High atmosphere-ocean exchange of organic carbon in the NE subtropical Atlantic

Jordi Dachs,1 Maria L. Calleja,2 Carlos M. Duarte,2 Sabino del Vento,1 Barbara Turpin,3 Andrea Polidori,3 Gerhard J. Herndl,4 and Susana Agusti2

Received 16 June 2005; revised 30 July 2005; accepted 5 October 2005; published 9 November 2005.

[1] The air-sea exchange of organic carbon (OC) remains largely unexplored, except for few organic compounds comprising a small fraction of the total aerosol and gaseous OC in the atmosphere. Observations of high atmospheric concentrations and diffusive air-sea exchanges for such individual organic compounds, suggest that air-sea exchange of total OC may contribute significantly to the oceanic carbon budget. Here we quantify the atmosphere-ocean exchanges of total OC in the NE Subtropical Atlantic. Average net gaseous diffusive air-water fluxes averaged –31 and –25 mmol C m⁻² d⁻¹ for the spring and fall, respectively, exceeding measured OC inputs by dry aerosol deposition (FDDOC, –0.98 mmol C m⁻² d⁻¹) and net CO₂ exchange (F₄⚽₂, –6.3 mmol C m⁻² d⁻¹). These fluxes are important to understand the regional carbon budget of the NE Subtropical Atlantic, and depict the atmosphere as a major dynamic vector for OC exchange with the ocean.


1. Introduction

[2] Anthropogenic emissions of un- or incompletely combusted organic carbon (OC) and biogenic emissions of volatile OC constitute significant carbon inputs to the atmosphere [Schauer et al., 2002; Fuentes et al., 2000]. Once organic compounds are released to the atmosphere they undergo atmospheric transport, degradation and deposition to the surface environments. The ocean plays a dual role as a source of some volatile compounds such as non-methane hydrocarbons [McKay et al., 1996], and as a major sink of many anthropogenic [Jurado et al., 2005] and biogenic organic compounds [Jacob et al., 2005]. There are three main mechanisms of exchange of OC between the ocean and the atmosphere; i) diffusive exchanges by volatilization (sea to air) and absorption (air to sea) of gas phase OC, ii) atmospheric aerosol OC dry deposition, and iii) by wet deposition of aerosol and gaseous OC. There are very few assessments of the magnitude and relevance of these mechanisms contributing to the atmosphere-ocean exchange of total OC. The few previous reports are limited to estimations of fluxes associated with aerosol dry and wet OC deposition [Willey et al., 2000; Durrieu de Madron et al., 2000; Kieber et al., 2002].

[3] Therefore, whereas the ocean is known to be a major sink for anthropogenic CO₂ [Sabine et al., 2004; Intergovernmental Panel on Climate Change (IPCC), 2001], the atmospheric inventory and air-sea exchange fluxes of OC remain largely unexplored, except for few organic compounds comprising a small fraction of the total OC in the atmosphere [Jacob et al., 2002; Jacob et al., 2005; Jurado et al., 2005; Lewis et al., 2000]. Observations of high atmospheric concentrations and diffusive air-sea exchange for some organic compounds [Singh et al., 2001; Duce et al., 1991; Jurado et al., 2005], especially the diffusive fluxes, suggest that air-sea exchange of total OC may contribute significantly to the oceanic carbon budget, although estimations of diffusive fluxes of total OC have not yet been reported.

[4] The objective of this study was to estimate the magnitude and direction, and assess the relevance of atmosphere-ocean exchanges of organic carbon, especially those associated with gas-phase organic compounds, in the north east subtropical Atlantic Ocean.

2. Sampling and Methods

[5] Sampling: We measured the atmospheric OC concentrations (gas and aerosol phase) and simultaneously, the dissolved concentrations and exchange fluxes of OC in the NE Subtropical Atlantic, an area subject to Saharan dust influence [Eglinton et al., 2002]. The dry depositional aerosol input (FDDOC), volatilization (F_OC,VOL) and absorption (F_OC,AB) components of the atmosphere-ocean exchange of organic carbon were quantified along with the air-sea CO₂ exchange, and the enrichment of the top-cm of the ocean in organic carbon. The study was conducted during the COCA and BADE cruises along the Subtropical NE Atlantic on-board the R/V Hespérides and R/V Pelagia, respectively. The COCA cruise took place in May–June 2003 and started from the Island of Gran Canaria, sailing along 26°N to reach 26°W, following south to reach 21°N, and then heading towards the W. African Coast at Cape Blanco along this parallel. The BADE cruise took place in September–October 2004 and started south of Cape Blanco and headed along a W-NW transect to reach 25°N, 31°W (Figure 1).

[6] Determination of dissolved organic carbon (DOC), CO₂ partial pressures, and atmospheric OC and EC aerosol...
concentrations were done using standard procedures as described in Table S1.\(^1\) In order to estimate air-water fluxes of OC, operational measurements of total volatile and semi-volatile OC in the gas phase and seawater dissolved phase are needed. Therefore, we developed here a novel procedure based on the definition of two operational measures, total gas-phase organic carbon (GOC) in the atmosphere and exchangeable dissolved organic carbon (EDOC) in seawater.

\[ [7] \] The total concentration of organic carbon in the gas phase (GOC) was determined indirectly by equilibrating air and water for 30 min by bubbling prefiltered air (QMA phase, Whatmann) through 50 ml of acidified (pH 1–2 with H\(_3\)PO\(_4\)) water (HPLC grade water, MERCK) upwind of the filter, Whatmann) through 50 ml of acidified (pH 1–2 with H\(_3\)PO\(_4\)) water (HPLC grade water, MERCK) upwind of the filter. Water was then transferred to 40 ml of pure acidified (pH 1–2 with H\(_3\)PO\(_4\)) water (HPLC grade water, MERCK). Water was then transferred to 40 ml of pure acidified (pH 1–2 with H\(_3\)PO\(_4\)) water (HPLC grade water, MERCK) and water for 30 min by bubbling prefiltered air (QMA phase (GOC) was determined indirectly by equilibrating air concentrations were corrected for field blanks.

\[ [10] \] For the spring sampling cruise, the concentration of dissolved OC exchangeable with the atmosphere (EDOC) in the coastal and open ocean surface averaged (±SE) 30 ± 6 \(\mu\)mol C L\(^{-1}\), corresponding to about 30–40% of the DOC concentration (Figure S1), while the dissolved OC concentration equilibrated with the gaseous organic carbon (GOC/H') averaged 40 ± 5 \(\mu\)mol C L\(^{-1}\). During the fall cruise, EDOC concentrations in the open ocean were not significantly different from those obtained during the spring cruise with an average EDOC concentration of 36 \(\mu\)mol C L\(^{-1}\.

\[ [9] \] The area nearest to the African coastal zone received dry deposition inputs of organic (FDD\(_{OC} = -1.02 ± 4.0 \times 10^6 \text{ mmol C m}^{-2} \text{ d}^{-1}\)) and elemental carbon two-fold higher than those in the open ocean and acted as a strong sink of aerosol-phase organic carbon, but with an important variability in fluxes (Figures S1 and S2) presumably due to large proximal land aerosol sources in the upwind NE direction, especially for the coastal sites (Figures S3–S10). The dry deposition flux of aerosol organic carbon was six fold higher than that of elemental (black) carbon (Figure S1), consistent with other reports \[ Lim et al., 2003 \].

\[ [11] \] This spatial covariance in exchangeable OC concentrations resulted in a significant correlation between GOC/H' and surface concentrations of EDOC, \(r^2 = 0.59 \text{ (} P < 0.01\)) and \(r^2 = 0.84 \text{ (} P < 0.01\)) for the spring and fall cruises, respectively (Figure 2). These two measurements are completely independent, so that the tight correlation between atmospheric and seasurface exchangeable OC concentrations suggests a dynamic coupling and cycling of these compounds between the surface ocean and lower atmosphere, similar to that reported for individual semivolatile organic compounds \[ Jaward et al., 2004 \]. This air-water coupling is therefore the result of exchanges between the
atmosphere and the ocean due to volatilization and atmospheric deposition.

[12] Atmospheric dry deposition (gaseous and particulate) and volatilization of organic carbon was consistently high [mean (±SE) FDDOC = 0.98 ± 0.22 mmol C m⁻² d⁻¹; mean FOC,AB = 104 ± 16 mmol C m⁻² d⁻¹; mean FOC,VOL 73 ± 11 mmol C m⁻² d⁻¹; Figures 1 and S1], with the average absolute magnitude of the gross volatilization and absorption fluxes exceeding the aerosol deposition by 70–100 fold. This ratio of gross diffusive to dry aerosol depositional flux of atmospheric organic carbon is comparable to that reported for hydrocarbons and other semivolatile organic compounds [Duce et al., 1991; Jurado et al., 2005] and is controlled by dynamic partitioning of organic compounds between the gas and aerosol phases [Jurado et al., 2005; Seinfeld and Pandis, 1998]. Indeed, the high ratio of dry gaseous to dry aerosol deposition fluxes suggests that atmospheric organic matter is dominated by gas-phase organic compounds.

[13] The gross diffusive fluxes were 2–8 times higher than the net air-sea fluxes (mean FOC = 31 ± 12 mmol C m⁻² d⁻¹) for the spring sampling cruise, and 2–15 times for the fall data set (mean FOC = 25 ± 23 mmol C m⁻² d⁻¹). Therefore, there are high diffusive volatilization and absorption fluxes which result in much smaller net air-water fluxes. This is consistent with the dynamic coupling of gas and dissolved organic compounds (Figure 2), especially in the open ocean. Consistent with the enrichments reported here during the two sampling cruises to the entire subtropical NE Atlantic an an aerial extent of 5.26 10⁶ km² yields an estimated input of 0.64 ± 0.3 Gt C yr⁻¹. This estimated diffusive net organic carbon exchange (mean net FOC = 28 mmol C m⁻² d⁻¹) measured here during the two sampling cruises to the entire subtropical NE Atlantic with an aerial extent of 5.26 10⁶ km² yields an estimated input of 0.64 ± 0.3 Gt C yr⁻¹. This estimated diffusive net organic carbon exchange is similar to the estimated organic carbon deficit for this region of 0.5 Gt C yr⁻¹ derived from the metabolic imbalance of the planktonic community [Duarte et al., 2001]. This imbalance cannot be accounted for by internal transport via oceanic circulation or wet deposition alone [Hansen et al., 2004]. This finding is consistent with previous suggestions that atmospheric input of OC may help explain net heterotrophy (i.e., excess organic carbon respiration over autotrophic production) in the NE Atlantic [del Giorgio and Duarte, 2002; Duarte et al., 1999]. The specific role of atmospheric OC inputs on regional carbon budgets depends, however, on the fraction of labile and refractory exchangeable organic carbon, which remains untested. Labile components would fuel heterotrophic processes, thereby yielding CO₂, whereas refractory and hydrophobic compounds would eventually add to the downward OC flux at the ultimate sink areas.

[14] Our results provide compelling evidence of high exchange fluxes of volatile and semivolatile organic carbon between the ocean and the atmosphere over the NE Atlantic. The origin of the exchanged organic carbon cannot be resolved here, however, likely contains products derived from incomplete combustion of fossil fuel which constitute a significant fraction of the total combustion products [Schauer et al., 2002] and is abundant in the atmosphere [Turpin et al., 2000]. Compounds released by land vegetation [Fuentes et al., 2000] and soil organic matter are also abundant in the atmosphere even over remote oceanic regions [Eglington et al., 2002] and might contribute to the pool of exchangeable OC, as well as biogenic marine OC [McKay et al., 1996]. Even if atmospheric organic carbon has a relatively short half-life of a few days is sufficient for transoceanic transport [Seinfeld and Pandis, 1998], allowing for their interaction with the ocean. The ocean has been identified as the dominant sink for gas-phase anthropogenic organic volatile contaminants [Dachs et al., 2002; Jurado et al., 2005], and biogenic organic compounds from land vegetation could also contribute to this sink as reported for specific compounds [Jacob et al., 2005].

[15] Since gross fluxes are significantly higher than net fluxes, relatively small changes in the former may trigger a change in the direction of the net air-sea fluxes and thus, some regions of the ocean may act as source and others as sink of organic C to the atmosphere. Such a dual sink-source role would support an internal redistribution of organic carbon within the ocean supplementing that mediated by water mass transport. Even for the NE Atlantic, our results show an important regional variability in net fluxes ranging from a net absorption flux of ~140 mmol m⁻² d⁻¹ to a net volatilization flux of 40 mmol m⁻² d⁻¹ across the region, considering the spring data set as an example. Extrapolating the average diffusive net organic carbon exchange (mean net FOC = 28 mmol C m⁻² d⁻¹) measured here during the two sampling cruises to the entire subtropical NE Atlantic with an aerial extent of 5.26 10⁶ km² yields an estimated input of 0.64 ± 0.3 Gt C yr⁻¹. This estimated diffusive net organic carbon exchange is similar to the estimated organic carbon deficit for this region of 0.5 Gt C yr⁻¹ derived from the metabolic imbalance of the planktonic community [Duarte et al., 2001]. This imbalance cannot be accounted for by internal transport via oceanic circulation or wet deposition alone [Hansen et al., 2004]. This finding is consistent with previous suggestions that atmospheric input of OC may help explain net heterotrophy (i.e., excess organic carbon respiration over autotrophic production) in the NE Atlantic [del Giorgio and Duarte, 2002; Duarte et al., 1999]. The specific role of atmospheric OC inputs on regional carbon budgets depends, however, on the fraction of labile and refractory exchangeable organic carbon, which remains untested. Labile components would fuel heterotrophic processes, thereby yielding CO₂, whereas refractory and hydrophobic compounds would eventually add to the downward OC flux at the ultimate sink areas.

[16] The exchange fluxes of volatile and semivolatile organic carbon between the atmosphere and the ocean reported here cannot be extrapolated to the global ocean, as these are likely to be particularly high for the subtropical NE Atlantic, due to proximate wind anthropogenic and
continental sources, marine regions with high primary productivity, and under strong and persistent wind speeds (about 10 m s\(^{-1}\)). A global estimate of OC air-sea exchanges can only be obtained once a cross-regional survey of fluxes, comparable to that available for CO\(_2\) fluxes [Takahashi et al., 2002], becomes available. However, exchange fluxes of total OC between the ocean and the atmosphere would remain of global significance even if the global-average flux would be an order of magnitude lower than that reported here for the NE Atlantic. Previous assessments of atmospheric deposition of organic C to the global oceans, considering wet deposition alone, arrived at an estimate of 0.1 Gt C yr\(^{-1}\) [Willey et al., 2000]. Yet, it is well known that diffusive volatilization and absorption fluxes for most organic compounds are up to 20 times higher than wet and dry aerosol deposition fluxes [Duce et al., 1991; Jurado et al., 2005]. Therefore, the global air-sea exchange flux of total organic carbon can be significantly higher than the modest flux reported due to wet deposition, which is already sizeable to the estimated oceanic CO\(_2\) uptake of about 2 Gt C yr\(^{-1}\) [IPCC, 2001; Takahashi et al., 2002].

Whereas these comparisons highlight the air-sea organic carbon exchange as major component of the global carbon cycle, the global direction of this flux, rendering the ocean a net source or sink of OC to the atmosphere, cannot be ascertained yet. The few previous attempts to estimate fluxes of total OC between the atmosphere and the ocean have been limited to assessments of wet and/or dry aerosol deposition [Willey et al., 2000; Durrieu de Madron et al., 2000; del Giorgio and Duarte, 2002], but neglected diffusive fluxes, which dominate the atmosphere-ocean exchange of individual organic compounds [Duce et al., 1991; Dachs et al., 2002; Jurado et al., 2005]. Here, we demonstrated an approach to estimate air-sea OC fluxes, and the significant of these in the Subtropical NE Atlantic. The evaluation of regional and global rates of air-sea organic carbon fluxes and elucidating the origin and fate of these materials must, therefore, receive urgent attention as an essential step to better understand the carbon budgets of the ocean and the atmosphere and test the suggested role of the atmosphere as a major vector for OC fluxes in the biosphere.

Acknowledgments. This research is part of the COCA, DEPO-CEC, and BADE-Spain projects, which were funded by the Spanish “Plan Nacional de I+D.” The BADE project is funded by the Dutch Science Foundation (NWO-ALW). S.d.V. and M.Ll.C. acknowledge PhD fellowships from “Generalitat de Catalunya” and Spanish Research Council (CSIC), respectively. We thank the crew of the R/V Hespérides and R/V Pelagia, the technical UTM personnel involved for professional assistance, J.C. Alonso, N. Cantero and R. Santiago for assistance in the laboratory. L. Méjanelle and R. Simó are acknowledged for helpful and insightful discussions.

References


Figure 1 of GRL 2005