Science of the Total Environment 609 (2017) 476–483

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

A 13-year study of dissolved organic carbon in rainwater of an agro-industrial region of São Paulo state (Brazil) heavily impacted by biomass burning

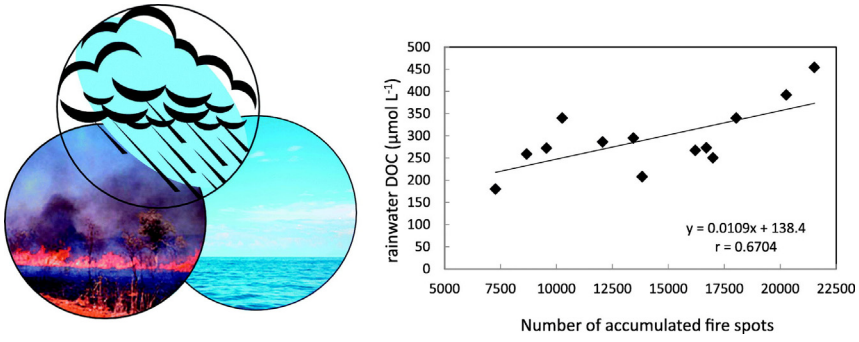
Daniely Godoy-Silva [a], Raquel F.P. Nogueira [a], M. Lucia A.M. Campos [b,*]

[a] Univ Estadual Paulista (UNESP), Departamento de Química Analítica, Instituto de Química, 14800-060 Araraquara, SP, Brazil
[b] Universidade de São Paulo (USP), Departamento de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, 14040-901 Ribeirão Preto, SP, Brazil

HIGHLIGHTS

- Biomass burning was the dominant source of DOC in rainwater.
- The wet deposition flux of DOC was 44% higher than the published world average.
- Volatile dissolved organic carbon comprised up to 53% of the DOC in rainwater.
- DOC in rainwater appeared to be mostly labile and rapidly bioavailable.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 April 2017
Received in revised form 10 July 2017
Accepted 16 July 2017
Available online xxxx

Editor: D. Barcelo

Keywords:
Biofuel
Vegetation fire
DOC bioavailability
Wet deposition
Carbon flux

ABSTRACT

This work presents the first comprehensive study of DOC in rainwater in a tropical agro-industrial region in central São Paulo State. The DOC concentrations ranged from 15 to 4992 µmol C L^{-1}, with an overall volume weighted mean (VWM) of 288 ± 17 µmol C L^{-1} (n = 881). The number of fire spots accumulated within each year of this study was positively correlated to the VWM concentration of DOC in rainwater. During the whole study period, higher VWM DOC concentrations were found during the dry months, despite the phasing out of agricultural fires in sugar cane plantations. The evidence suggested that inputs of atmospheric soluble organic carbon from biomass burning exceeded those from vehicular fuel combustion and biogenic sources. In most cases, dilution of DOC according to precipitation volume was minimal, showing that in-cloud processes were dominant for this species. In contrast, most of the volatile dissolved organic carbon (VDOC) appeared to be removed from the atmosphere in the first milliliter or so of rain, showing a dominance of below-cloud scavenging. VDOC contributed a significant fraction of the DOC for 62% of the samples analyzed, ranging from 5.1 to 488 µmol C L^{-1} (n = 552). The average wet deposition flux of DOC was 49 kg C ha^{-1} yr^{-1}, with VDOC accounting for 10% of the total. This dissolved carbon flux is higher than the estimated world average (34 kg C ha^{-1} yr^{-1}). The DOC in the rainwater was mostly labile (75% on average) and rapidly bioavailable (within days to weeks), in contrast to refractory dissolved carbon found in rainwater from regions where fossil fuel combustion is the dominant source. The findings of this work indicate that biomass burning can lead to important atmospheric inputs of readily available organic matter to land and to the open ocean.

* Corresponding author.
E-mail address: lcampos@ffclrp.usp.br (M.L.A.M. Campos).

http://dx.doi.org/10.1016/j.scitotenv.2017.07.145
0048-9697/

1. Introduction

The atmosphere is an important reservoir of carbon that plays a key role in global radiative forcing. Atmospheric organic carbon (OC) originates from multiple sources. On a global scale, biogenic emissions are the most significant source category, consisting mainly of volatile organic carbon (VOC) emitted by vegetation (dominated by isoprene and monoterpenes), together with particles such as pollen, fungal spores, and plant debris released into the atmosphere (Kanakidou et al., 2012).

Regionally, anthropogenic emissions of OC due to fossil fuel combustion can overwhelm natural sources, especially in highly urbanized regions (Wang et al., 2016). Biomass burning, as either a natural (10%) or intentional (90%) process, is an important source of atmospheric OC (including volatile species), especially in the tropics (Iavorivska et al., 2016). In such regions, fire is intensively used for deforestation, land clearance for temporary cultivations, and removal of dry vegetation to improve productivity. It has been estimated that globally, wildfires contribute to an amount of carbon equivalent to about 20% of the fossil fuel carbon emitted to the atmosphere, although the increasing demand for food, together with changes in the global climate, may increase the contribution of biomass burning in the near future (Keywood et al., 2013).

Since the early 1990s, emissions of gases and particles to the atmosphere due to biomass burning have been linked to ozone formation, changes in tropospheric chemistry, and impacts on climate (Crutzen and Andreae, 1990). In the past decades, numerous studies have shown that primary smoke particles and secondary organic aerosols affect the number of cloud condensation nuclei, cloud droplet size, and precipitation (Kanakidou et al., 2012, and references therein). Clouds are important in controlling the Earth's heat balance, so large-scale changes in their properties are likely to strongly affect the climate. Secondary particles can be formed by condensation of VOC molecules that contain multiple functional groups. The primary VOC compounds emitted can also be oxidized during photochemical processes in the atmosphere, forming less volatile species that are subsequently transformed into solid-phase particles (Hallquist et al., 2009).

Kanakidou et al. (2012), using a tridimensional global model, estimated that annually 1108 Tg C (values reported in the literature range from 427 to 1371 Tg C yr^{-1}) are transferred to the atmosphere as gaseous and particulate OC. Approximately 90% of this carbon is in the form of VOC and 10% is in the particulate organic form. Atmospheric OC species are removed from this compartment by means of wet precipitation (60%) and dry deposition (40%). Of the total amount of OC emitted, 489 Tg C yr^{-1} are deposited back onto the Earth's surface as soluble OC (dissolved organic carbon – DOC), leading to a deposition of about 50% onto land and 50% into the ocean. The remaining OC emitted is transformed in the atmosphere into secondary organic products, carbon monoxide, and ultimately carbon dioxide.

In an earlier study, Raymond (2005) suggested that the net transfer of continental OC to the ocean could be close to zero, considering the exchange fluxes between the two ecosystems. However, this calculation could underestimate the terrestrial transfer of organic carbon, because it assumed an average concentration of dissolved organic carbon (DOC) in continental rainwater of 90 μmol C L^{-1}, which is well below the global continental average of 239 μmol C L^{-1}, estimated by Iavorivska et al. (2016).

The concentration of DOC in rainwater can be highly variable, both spatially and temporally, and biomass burning emissions are especially associated with the southern hemisphere, where the paucity of data on rainwater DOC is notorious. Several studies have noted that global estimates of the transfer of atmospheric organic carbon to the Earth's surface have large uncertainties, due to a lack of knowledge concerning DOC in precipitation (Iavorivska et al., 2016, and references therein). Terrestrial inputs of bioavailable organic carbon to fuel oceanic primary productivity are a subject of increasing interest (Hansell et al., 2004). However, in order to improve understanding of the role of wet deposition of DOC to terrestrial and marine ecosystems, it is essential to investigate the sources, concentrations, and reactivity of the organic matter present in rainwater, especially in the southern hemisphere.

This study was conducted in an agro-industrial region of São Paulo State (Brazil), where sugar cane plantation and processing is the main economic activity. Brazil is the world leader in sugar cane production, and about half of the total is used to produce ethanol fuel (UNICA, 2016; FAO, 2017). Vehicular ethanol fuel has been produced in Brazil since the 1970s and is used either directly or as a gasoline additive (23–28%, v/v; Anderson, 2009). Since 2013, approximately 88% of all light duty vehicles in Brazil have been produced with dual-fuel technology, enabling the use of any proportion of gasoline and ethanol. The high internal and external demand for ethanol fuel has resulted in a doubling of the area planted with sugar cane in Brazil in the past 10 years or so, reaching over 10 million ha in 2016 (IBGE, 2016).

Prior to 2006, sugar cane harvesting was performed exclusively using manual labor, requiring burning of the plant foliage before cutting in order to protect workers from injuries and increase productivity. Subsequently, a mechanized process, which does not require the use of fire, has progressively substituted manual harvesting, reaching about 91% of the planted area in São Paulo State in 2016 (SMA, 2016). It is important to point out that the law that imposes phasing-out of manual harvesting only applies to São Paulo State, which accounts for around 50% of the country's sugar cane production. Remote sensing data show that fire in rural regions of Brazil and in the savanna biome is still very common, either for expansion of agriculture and pasture, or for removal of waste and renewal of agricultural areas (INPE, 2017).

In the past decade, the study region has experienced a major shift in agricultural practices, while at the same time there has been important regional economic growth, resulting in increases in the number of inhabitants and the size of the vehicle fleet. The temporally-resolved assessment of DOC in rainwater can provide important information about the sources of carbon emissions to the atmosphere, as well as possible shifts over time.

The aims of this work were to identify the main regional sources of organic carbon emissions, calculate the wet deposition fluxes of dissolved organic carbon, and evaluate its bioavailability. This is the first long-term assessment of DOC and volatile dissolved organic carbon (VDOC) in rainwater from a Brazilian region where fire is a common practice in agricultural management. The use of fire in farming is part of the culture of several countries of Latin America and Africa, so the data provided here can serve as a basis for improving regional and global carbon cycle models. Keywood et al. (2013) drew attention to the fact that extreme weather events associated with a warming climate are likely to increase wildfires (such as those seen in the western United States, Australia, and Portugal), so it is imperative to improve understanding of the impacts of biomass burning on global atmospheric chemistry.

2. Experimental

2.1. Collection sites and meteorological information

The rainwater sampling sites were located on the UNESP and USP campuses in the municipalities of Araraquara (AQA) (21°47′37″S, 48°10′52″W) and Ribeirão Preto (RP) (21°10′42″S, 47°48′24″W), respectively. Both sites were around 1 km distant from extensive sugar cane plantations (Fig. 1).

AQA and RP were chosen for this study because they are both located within the sugar cane belt of the State and their main economic activities are based on sugar cane plantation and processing. Although they have different populations, which could influence organic carbon emissions (AQA has 228,000 inhabitants and RP has 674,000; IBGE, 2016), as this time series evolved, it became clear there were no significant differences between the rainwater DOC concentration ranges or averages for the two sites. Nevertheless, sample collections were maintained at both sites in order to obtain a larger data set and enable a more