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Atmospheric deposition of organic carbon via precipitation

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HIGHLIGHTS

- Atmospheric deposition is the major pathway for removal of organic carbon from the atmosphere.
- Our synthesis from 83 contemporary studies shows the magnitude and regional variability of organic carbon in precipitation.
- This dataset (shared as a supplement) provides a benchmark of current conditions toward exploring past and future changes.
- The information will be useful for carbon budgets, environmental modeling, and ecosystem studies.

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ABSTRACT

Atmospheric deposition is the major pathway for removal of organic carbon (OC) from the atmosphere, affecting both atmospheric and landscape processes. Transfers of OC from the atmosphere to land occur as wet deposition (via precipitation) and as dry deposition (via surface settling of particles and gases). Despite current understanding of the significance of organic carbon inputs with precipitation to carbon budgets, transfers of organic matter between the atmosphere and land are not explicitly included in most carbon cycle models due to limited data, highlighting the need for further information. Studies regarding the abundance of OC in precipitation are relatively sparse, in part due to the fact that concentrations of organics in precipitation and their associated rates of atmospheric deposition are not routinely measured as a part of major deposition monitoring networks. Here, we provide a new data synthesis from 83 contemporary studies published in the peer reviewed literature where organic matter in precipitation was measured around the world. We compiled data regarding the concentrations of organic carbon in precipitation and associated rates of atmospheric deposition of organic carbon. We calculated summary statistics in a common set of units, providing insights into the magnitude and regional variability of OC in precipitation. A land to ocean gradient is evident in OC concentrations, with marine sites generally showing lower values than continental sites. Our synthesis highlights gaps in the data and challenges for data intercomparison. There is a need to concentrate sampling efforts in areas where anthropogenic OC emissions are on the rise (Asia, South America), as well as in remote sites suggesting background conditions, especially in Southern Hemisphere. It is also important to acquire more data for marine rainwater at various distances from the coast in order to assess a magnitude of carbon transfer between the land and the ocean. Our integration of the recent published information on OC in precipitation provides a unique data set (shared here as supplemental information) and a regional perspective that will be useful in carbon budgets, environmental modeling, and ecosystem studies. This can be used for comparison with past conditions and as a baseline toward exploring future changes, since changes in emissions, land use, and climatic variability are reflected in the amount and quality of OC deposited to ecosystems.

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1. Introduction

Carbon in the atmosphere affects air quality and climate. The ultimate fate of atmospheric organic carbon is to be oxidized to inorganic forms of carbon dioxide and carbon monoxide (30% of global organic carbon emissions, Hallquist et al., 2009), or to be removed from the atmosphere and deposited to the landscape through deposition (Dachs et al., 2005; Goldstein and Galbally, 2007). Deposition is the major pathway for removal of organic carbon (OC) from the atmosphere, affecting both atmospheric and

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landscape processes. Transfers of OC from the atmosphere to land occur as wet deposition (via precipitation) and as dry deposition (via surface settling of particles and gases).

Compared to a large body of research on atmospheric deposition of acidic compounds and persistent organic pollutants, studies regarding the abundance of OC in precipitation are relatively sparse. One reason is that concentrations of organics in precipitation and their associated rates of atmospheric deposition are not routinely measured as a part of major deposition monitoring networks such as those in the USA (National Atmospheric Deposition Program), in Canada (Canadian Air and Precipitation Monitoring Network), or the European Union (European Monitoring and Evaluation Program). Despite a lack of operational monitoring, considerable progress has been made in recent decades in research studies toward understanding the chemical nature of precipitation OC, and its seasonal patterns of variation. The magnitude of the global flux of OC was addressed by Willey et al. (2000) in a seminal work showing the significance of precipitation OC in the global carbon budget, which sparked interest from the scientific community to further explore the organic fraction of precipitation. Transfer of organics between the atmosphere and land are not explicitly included in global carbon cycle models due to limited data (Jurado et al., 2008), highlighting the need for further information.

Our objective was to synthesize recent information on measurements of OC in precipitation, providing insights regarding inputs of organics from the atmosphere to the landscape. We developed a new data set on wet atmospheric deposition of organic matter and/or the associated precipitation concentrations of organic carbon published in peer reviewed literature over the last three decades. This allows us to consider questions of how much OC is there in precipitation; and how does it vary regionally? Our synthesis updates previous work by Mazurek and Simoneit (1986) who reviewed studies published through 1985 regarding organic chemistry and abundance of organic carbon in precipitation. Concerns they expressed two decades ago about the comparability of earlier datasets and the lack of established sampling and analytical techniques are still true today. With perturbations of the carbon cycle now widely recognized, the need for synthesis of existing datasets is great. Our integration of the recent published information on OC in precipitation provides a unique data set (shared here as supplemental information) and a regional perspective that will be useful in carbon budgets, environmental modeling, and ecosystem studies. This synthesis highlights gaps in data availability and challenges for data intercomparison.

Various terms are used to describe different pools within the organic matter (OM) continuum depending on the chemical or physical properties of interest. Unlike inorganic constituents that consist of single compounds, OM is a blend of multiple organic compounds. OM refers to all organic compounds in a sample; where the carbon provides a structural backbone (about 50%) being bonded with other elements such as hydrogen, nitrogen, oxygen, phosphorous, and sulfur (Thurman, 1985). The magnitude of OM is generally quantified through measurements of the organic carbon (OC) concentration (mass per unit volume). Organic compounds that are water-soluble and pass through a filter are referred to as dissolved organic matter (DOM) or dissolved organic carbon (DOC), while compounds that are insoluble are referred to as particulate organic matter (POM) or particulate organic carbon (POC). Bulk, total organic carbon (TOC = DOC + POC) refers to measurements of the total pool of organic carbon. OC is ubiquitous in the atmosphere and is present as particulate airborne aerosols and as gaseous volatile organic compounds (VOCs).

There are numerous inorganic and organic compounds present in atmospheric water that affect atmospheric deposition of OC (Fig. 1). Primary sources of OC are directly emitted into the atmosphere in the form of both gases and particles. They are further divided into biogenic (emitted by natural systems) and anthropogenic (emitted by human activities). Biogenic primary sources are related to emissions of volatile organic compounds from vegetation, wind-lifted biological particles (pollen, plant debris, soil, dust, bacteria, and viruses), forest fires, emissions from marine environments (degassing from ocean and bursting of ocean bubbles enriched in organic material from plankton activity), volcanoes, etc. Anthropogenic primary sources include: combustion and production of fossil and ethanol fuels (motor vehicle exhaust, electric generation units), biomass burning, domestic heating and cooking, tire and asphalt wear, solvent use, emissions from agriculture (such as pesticides), and natural gas exploration. Globally, primary sources are mostly biogenic in origin (80%) and are dominated by isoprene and monoterpene emissions from vegetation (de Gouw and Jimenez, 2009; Donahue et al., 2009). The distinction biogenic and anthropogenic categories is not always clear. Emissions from burning of different biomass types have similar physicochemical properties and are usually lumped into a separate third category, which includes emission sources that can have both natural (forest fires, savannah bushfires) and man-made origin (burning of sugar cane plantations, burning coal and wood for domestic heating and cooking), and are hard to estimate separately.

Primary emission sources display marked zonal and seasonal variability. Biogenic and biomass burning emissions mostly originate in the tropics, while anthropogenic emissions occur in the northern latitudes, where they can reach 50% of total OC emissions, especially in the winter when vegetation emissions are low (Tsigaridis and Kanakidou, 2003). Over the ocean in southern latitudes marine sources can be up to 100% of all OC emissions (de Gouw and Jimenez, 2009). Oceanic sources can be almost the same magnitude as fossil fuel sources (Spracklen et al., 2008) and are equally important in storms with marine origin and in remote places. Despite the global prevalence of biogenic emissions, significant correlations of rainwater OC with pollutants and substantial contributions of fossil-derived carbon in the rain at some sites underscores the important role of anthropogenic emissions in formation of precipitation OC.

At least a half of global primary emissions of OC are chemically transformed in the atmosphere to form secondary organic aerosols (Hallquist et al., 2009; Kanakidou et al., 2005). Organic aerosols have been extensively studied in recent decades. Volatile organic precursor gases partition into aerosol particles by participating in chemical reactions that happen both in air and in aqueous phase of clouds, fog, and rain droplets (Ervens et al., 2011). The chemical reactions are mediated by oxidants and/or solar irradiation, and generally follow either of two pathways (Rudich et al., 2007 and references therein): 1) generation of secondary organic compounds with higher molecular weight and decreased water solubility through oligomerization reactions; or 2) degradation of large molecules via oxidation reactions. The second pathway generates compounds with lower molecular weight, making organics more water-soluble and less volatile by increasing oxidation state (Fuzzi et al., 2006 and references therein). Such chemical transformations facilitate their incorporation into cloud droplets as cloud condensation nuclei and removal through precipitation (Hallquist et al., 2009; Jimenez et al., 2009; Pöschl, 2005). Numerous studies highlight that some organic species found in the atmosphere are surface active and may serve as cloud condensation nuclei (Decesari et al., 2005; Novakov and Penner, 1993; Orlović-Leko et al., 2011, 2009). The most efficient nuclei are comprised of humic-like substances such as polycarboxylic acids (Facchini et al., 2000), which have been observed in rainwater in many studies. They influence the growth and nucleation of cloud water droplets by lowering their surface

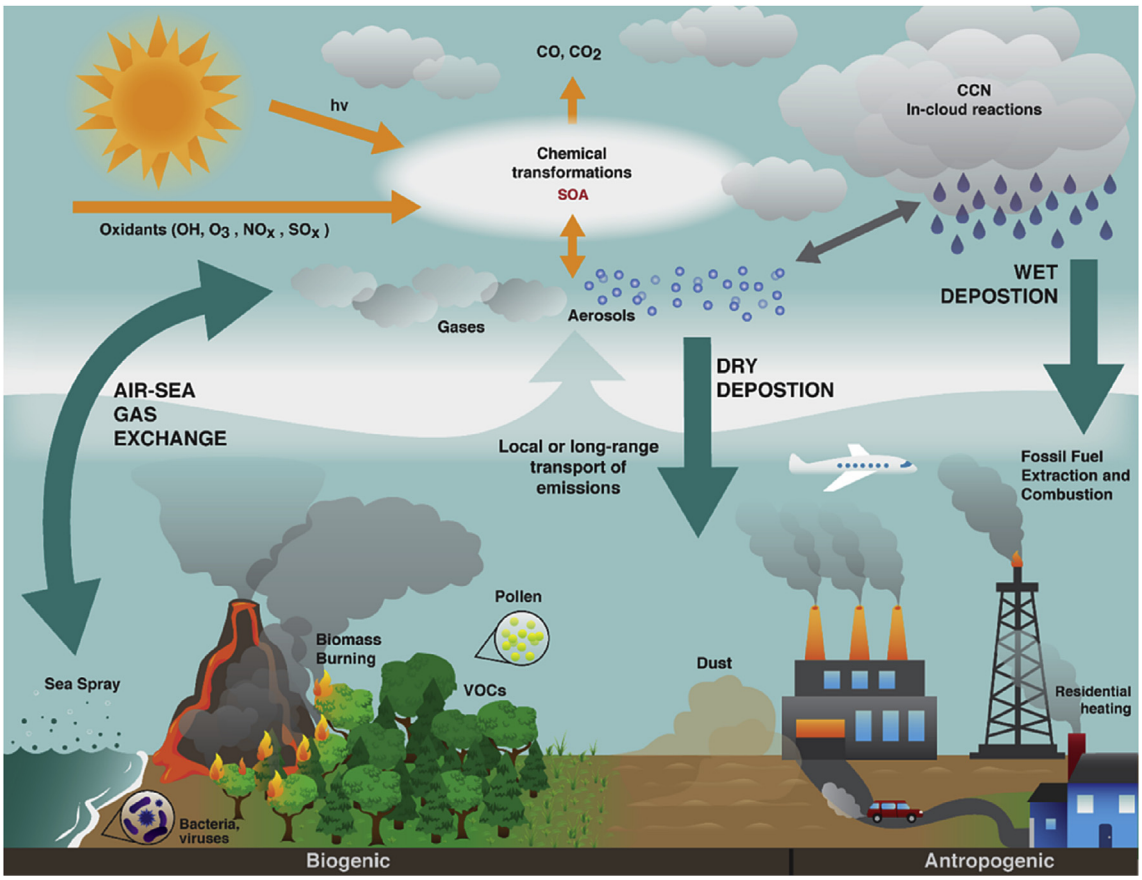

Fig. 1. Major sources and processes affecting the amount and quality of organic carbon found in wet deposition. SOA refers to secondary organic aerosols, CCN are cloud condensation nuclei, VOCs are volatile organic compounds, CO is carbon monoxide gas, and CO_2 is carbon dioxide gas.

tension and critical supersaturation levels (Shulman et al., 1996), and change the hygroscopicity of inorganic particles (Saxena et al., 1995).

Global scale models suggest that most atmospheric OC emissions are delivered back to the landscape through atmospheric deposition. Of the recently estimated ~1108 Tg C yr^{-1} (literature range 427–1371 Tg C yr^{-1}) of gaseous and particulate OC that are emitted annually around the world (Kanakidou et al., 2012), between 305 and 950 Tg C yr^{-1} of OC are deposited to the surface (Goldstein and Galbally, 2007; Hallquist et al., 2009; Jurado et al., 2008; Kanakidou et al., 2012). The majority of this OC flux is in the form of wet atmospheric deposition (60%) with the rest in dry deposition (40%); and the majority of the wet atmospheric deposition flux is water soluble DOC (over 90%) in precipitation (Kanakidou et al., 2012). Global estimates of wet atmospheric DOC deposition based on sampled precipitation data and a chemistry-transport model converge around 306–580 Tg C yr^{-1} (Kanakidou et al., 2012; Willey et al., 2000). While 90% of OC is emitted from terrestrial ecosystems, around 30–50% of OC is deposited into the oceans (Jurado et al., 2008; Kanakidou et al., 2012; Willey et al., 2000). Estimates suggest that there is a net, albeit small, transfer of terrestrial OC to the ocean, while most OC in rainwater deposited over the oceans is from recycled marine sources (Raymond, 2005). Wet deposition of OC to the global ocean surface (90–246 Tg C yr^{-1}) (Kanakidou et al., 2012; Willey et al., 2000) is about 10% of the net annual uptake of CO_2 by the ocean (2000 ± 1000 Tg C yr^{-1} in 2000) (Takahashi et al., 2009) and close to the amount of terrestrial POC exported by the rivers to the ocean (200 ± 135 Tg C yr^{-1}) (Galy et al., 2015). It has been demonstrated that wet deposition is also a sink for OC emitted to the atmosphere from incomplete combustion of fossil fuels. The fossil fuel combustion represents a human-induced disturbance to the carbon cycle (Ciais et al., 2013), by introducing additional old (relic) carbon that has been locked away for millennia into the present-day ecosystems. Specifically, between 4 and 52% of DOC in precipitation is relic carbon (Avery et al., 2006; Raymond, 2005; Wang et al., 2015). This results in wet deposition of DOC annually removing around 6–46 Tg C yr^{-1} of fossil OC (Avery et al., 2006; Yan and Kim, 2012), an estimate that is close to a range of annual primary OC emissions from fossil fuel (3.2–33.9 Tg C yr^{-1}) (Bond, 2004; Hallquist et al., 2009; Spracklen et al., 2011).

Organic species are removed from the atmosphere and delivered to terrestrial and aquatic landscapes via both wet atmospheric deposition (via precipitation) and dry atmospheric deposition (via settling of gases and particles). Wet atmospheric deposition, which includes liquid and solid forms of precipitation such as rain, snow, hail, and fog, is the main pathway of removing the organic carbon from the atmosphere (Kanakidou et al., 2005). In precipitation, most of the carbon is organic (76–96%) (Fahey et al., 2005; Pan et al., 2010); the inorganic part is comprised of the disassociated carbonic acid. Incorporation of OC into precipitation can go through one of two scavenging mechanisms: 1) included into aqueous phase of clouds (in-cloud scavenging, rainout); or 2) picked up by rain droplets or snow crystals below the cloud base on their way to the surface (below-cloud scavenging, washout). Different forms of wet deposition differ in their efficiency of scavenging solutes from the atmosphere. Some authors report that snow has significantly higher OC concentrations than rain (Pan et al., 2010; Sempere and

Kawamura, 1994) due to the larger surface area of snowflakes relative to rain drops. The same pattern was observed for cloud water, which on average had 2 to 3 times higher OC concentrations than rain (Gioda et al., 2008; Neal et al., 2001; Reynolds et al., 1996). In addition to differences in scavenging processes for deposition forms, the efficiency with which wet deposition removes constituents from the atmosphere also depends on their chemical characteristics, such as polarity and solubility (Duce et al., 1983; Kanakidou et al., 2005). These characteristics define the potential of organics to be included into cloud and rain droplets. For example, based on estimates of scavenging ratios Cerqueira et al. (2010) concluded that sulfate is removed more efficiently than POC, and POC is removed more efficiently than elemental carbon due to the differences in their solubility in water.

2. Methods

We scoured peer-reviewed literature published in the past three decades (since 1985); compiling information on measured concentrations of OC in precipitation and/or rates of atmospheric OC deposition. Important differences among studies make it challenging to compare the reported concentration and deposition values. Tracking this ancillary information was a goal of our data synthesis, and all such information are included in our data compilation (provided as supplemental information). The studies investigate a wide spectrum of wet deposition forms; including precipitation of snow (Grannas et al., 2004; Laniewski et al., 1999; Legrand et al., 2013; Lyons et al., 2007; Meyers and Hitls, 1982; Twickler et al., 1986), cloud water (Deguillaume et al., 2014; Fuzzi et al., 2002; Gelencser et al., 2003; Hadi et al., 1995; Hegg et al., 2002; Loflund et al., 2002; Marinoni et al., 2004; Reyes-Rodríguez et al., 2009), fog (Birdwell and Valsaraj, 2010; Collett et al., 2008; Herckes et al., 2013, 2007; Raja et al., 2009), and dew (Scheller, 2001). The majority of the published data on dissolved and particulate OC in precipitation is on rainwater, which is the focus of this synthesis. Studies also vary in terms of whether DOC, TOC, or both were quantified, and the spatial and temporal scales over which data were reported. Additionally, studies expressed DOC differently, given differences in the pore sizes of filters that were used to define the dissolved fraction, with pore sizes ranging from 0.2 to 1.0 μm. Many researchers use carbon-free and binder-free glass fiber filters where the smallest nominal pore size available is 0.7 μm (Cory et al., 2011). The standard classification of dissolved constituents is 0.45 μm, and numerous studies used membrane filters of this pore diameter. Recognizing that the filtrate can contain colloidal and fine particles in addition to soluble organic matter, some researchers use a smaller filter size of 0.2 μm to best represent non-colloidal DOC (Kaplan, 1994; Nebbioso and Piccolo, 2013). We include information on the types of filters used in each study in our summary data table (see Supplemental information).

There are differences among studies in terms of whether average concentrations were calculated as simple arithmetic average of the concentration data, or if the averages were adjusted (weighted) for precipitation volume. The non-linear, inverse relationship between OC concentration and precipitation volume generally causes a decrease in concentrations when precipitation volumes are large. This dilution effect is especially marked in regions with varying dry and wet climatic seasons, when the difference in rainwater OC levels can be many-fold (Andreae et al., 1990; Coelho et al., 2008; Germer et al., 2007a; Guo et al., 2005; Laclau et al., 2003; Williams et al., 1997; Zafiriou et al., 1985). To account for the influence of rain volume on concentration when comparing seasons and years, it is best to use volume-weighted average (VWA) concentrations (e.g., Mladenov et al., 2012). For calculations of summary statistics we used average concentrations reported by authors of the individual studies included in the data synthesis table regardless of their weighting; however the preference was given to VWA concentrations if both simple arithmetic average and volume-adjusted concentration values were available.

Further, there are considerable methodological differences among the studies published in recent decades in terms of how TOC and DOC were measured (Fig. 2). Methods to quantify bulk TOC (on an unfiltered sample) or DOC (on a filtered sample) are generally based on oxidation of organic matter to CO_2 gas. The amount of evolved gas is quantified by a detector and expressed as a concentration of organic carbon. Earlier studies (through mid-1980s) mostly used wet chemical or ultraviolet (UV) oxidation with spectrophotometric, colorimetric, gravimetric or infra-red (IR) detection of evolved CO_2; elemental analysis with automated analyzer; or high-temperature combustion (HTC) of dried samples (Mazurek and Simoneit, 1986). Development of new methods allowed performing analysis on liquid samples without the need to evaporate. More recent studies, which are featured in this review, report using wet chemical (mostly persulfate) or UV oxidation with IR detection and automated HTC. Efforts to evaluate the efficiency of these methods for determination of OC in seawater (Lee and Henrichs, 1993; Peltzer et al., 1996; Sharp et al., 1995, 2002; Sharp, 1997; Spyres et al., 2000; Wang et al., 2000; Wangersky, 1993; Watanabe et al., 2007), freshwater (Aiken et al., 2002; Benner and Hedges, 1993; Kaplan, 2000; Koprivnjak et al., 1995), and rainwater (Torres et al., 2014) are still ongoing and do not decisively show systematic differences among the methods. Currently HTC is the most widely used method and is considered a standard method for OC analysis of natural waters (Fig. 2). Depending on the HTC analytical approach OC can be measured as total organic carbon (TOC) or non-purgeable organic carbon (NPOC), such that TOC = NPOC + VOC (volatile organic compounds) and TOC = TC − IC (inorganic carbon, in the form of carbonate and bicarbonate) (Findlay et al., 2010). We include information on the analytical methods used in each study in our data compilation, provided as Supplemental Information.

We made minor modifications and/or conversions of the reported data in order to estimate average values (e.g. from ranges or multiple samples) and to present data in a uniform set of units. Concentrations are expressed in mg C L^{-1} (original units of μM were converted to mg C L^{-1} by multiplying by 0.012), and deposition fluxes are expressed as kg C ha^{-1} yr^{-1}. A list of decisions made on a case-by-case basis that were needed to facilitate the data intercomparison; the original values for concentration and deposition flux reported in the manuscripts; and the modified values used to calculate summary statistics are included in the Supplemental Information. For example, when both wet and total deposition values were reported for the same site, only wet deposition values were retained. When both DOC and TOC values were available, then only values for DOC were used. Overall, summary calculations were based on a combination of DOC and TOC reports: for concentration 66 DOC and 15 TOC values, for deposition flux 33 DOC and 7 TOC values. In some publications only ranges on concentrations or deposition were reported, in which case a median was calculated and used as an average for summary statistics. The same applied when only the means for two distinct precipitation seasons (wet and dry) were given; then a median between the seasonal means was used as a single average for that site. In case where DOC measurements for one sampling site were reported for multiple years in several publications, and the authors did not provide a multi-year average (Wilmington, NC, USA and Aveiro, Portugal), a simple average value between years was calculated to represent that site. The data for hurricanes was not included into summary statistics and is presented separately, since hurricanes represent extreme weather events and thus would bias the description of

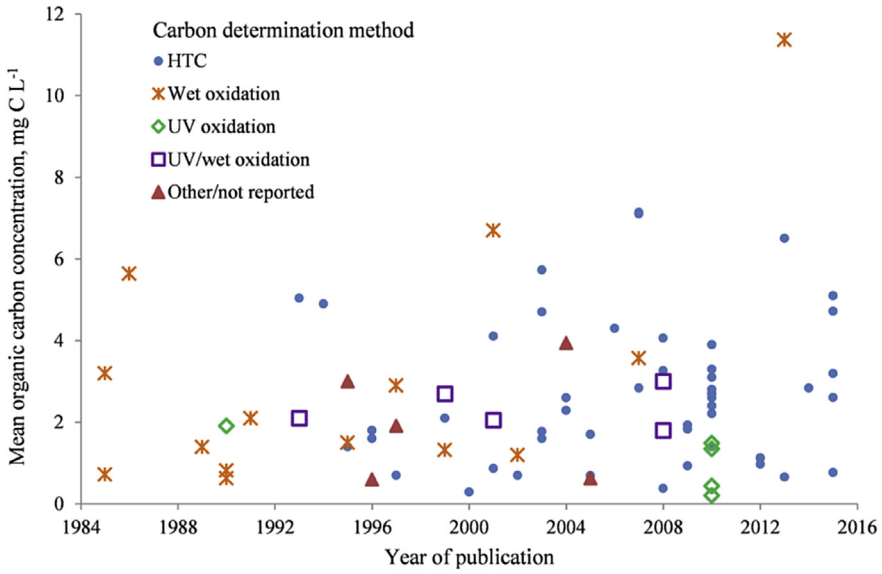

Fig. 2. The progression of analytical methods of organic carbon analysis in studies published between 1985 and 2015, and the measured mean concentrations.

"average" conditions.

3. Results

Our synthesis includes 83 studies of OC in precipitation (wet and total atmospheric deposition) that were published in the last 3 decades. We provide our data compilation (as Supplemental Information) with information on the reported concentrations of OC in precipitation (mass/volume) and rates of atmospheric OC deposition (mass/area/time). We include information on the geographic locations, sampling methods, and analytical methods used for each study.

We grouped the datasets by environment type (Table 1) where the samples were divided into continental (sampled inland), coastal/island (sampled within 100 km from the shore) and marine (sampled aboard a ship or on a remote offshore island). The data show great variability and are log-normally distributed; with overlapping ranges of concentration and deposition flux values, and standard deviations that are almost equal to average values. Comparing values of deposition flux by environmental types cannot be made since the marine type consists of only a single study, which was conducted at the Enewetak Atoll in the North Pacific Ocean (Zafiriou et al., 1985). There is a land to ocean gradient in concentrations: marine sites show significantly lower values than continental (Kruskal-Wallis test, $p < 0.01$), and continental and coastal/island sites are generally higher but not statistically different from one another. A similar gradient has been reported for a global compilation of datasets on rainwater organic nitrogen (Cornell, 2011; Cornell et al., 2003), as well as by a number of individual studies of rainwater OC that used back-trajectory analysis in various parts of the world. This may be due to the fact that most of the known emission sources are on the land. Oceanic sources are also considered important, but their strength and extent of influence yet has to be estimated.

Additionally, we grouped the OC data by the regions of the world (Table 2, Fig. 3). The highest concentrations are observed in Africa, South America, and Asia. Though the differences between groups are not statistically significant, and observations are sparse, this global pattern is consistent with reports of elevated emissions in those regions from various sources. High OC concentrations in African rainwater are potentially associated with strong emissions from biomass burning (Liousse et al., 2010; Roberts et al., 2009) or dust particles (Mladenov et al., 2011). In South America, high levels of OC in rainwater may be due to biomass/biofuel burning (Campos et al., 2007; Coelho et al., 2011), and in Asia OC is associated with fossil fuels combustion (Pan et al., 2010; Yan and Kim, 2012).

Table 1
Summary statistics for concentrations and deposition flux of organic carbon (TOC and DOC) in rainwater grouped by the types of environment.

Rainwater concentration of OC			
Environment type	Mean ± SD, mg C L^{-1}	Median, mg C L^{-1}	No. of sites
Continental	2.87 ± 1.9	2.65	54
Coastal/Island	2.48 ± 2.1	1.87	22
Marine	0.92 ± 0.7	0.72	5
All data	2.64 ± 1.9	2.21	81
Inter-quartile range, all data	1.33–3.28		
Rainwater deposition flux of OC			
Environment type	Mean ± SD, kg C ha^{-1} yr^{-1}	Median, kg C ha^{-1} yr^{-1}	No. of sites
Continental	35 ± 34	20	28
Coastal/Island	32 ± 32	21	11
Marine	6	–	1
All data	33 ± 33	20	40
Inter-quartile range, all data	15–44		

Table 2
Mean organic carbon concentrations in rainwater grouped by world regions, from studies of DOC and TOC published between 1985 and 2015.

Region	OC concentration		OC deposition flux	
	Mean ± SD, mg C L^{-1}	No. of sites	Mean ± SD, kg C ha^{-1} yr^{-1}	No. of sites
Africa	5.01 ± 1.0	2	101	1
Asia	2.65 ± 0.9	19	19 ± 4	11
Atlantic	0.99 ± 1.1	2	–	–
Australia/New Zealand	1.05 ± 0.5	2	35	1
Central America	2.90 ± 2.5	7	65 ± 61	5
Europe	2.60 ± 2.4	22	18 ± 13	8
North America	2.63 ± 2.1	14	21 ± 19	7
Pacific	1.16 ± 0.6	2	6	1
South America	2.98 ± 1.8	11	62 ± 31	6
All data	2.64 ± 1.9	81	34 ± 33	40

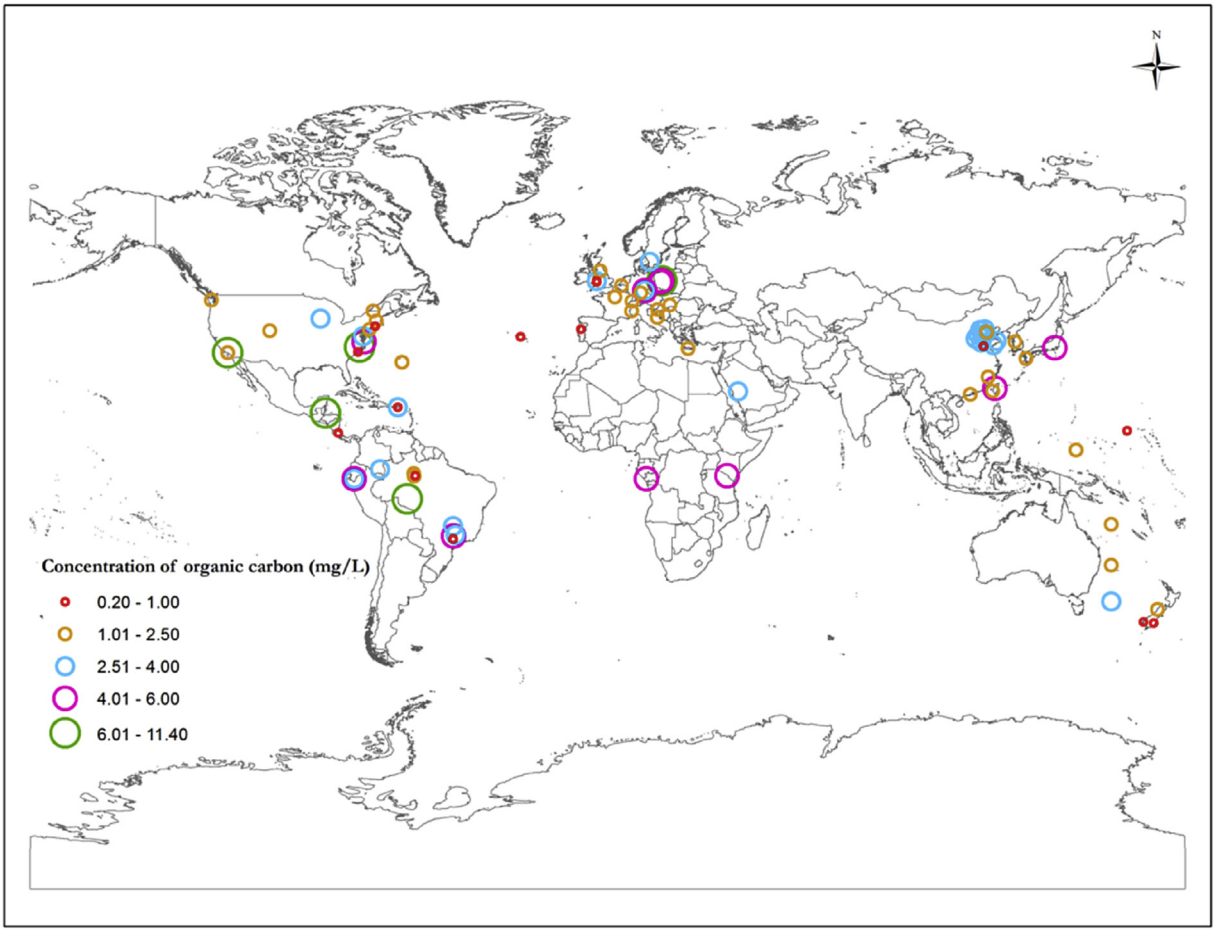

Fig. 3. Mean concentrations of organic carbon in rainwater around the world from studies of DOC and TOC published between 1985 and 2015.

Global estimates of organic carbon concentration and wet deposition flux based on the datasets available at the time of this review (Table 1) yielded a mean concentration of 2.64 ± 1.9 mg C L^{-1}, and a deposition flux of 34 ± 33 kg C ha^{-1} yr^{-1}. These flux estimates are of similar magnitude to a global flux estimate of 29 kg C ha^{-1} yr^{-1}, while the concentrations are higher than DOC concentrations for global marine (0.28 mg C L^{-1}) and continental (1.99 mg C L^{-1}) rainwater provided by Willey et al. (2000) more than a decade ago.

4. Discussion

Organic matter is ubiquitous in precipitation in samples collected around the world, highlighting that atmospheric deposition is an important pathway providing inputs of OC to terrestrial and aquatic ecosystems of the landscape. We were able to find 83 contemporary studies reporting OC concentrations in precipitation and/or associated rates of wet atmospheric OC deposition, measured at sites around the world. The available data are highly scattered in space and time (Figs. 2 and 3). Continents in the Northern Hemisphere have noticeably more data points than in the Southern Hemisphere. The number of studies in Asia and South

America has increased in recent years, while Africa and Australia/New Zealand remain poorly represented on the global map. There is a need to concentrate sampling efforts in areas where anthropogenic organic carbon emissions are on the rise, as well as in background remote sites. It is especially important to acquire more data for marine rainwater at various distances from the coast in order to assess a magnitude of carbon transfer between the land and the ocean, since the direction of this flux is currently unclear (Dachs et al., 2005; Raymond, 2005). The sparseness of measurements of OC in precipitation and associated rates of wet atmospheric OC deposition hinders understanding of inputs of OC to watersheds for ecosystem studies, and hinders the refinement of atmospheric carbon transport models.

Including OC measurements into precipitation analyses made at atmospheric deposition monitoring networks would help to address these gaps, and would provide a platform for acquiring long-term data in order to evaluate the impact of changes in emissions of OC on atmospheric, terrestrial, and aquatic ecosystems. One of the factors that complicates integration of OC measurements into existing monitoring networks is ensuring that the samples remain unchanged during sampling. It has been shown that rainwater organic carbon is prone to biodegradation by microbial activity (Avery et al., 2003; Keene and Galloway, 1984; Mitra et al., 2013) because it contains a large amount of labile compounds such as carboxylic organic acids, which can comprise up to 40% of DOC (Andreae et al., 1990; Kieber et al., 2002a; Willey et al., 2000). And since most of the networks use longer sampling frequency (weekly vs daily or event), measures should be taken to slow the microbial digestion of rainwater organics during collection. One of the methods that can used is to add biocides (for example, mercuric chloride, thymol, concentrated hydrochloric acid, chloroform) to sampling containers (Gillett and Ayers, 1991; Kawamura et al., 2001; Matsumoto and Hanya, 1980; Neumann et al., 1959; Sakugawa et al., 1993).

Though in any individual study TOC concentrations are necessarily higher than DOC concentrations in precipitation (where TOC − POC = DOC), there was no significant difference between concentrations of DOC and TOC in this dataset when considered at large spatial scales (e.g., by continent or world region). This is attributed to the fact that DOC (the dissolved form) makes up between 65% and 99% of TOC depending on location, emission sources, and prevalent meteorological conditions (Cerqueira et al., 2010; Economou and Mihalopoulos, 2002; Gioda et al., 2008; Likens et al., 1983; Sempere and Kawamura, 1994; Willey et al., 2000). The contribution of the particulate fraction varies between sampling locations. Some studies find no substantial differences between DOC and TOC concentrations (Raymond, 2005; Willey et al., 2000 in Wilmington, NC, USA), while others measure high levels of POC, and suggest that for their location filtration was necessary for reporting concentrations as DOC (Pan et al., 2010; Willey et al., 2000 in New Zealand).

A lack of difference between dissolved and total deposition fractions in this dataset suggests a relatively minor contribution of dry atmospheric OC deposition at the sampling sites compared to the dominance of wet atmospheric OC deposition. This may reflect a systematic bias in the siting of the precipitation sampling locations, since they are found mostly in areas with ample rainfall (i.e. an average annual precipitation amount in this dataset is 1433 ± 990 mm). Ground-based measurements of dry atmospheric OC deposition are scarce, but some papers suggest that it can be as much as wet deposition in arid regions (i.e. Lohse et al., 2008); and global estimates based on satellite data (Jurado et al., 2008) indicate its appreciable proportion in the carbon cycle.

Data for hurricanes were not included in summary statistics, since hurricanes represent extreme weather events with usually much lower OC concentrations and thus would bias the description of "average" conditions. Several publications pointed to the importance of hurricanes and tropical storms as large weather systems capable of delivering significant amount of marine organic carbon with precipitation (Avery et al., 2004; Miller et al., 2008; Mitra et al., 2013; Mullaugh et al., 2013; Willey et al., 2000). The data from the seven hurricanes reported in the studies reviewed give a mean OC concentration of 0.82 ± 0.7 mg C L^{-1} (median 0.94 mg C L^{-1}), which is comparable to levels found in marine rain. If the hurricane data are included in the global summary statistics, then it brings the average OC concentration for the whole dataset to 2.49 ± 1.9 mg C L^{-1} (median 2.1 mg C L^{-1}), and the Marine environment type to 0.86 ± 0.7 mg C L^{-1} (median 0.83 mg C L^{-1}).

Only a few studies included observations of long term data allowing consideration of trends. Two detailed studies from Wilmington (North Carolina, USA) (Willey et al., 2011, 2006) examined long-term changes in rainwater chemistry. Rainwater DOC showed a 50% decrease over a 20 year period (between 1988 and 2003), carboxylic organic acids also decreased in concentration by half. The authors suggest that there may be several explanations to such patterns. The primary reason for a downward trend in DOC concentrations was a decrease in emissions of VOCs. This could be due to the introduction of new policies for control of vehicular VOCs emissions in 1996 in the USA, and also local deforestation. The decrease in DOC rainwater concentrations could also be caused by the changing redox chemistry of rainwater, for example a two-fold increase in hydrogen peroxide, which is a main reductant of organic molecules in the atmosphere (Willey et al., 2012). Another study from Wales, UK (Neal et al., 2005) reported an overall slightly increasing trend in rainwater DOC from 1983 to 2003. However, the trend was mainly due to increase in the first half of the record while later years showed a decline in rainwater DOC, and the authors attribute this temporal pattern to a long amplitude cyclical trend.

Methods of sampling and chemical analysis for OC in rainwater were highly variable among the studies published in the past three decades; stemming from differences in research questions, traditions of various research communities, and equipment availability. To best ensure seamless integration of future datasets into global and regional compilations, standardized assessment protocols or best practices for determination of organic constituents in atmospheric waters should be developed. Though the HTC analytical methods of OC determination has become widely used in recent decades (Fig. 2), an overall comparison of OC concentrations in wet and total deposition from the studies included in this review did not show a statistically significant difference between these and earlier methods (Kruskal-Wallis test, $p > 0.1$).

Current research benefits greatly from recent advances in analytical methods, which are now capable of identifying specific organic compounds, and their physical properties. This brings the scientific community closer to addressing key research questions about atmospheric OC regarding its chemical composition. The multitude of emission sources and subsequent transformations in the atmosphere lead to an extreme chemical complexity of rainwater OC. Combining quality and quantity measurements of rainwater OC can help address the main gaps in current knowledge: identify multiple precursor sources of OC in the atmosphere, and its post-deposition fate and ecological relevance. Individual organic compounds in precipitation are measured because of their functions in atmospheric chemistry, their toxicity, or biological availability. Due to current constraints in analytical capabilities, and the large heterogeneous pool of organic matter, measurable identifiable classes of organic compounds do not add up to the total mass of organic carbon in precipitation. Quantifying the thousands of unidentified organic compounds present in low abundance still exceeds current analytical capabilities; and measurements of DOC,

POC, and TOC remain the best indicators of the total mass of carbon comprising the organic matter in water samples (Cory et al., 2011).

Our contemporary dataset provides insights into the magnitude and regional variability of OC in precipitation. This can be used for comparison with past conditions (Mazurek and Simoneit, 1986). Further, the data can be used as a baseline toward exploring future changes in the volume and composition of precipitation; where changes in emissions, land use, and climatic variability will be reflected in the amount and quality of OC deposited to ecosystems.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2016.06.006.

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[1] References provided in this section are included in the data synthesis table provided as Supplemental information; and have data within them that were used for generating the summary statistics shown in Table 1, Table 2, Fig. 2, and Fig. 3.

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