, 148, and 213. In Bermuda, in general there were more high molecular weight peaks and prominent peaks corresponding to molecular weights of 167, 182, 198, and 213 and 241 in most air and water samples. These peaks share retention times with the n-alkane wax standards used in this study; n-alkanes have been previously measured in marine atmospheres and surface waters [Bendale et al., 2007; Bravo-Linares et al., 2007; Zafiriou et al., 1985]. If these are n-alkanes, they would correspond to C_{12}-C_{15} and C_{17} compounds and these relatively short chain n-alkanes could be algal or bacterial markers [Emerson and Hedges, 2008]. None of the Gloucester Point samples showed the same regular intervals in molecular weight of prominent peaks, although these C_{12}-C_{15} peaks were occasionally present in air samples. Air samples were generally characterized by a few prominent, very large peaks, while water samples had a much larger range of less abundant compounds.

Future Work

One of the most potentially questionable features of the data obtained is the fact that VOC concentrations and fluxes were measured to be so much higher in Bermuda than in Gloucester Point, as this is inconsistent with VOC sources as well as other studies comparing coastal and open ocean sites [Beale et al., 2010; Dachs et al., 2005]. In the
future, the field blank for shipboard measurements should be taken before any samples are collected, but after all the equipment is set up on the ship. The high-H field blank for Bermuda was taken after 3 samples had been collected, and was higher than the first samples. Blanks previously collected in Gloucester Point were then used to correct these data, but there is reason to believe a true shipboard field blank would have been considerably higher. In addition, the water trap storage vial cracking may have made the Bermuda low-H concentration and flux estimates erroneously high. Clean Teflon bags were used in all samples afterwards, and would be necessary for any kind of remote field sampling where samples need to be frozen and transported before analysis. The results presented for Bermuda were the first attempt to complete this experiment shipboard, and should be interpreted bearing in mind the improvements that need to be made. However, the experiments validated the use of the simultaneous air-water VOC measurement method on research cruises, offering the possibility of obtaining increased spatial coverage for VOC fluxes. The method is low-maintenance and could be implemented in many situations. Although low-H VOC measurements were overall much higher than those obtained by other methods, the studies used for comparison for the most part only measured specific compounds. The one study that attempted to measure total VOC might have been underestimating VOC in the water due to non-equilibrium conditions.

One shortcoming of the method presented here is relatively low signal:noise, especially for low-H VOC measurement. Before each experiment, high-H TD tube blanks were taken using pure air and the exact apparatus used in the field. However, signal:noise was always less than 10, so in many cases, VOC concentration and flux
estimates depended in large part on the value of the system blanks. Further, all TD tubes had their own history and were not identical, so the cleanliness of the sampling systems were not the only factor in determining the value of the blanks. Therefore, for high-H VOC, the average air system and water system blanks taken over the year were used for correction of sample concentrations before relating FID signal to total carbon. For low-H VOC, a water trap field blank was placed next to the air sampler for the duration of the sample. However, these blanks displayed high variability, and signal:noise was as low as 2 in some cases. Since field blanks were unpredictable and had the potential to be high, the blank value used to subtract from sample measurements was the average field blank concentration plus 2 standard deviations. Therefore, a 95% confidence value for the field blank was used. This eliminated the dependence of samples on particular field blank concentrations. The exception was for the April and May low-H VOC samples, which had to be run on a different instrument than the one normally used, so sample-specific field blanks were used in this case. Overall, the blank averaging eliminated sample dependence on blank values, but this is only desirable if blank values depend on other factors besides equipment cleanliness, like differences in tube history. If these other factor were negligible compared to differences in system cleanliness, individual samples could have been erroneously altered by blank averaging.

Complete retention of low-H VOC in the water traps is questionable given some of the field data where an appreciable amount of VOC was dissolved in a third trap. Although the experiments outlined in the Methods section indicated that 2 water traps were sufficient, 3 traps were used in the January 31 and April samples, and it was found
when the samples were analyzed later that in some cases, there was an appreciable amount of organic matter in impinger 3. Further experimentation is ongoing to investigate whether 3 traps should be used for all future samples using this method.

In conclusion, gaseous VOC flux has the potential to be quite significant in the context of the global carbon cycle. Greater spatial and temporal variability in sampling is required in estuaries, especially, where small scale variation in physical and biological forces cause high variability in biogeochemistry. VOC sampling needs to be conducted in environments of different productivities, salinities, and at different times throughout the day to determine an estuary-wide, and eventually global, VOC flux estimate. In addition, the differences in partitioning behavior between different VOC compounds needs to be taken into account. In previous studies attempting to measure total VOC flux, only material in the low-H fraction was sampled. Impacts of the sampling method on which fractions of VOC are actually collected are enormous. Thus far, no attempt has been made to separate compounds based on differences in Henry’s Law constant, even though this parameter helps dictate their behavior at the air-sea interface. Although low-H VOC dominated in this study, this might not be true for all sites and more effort should be made to sample the entire range of VOC. The novelty in this study is the use of difference mass transfer coefficients for different VOC fractions, which is important since mass transfer coefficients vary by 4-5 orders of magnitude for high-H VOC. This study has shown that air-film limited and water-film limited compounds behave very differently, and the use of one “average” mass transfer coefficient for all material is insufficient.
TABLE 1. Chemical standards used for calibration of FID signal.

<table>
<thead>
<tr>
<th>Compound</th>
<th>MW</th>
<th>H (L atm mol⁻¹)</th>
<th>RT (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-butadiene</td>
<td>54.1</td>
<td>69</td>
<td>5.5</td>
</tr>
<tr>
<td>o-xylene</td>
<td>106.2</td>
<td>4.5</td>
<td>4.4</td>
</tr>
<tr>
<td>p-xylene</td>
<td>106.2</td>
<td>7.1</td>
<td>4</td>
</tr>
<tr>
<td>heptanal</td>
<td>114.2</td>
<td>0.3</td>
<td>4.6</td>
</tr>
<tr>
<td>4-ethyltoluene</td>
<td>120.2</td>
<td>5</td>
<td>8.7</td>
</tr>
<tr>
<td>4-isopropyltoluene</td>
<td>134.2</td>
<td>7.7</td>
<td>6.6</td>
</tr>
<tr>
<td>n-butylbenzene</td>
<td>134.2</td>
<td>12.8</td>
<td>7.2</td>
</tr>
<tr>
<td>nonanal</td>
<td>142.2</td>
<td>1.3</td>
<td>7.9</td>
</tr>
<tr>
<td>decanal</td>
<td>156.2</td>
<td>1.6</td>
<td>9.5</td>
</tr>
<tr>
<td>tridecane</td>
<td>184.4</td>
<td>2326</td>
<td>10.9</td>
</tr>
<tr>
<td>tetradecane</td>
<td>198.4</td>
<td>1136</td>
<td>12.4</td>
</tr>
<tr>
<td>pentadecane</td>
<td>212.4</td>
<td>476</td>
<td>13.7</td>
</tr>
</tbody>
</table>
TABLE 2. Experiments (single replicate) used to assess low-H VOC breakthrough with varying number of water traps and clean air purge time.

<table>
<thead>
<tr>
<th>Impinger</th>
<th>Expt 1</th>
<th>Expt 2</th>
<th>Expt 3</th>
<th>Expt 4</th>
<th>Expt 5</th>
<th>Expt 6</th>
<th>Expt 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.47</td>
<td>5.58</td>
<td>6.83</td>
<td>8.38</td>
<td>13.74</td>
<td>44.3</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>6.06</td>
<td>6.34</td>
<td>4.71</td>
<td>4.12</td>
<td>b.d.</td>
<td>32.1</td>
<td>0.41</td>
</tr>
<tr>
<td>3</td>
<td>2.5</td>
<td>11.5</td>
<td>b.d.</td>
<td>21.0</td>
<td>3.57</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Experiments
1. (Control) 1 L sample purge, 3 L clean air purge
2. 1 L sample purge, 1 L clean air purge
3. 1 L sample purge, 3rd impinger added before 3 L clean air purge
4. 1 L sample purge, 3rd impinger added before 1 L clean air purge
5. 3rd impinger added before 1 L sample purge, no clean air purge
6. 3rd impinger added before 1 L sample purge, 1 L clean air purge
7. 3rd impinger added before 1 L sample purge, 3 L clean air purge
TABLE 3. High-H VOC concentrations in air and surface seawater. Errors reflect 20% uncertainty in air flow rate.

<table>
<thead>
<tr>
<th>Date</th>
<th>CA</th>
<th>Error</th>
<th>HCw</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bermuda</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19-Aug-2010</td>
<td>212</td>
<td>42</td>
<td>1340</td>
<td>268</td>
</tr>
<tr>
<td>20-Aug-2010</td>
<td>209</td>
<td>42</td>
<td>3230</td>
<td>645</td>
</tr>
<tr>
<td>21-Aug-2010</td>
<td>115</td>
<td>23</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td><strong>Gloucester Point</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Jul-2010</td>
<td>15.4</td>
<td>3.1</td>
<td>507</td>
<td>101</td>
</tr>
<tr>
<td>28-Jul-2010</td>
<td>97.4</td>
<td>19.5</td>
<td>439</td>
<td>88</td>
</tr>
<tr>
<td>15-Oct-2010</td>
<td>43.8</td>
<td>8.8</td>
<td>78.7</td>
<td>16.0</td>
</tr>
<tr>
<td>9-Nov-2010</td>
<td>31.7</td>
<td>6.3</td>
<td>114</td>
<td>23</td>
</tr>
<tr>
<td>3-Dec-2010</td>
<td>19.3</td>
<td>3.9</td>
<td>75.6</td>
<td>15.3</td>
</tr>
<tr>
<td>13-Apr-2011</td>
<td>49.4</td>
<td>9.9</td>
<td>109</td>
<td>22</td>
</tr>
<tr>
<td>2-May-2011</td>
<td>101</td>
<td>22.3</td>
<td>50.5</td>
<td>14.8</td>
</tr>
</tbody>
</table>
TABLE 4. Low-H VOC concentrations in air and surface seawater. Error reflects 20% uncertainty in air flow rate and uncertainty associated with the use of linear regression.

<table>
<thead>
<tr>
<th>Date</th>
<th>$C_A$ (ng C L$^{-1}$)</th>
<th>Error</th>
<th>$HC_w$ (ng C L$^{-1}$)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bermuda</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19-Aug-2010</td>
<td>546</td>
<td>109</td>
<td>9,960</td>
<td>1,990</td>
</tr>
<tr>
<td>20-Aug-2010</td>
<td>1,670</td>
<td>334</td>
<td>43,000</td>
<td>8,590</td>
</tr>
<tr>
<td>Gloucester Point</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28-Jul-2010</td>
<td>632</td>
<td>126</td>
<td>12,200</td>
<td>2,450</td>
</tr>
<tr>
<td>15-Oct-2010</td>
<td>719</td>
<td>144</td>
<td>9,750</td>
<td>1,950</td>
</tr>
<tr>
<td>9-Nov-2010</td>
<td>444</td>
<td>89</td>
<td>9,820</td>
<td>1,960</td>
</tr>
<tr>
<td>3-Dec-2010</td>
<td>b.d.</td>
<td>--</td>
<td>4,330</td>
<td>866</td>
</tr>
<tr>
<td>19-Jan-2011</td>
<td>506</td>
<td>101</td>
<td>11,900</td>
<td>2,390</td>
</tr>
<tr>
<td>31-Jan-2011</td>
<td>--</td>
<td>--</td>
<td>1,760</td>
<td>353</td>
</tr>
<tr>
<td>23-Feb-2011</td>
<td>491</td>
<td>98</td>
<td>723</td>
<td>145</td>
</tr>
<tr>
<td>14-Mar-2011</td>
<td>150</td>
<td>30.0</td>
<td>3,910</td>
<td>781</td>
</tr>
<tr>
<td>13-Apr-2011</td>
<td>1,060</td>
<td>213</td>
<td>25,000</td>
<td>4,990</td>
</tr>
<tr>
<td>2-May-2011</td>
<td>511</td>
<td>102</td>
<td>30,500</td>
<td>6,110</td>
</tr>
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</table>
TABLE 5. High-H VOC concentration gradients. Error was propagated from both air and water VOC concentration estimates.

<table>
<thead>
<tr>
<th>Date</th>
<th>Concentration (ng C L⁻¹)</th>
<th>Error (ng C L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bermuda</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19-Aug-2010</td>
<td>1130</td>
<td>271</td>
</tr>
<tr>
<td>20-Aug-2010</td>
<td>3020</td>
<td>646</td>
</tr>
<tr>
<td>Gloucester Point</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Jul-2010</td>
<td>492</td>
<td>101</td>
</tr>
<tr>
<td>28-Jul-2010</td>
<td>342</td>
<td>90</td>
</tr>
<tr>
<td>15-Oct-2010</td>
<td>34.9</td>
<td>18.2</td>
</tr>
<tr>
<td>9-Nov-2010</td>
<td>81.9</td>
<td>23.6</td>
</tr>
<tr>
<td>3-Dec-2010</td>
<td>56.3</td>
<td>15.8</td>
</tr>
<tr>
<td>13-Apr-2011</td>
<td>60.0</td>
<td>24.6</td>
</tr>
<tr>
<td>2-May-2011</td>
<td>-50.8</td>
<td>26.7</td>
</tr>
</tbody>
</table>
TABLE 6. Low-H VOC Concentration Gradients. Error is cumulative from air and water VOC concentration estimates.

<table>
<thead>
<tr>
<th>Date</th>
<th>(CA-HCW) ng C L⁻¹</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bermuda</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19-Aug-2010</td>
<td>9,420</td>
<td>2,000</td>
</tr>
<tr>
<td>20-Aug-2010</td>
<td>41,300</td>
<td>8,600</td>
</tr>
<tr>
<td><strong>Gloucester Point</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28-Jul-2010</td>
<td>11,600</td>
<td>2,450</td>
</tr>
<tr>
<td>15-Oct-2010</td>
<td>9,030</td>
<td>1,960</td>
</tr>
<tr>
<td>9-Nov-2010</td>
<td>9,380</td>
<td>1,970</td>
</tr>
<tr>
<td>3-Dec-2010</td>
<td>4,330</td>
<td>866</td>
</tr>
<tr>
<td>19-Jan-2011</td>
<td>11,400</td>
<td>2,390</td>
</tr>
<tr>
<td>23-Feb-2011</td>
<td>235</td>
<td>175</td>
</tr>
<tr>
<td>14-Mar-2011</td>
<td>3,760</td>
<td>782</td>
</tr>
<tr>
<td>13-Apr-11</td>
<td>23,900</td>
<td>5,000</td>
</tr>
<tr>
<td>2-May-11</td>
<td>30,000</td>
<td>6,110</td>
</tr>
</tbody>
</table>
TABLE 7. High-H VOC fluxes and mass transfer coefficients and fluxes.

<table>
<thead>
<tr>
<th></th>
<th>Flux</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ng C m⁻² s⁻¹</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Error</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>v_water cm s⁻¹</th>
<th>Flux</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bermuda</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19-Aug-2010</td>
<td>0.00139</td>
<td>15.7</td>
<td>0.4</td>
</tr>
<tr>
<td>20-Aug-2010</td>
<td>0.00139</td>
<td>42.0</td>
<td>0.9</td>
</tr>
<tr>
<td><strong>Gloucester Point</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Jul-2010</td>
<td>0.00128</td>
<td>6.29</td>
<td>0.13</td>
</tr>
<tr>
<td>28-Jul-2010</td>
<td>0.00139</td>
<td>4.77</td>
<td>0.13</td>
</tr>
<tr>
<td>15-Oct-2010</td>
<td>0.00117</td>
<td>0.408</td>
<td>0.021</td>
</tr>
<tr>
<td>9-Nov-2010</td>
<td>0.00107</td>
<td>0.873</td>
<td>0.025</td>
</tr>
<tr>
<td>3-Dec-2010</td>
<td>0.00097</td>
<td>0.543</td>
<td>0.015</td>
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<tr>
<td>13-Apr-2011</td>
<td>0.00107</td>
<td>0.639</td>
<td>0.026</td>
</tr>
<tr>
<td>2-May-2011</td>
<td>0.00117</td>
<td>-0.595</td>
<td>0.031</td>
</tr>
</tbody>
</table>
TABLE 8. Low-H VOC estimates of mass transfer coefficients and fluxes. Mass transfer coefficient was estimated to be 1 cm s\(^{-1}\).

<table>
<thead>
<tr>
<th></th>
<th>Flux</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bermuda</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19-Aug-2010</td>
<td>94,200</td>
<td>6,760</td>
</tr>
<tr>
<td>20-Aug-2010</td>
<td>413,000</td>
<td>13,400</td>
</tr>
<tr>
<td><strong>Gloucester Point</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28-Jul-2010</td>
<td>116,000</td>
<td>2,570</td>
</tr>
<tr>
<td>15-Oct-2010</td>
<td>90,300</td>
<td>6,600</td>
</tr>
<tr>
<td>9-Nov-2010</td>
<td>93,800</td>
<td>5,220</td>
</tr>
<tr>
<td>3-Dec-2010</td>
<td>43,300</td>
<td>3,320</td>
</tr>
<tr>
<td>19-Jan-2011</td>
<td>114,000</td>
<td>4,780</td>
</tr>
<tr>
<td>23-Feb-2011</td>
<td>2,350</td>
<td>4,150</td>
</tr>
<tr>
<td>14-Mar-2011</td>
<td>37,600</td>
<td>2,950</td>
</tr>
<tr>
<td>13-Apr-11</td>
<td>239,000</td>
<td>4,440</td>
</tr>
<tr>
<td>2-May-11</td>
<td>300,000</td>
<td>5,450</td>
</tr>
</tbody>
</table>
TABLE 9. Environmental conditions during samples.

<table>
<thead>
<tr>
<th>Date</th>
<th>Air start</th>
<th>Air end</th>
<th>Air vol L</th>
<th>Water</th>
<th>Tide</th>
<th>Low air T deg. C</th>
<th>High air T deg. C</th>
<th>Avg. air T deg. C</th>
<th>Air T at sample deg. C</th>
<th>Water T at sample deg. C</th>
<th>Avg. wind speed m/s</th>
<th>Avg. wind direction deg T</th>
<th>Sorbents used</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gloucester Point</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Jul-10</td>
<td>6:45 AM</td>
<td>4:45 PM</td>
<td>30</td>
<td>1:00 PM</td>
<td>flood high</td>
<td>20.4</td>
<td>24.4</td>
<td>21.0</td>
<td>21.4</td>
<td>28.8</td>
<td>4.8</td>
<td>155</td>
<td>Tena5, CSII</td>
<td>high-H VOC only</td>
</tr>
<tr>
<td>29-Jul-10</td>
<td>7:00 AM</td>
<td>5:00 PM</td>
<td>30</td>
<td>10:30 AM</td>
<td>flood high</td>
<td>25.4</td>
<td>30.5</td>
<td>26.9</td>
<td>25.4</td>
<td>27.9</td>
<td>3.7</td>
<td>222</td>
<td>Tena5, CSII</td>
<td></td>
</tr>
<tr>
<td>15-Oct-10</td>
<td>7:45 AM</td>
<td>2:30 PM</td>
<td>20</td>
<td>12:00 PM</td>
<td>flood flow</td>
<td>10.6</td>
<td>15.1</td>
<td>12.1</td>
<td>11.2</td>
<td>19.9</td>
<td>4.3</td>
<td>246</td>
<td>Tena5, CSII</td>
<td>rain started 2:30 PM</td>
</tr>
<tr>
<td>9-Nov-10</td>
<td>7:45 AM</td>
<td>3:45 PM</td>
<td>24</td>
<td>12:00 PM</td>
<td>ebb/high</td>
<td>8.7</td>
<td>12.2</td>
<td>10.2</td>
<td>8.8</td>
<td>13.7</td>
<td>6.1</td>
<td>339</td>
<td>Tena5, CT</td>
<td></td>
</tr>
<tr>
<td>5-Dec-10</td>
<td>8:00 AM</td>
<td>3:00 PM</td>
<td>21</td>
<td>10:00 AM</td>
<td>ebb</td>
<td>3.0</td>
<td>4.9</td>
<td>3.6</td>
<td>2.3</td>
<td>12.2</td>
<td>5.0</td>
<td>703</td>
<td>Tena5, CT</td>
<td>water sample 12-2, air 12-3</td>
</tr>
<tr>
<td>18-Jan-11</td>
<td>8:30 AM</td>
<td>3:30 PM</td>
<td>21</td>
<td>10:00 AM</td>
<td>ebb/high</td>
<td>4.8</td>
<td>7.0</td>
<td>5.5</td>
<td>5.3</td>
<td>2.6</td>
<td>2.5</td>
<td>255</td>
<td>--</td>
<td>low-H VOC only</td>
</tr>
<tr>
<td>31-Jan-11</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>9:30 AM</td>
<td>ebb</td>
<td>1.5</td>
<td>2.9</td>
<td>2.0</td>
<td>2.1</td>
<td>3.0</td>
<td>5.6</td>
<td>44.6</td>
<td>--</td>
<td>low-H VOC only, water only</td>
</tr>
<tr>
<td>25-Feb-11</td>
<td>7:00 AM</td>
<td>2:00 PM</td>
<td>21</td>
<td>8:30 AM</td>
<td>flood flow</td>
<td>-1</td>
<td>2.2</td>
<td>0.2</td>
<td>0.6</td>
<td>6.2</td>
<td>3.7</td>
<td>290</td>
<td>--</td>
<td>low-H VOC only</td>
</tr>
<tr>
<td>14-Mar-11</td>
<td>8:00 AM</td>
<td>4:00 PM</td>
<td>24</td>
<td>1:45 PM</td>
<td>flood</td>
<td>5.2</td>
<td>8.6</td>
<td>6.6</td>
<td>6.7</td>
<td>9.9</td>
<td>4.6</td>
<td>136</td>
<td>--</td>
<td>low-H VOC only</td>
</tr>
<tr>
<td>13-Apr-11</td>
<td>8:00 AM</td>
<td>3:30 PM</td>
<td>22.5</td>
<td>9:40 AM</td>
<td>high</td>
<td>13.4</td>
<td>15.8</td>
<td>14.3</td>
<td>14.4</td>
<td>14.3</td>
<td>3.8</td>
<td>240</td>
<td>Tena5, CSII</td>
<td>high-H air analyzed after 2 weeks</td>
</tr>
<tr>
<td>2-May-11</td>
<td>8:45 AM</td>
<td>4:30 PM</td>
<td>33</td>
<td>10:00 AM</td>
<td>flood</td>
<td>13.7</td>
<td>21.8</td>
<td>16.0</td>
<td>14.1</td>
<td>18.8</td>
<td>3.1</td>
<td>187</td>
<td>Tena5, CSII</td>
<td></td>
</tr>
</tbody>
</table>

Bermuda

| Date       | Air start | Air end  | Air vol L | Water | Tide | Low air T deg. C | High air T deg. C | Avg. air T deg. C | Air T at sample deg. C | Water T at sample deg. C | Avg. wind speed m/s | Avg. wind direction deg T | Sorbents used | Notes                  |
|------------|-----------|----------|------------|-------|------|------------------|------------------|-------------------|-------------------------|--------------------------|                |                         |              |                       |
| 15-Aug-10  | 11:00 AM  | 9:00 PM  | 30         | 3:30 PM | --   | 26.9             | 30.6             | 28.5              | 27.6                    | 28.6                     | 3.3             | 143.0                  | Tena5, CSII |                       |
| 20-Aug-10  | 9:30 AM   | 8:30 PM  | 33         | 10:30 AM| --   | 25.1             | 31.9             | 28.4              | 28.2                    | 28.9                     | 5.1             | 137.2                  | Tena5, CSII |                       |
| 21-Aug-10  | 8:30 AM   | 7:00 PM* | 37         | 9:30 AM | --   | 27.4             | 31.7             | 28.9              | 28.1                    | 28.9                     | 4.9             | 122.6                  | Tena5, CSII | * air stopped 7 PM on 22-Aug |
TABLE 10. P-values and adjusted R² values for regressions with VOC measurements and environmental parameters. The direction of the relationship is given as “+” and “−” for positive and negative relationships, respectively.

<table>
<thead>
<tr>
<th></th>
<th>High-H VOC</th>
<th></th>
<th></th>
<th>Flux</th>
<th>Low-H VOC</th>
<th></th>
<th></th>
<th>Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CA ng C L⁻¹</td>
<td>HCW ng C L⁻¹</td>
<td>Gradient ng C L⁻¹</td>
<td>Flux ng C m² s⁻¹</td>
<td>CA ng C L⁻¹</td>
<td>HCW ng C L⁻¹</td>
<td>Gradient ng C L⁻¹</td>
<td>Flux ng C m² s⁻¹</td>
</tr>
<tr>
<td>Avg. Air T (deg. C)</td>
<td>p=0.036</td>
<td>p=0.028</td>
<td>p=0.042</td>
<td>p=0.044</td>
<td>R²=0.541</td>
<td>R²=0.581</td>
<td>R²=0.350</td>
<td>R²=0.344</td>
</tr>
<tr>
<td>Sample Air T (deg. C)</td>
<td>p=0.027</td>
<td>p=0.049</td>
<td>p=0.025</td>
<td></td>
<td>R²=0.591</td>
<td>R²=0.487</td>
<td>R²=0.602</td>
<td></td>
</tr>
<tr>
<td>Sample Water T (deg C)</td>
<td>p=0.014</td>
<td>p=0.018</td>
<td>p=0.0068</td>
<td></td>
<td>R²=0.679</td>
<td>R²=0.644</td>
<td>R²=0.757</td>
<td></td>
</tr>
<tr>
<td>Avg. Wind Speed (m s⁻¹)</td>
<td>p=0.041</td>
<td></td>
<td></td>
<td></td>
<td>R²=0.52</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Avg. Wind Dir. (Deg. T)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 1. Air-Sea Film Model, adapted from Liss and Slater 1974. $C_W$ is VOC concentration in water, $C_A$ is VOC concentration in air, $C_{WA}$ is concentration in water film at film interface, $C_{AW}$ is concentration in air film at film interface, and $\delta_w$ and $\delta_A$ are the water and air film thicknesses, respectively.
FIGURE 2. Schematic of air sampling set-up. VOC in water traps was quantified using a DOC analyzer, and VOC on the Tenax and Carbosieve sorbent tubes was analyzed using TD-GC-FID.
FIGURE 3. Schematic of water sampling set-up. VOC in water traps was quantified using a DOC analyzer, and VOC on the Tenax and Carbosieve sorbent tubes was analyzed using TD-GC-FID.
FIGURE 4. Calibration curve used for quantification of FID signal.
FIGURE 5. a) Declining FID signal of chemical standards in air purged out of the water tank. B) Purge time vs. VOC concentration in purged air.
FIGURE 6. Sampling Locations.
FIGURE 7. Gloucester Point sampling site on VIMS pier.
FIGURE 8. Atlantic Ocean sampling sites near Bermuda.
FIGURE 9. Relationship between Henry’s Law constant and mass transfer coefficient of some representative compounds.
FIGURE 10. Relationship between retention time and molecular weight of chemical standards used for calibration.

The graph shows a linear relationship between retention time (y) and molecular weight (x), with the equation:

\[ y = 0.0874x - 5.0181 \]
FIGURE 11. Representative high-H VOC air sample.
FIGURE 12. Gloucester Point High-H VOC Concentrations. $C_A$ is VOC concentration in air and $HC_W$ is VOC concentration in seawater-equilibrated air.
FIGURE 13. Gloucester Point Low-H VOC Concentrations. \( C_A \) is VOC concentration in air and \( H C_W \) is VOC concentration in seawater-equilibrated air.
FIGURE 15. Gloucester Point Low-H VOC Concentration Gradients.
Figure 16. Gloucester Point High-H VOC fluxes.
FIGURE 17. Gloucester Point Low-H VOC fluxes.
FIGURE 18. Low-H VOC HC$_w$ vs. C$_A$ with adjusted R$^2$ and p-value.

R$^2$ = 0.236
p = 0.105
APPENDIX. Regressions of purged VOC with time used for determining initial high-H and low-H VOC concentrations in seawater samples. Only the August 19 high-H VOC sample had a significant change in VOC concentration over time ($\alpha=0.05$).

High-H VOC in Water:

Bermuda:

![Graph showing regression line for August 19 sample with equation: $y = 0.0217x + 7.1987$, $R^2 = 0.8908$]

![Graph showing regression line for August 20 sample with equation: $y = -0.032x + 8.0789$, $R^2 = 0.0642$]

Gloucester Point:

![Graph showing regression line for July 1 sample with equation: $y = -0.0099x + 2.284$, $R^2 = 0.7652$]

![Graph showing regression line for July 28 sample with equation: $y = -0.0195x + 0.6856$, $R^2 = 0.4509$]

![Graph showing regression line for October 15 sample with equation: $y = -0.0077x + 2.365$, $R^2 = 0.0483$]

![Graph showing regression line for November 9 sample with equation: $y = -0.0983x + 2.725$, $R^2 = 0.7174$]

![Graph showing regression line for December 3 sample with equation: $y = -0.052x + 3.326$, $R^2 = 0.3596$]

![Graph showing regression line for April 13 sample with equation: $y = -0.039x + 4.6945$, $R^2 = 0.1556$]
Low-H VOC in Water:

Bermuda:

August 19:

\[ y = 0.0152x + 9.2067 \]
\[ R^2 = 0.28752 \]

August 20:

\[ y = -0.0466x + 10.668 \]
\[ R^2 = 0.36836 \]

Gloucester Point:

July 28:

\[ y = -0.0067x + 9.4131 \]
\[ R^2 = 0.69882 \]

October 15:

\[ y = -0.0077x + 9.1853 \]
\[ R^2 = 0.08276 \]

November 9:

\[ y = -0.0165x + 9.1924 \]
\[ R^2 = 0.13617 \]

December 3:

\[ y = -0.0113x + 8.3737 \]
\[ R^2 = 0.04056 \]
References

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VITA

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