Dissolved organic carbon in rainwater: Glassware decontamination and sample preservation and volatile organic carbon

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Abstract

The efficiency of different methods for the decontamination of glassware used for the analysis of dissolved organic carbon (DOC) was tested using reported procedures as well as new ones proposed in this work. A Fenton solution bath (1.0 mmol L\textsuperscript{-1} Fe\textsuperscript{2+} and 100 mmol L\textsuperscript{-1} H\textsubscript{2}O\textsubscript{2}) for 1 h or for 30 min employing UV irradiation showed to combine simplicity, low cost and high efficiency. Using the optimized cleaning procedure, the DOC for stored UV-irradiated ultra-pure water reached concentrations below the limit of detection (0.19 \textmu mol C L\textsuperscript{-1}). Filtered (0.7 \textmu m) rain samples maintained the DOC integrity for at least 7 days when stored at 4 °C. The volatile organic carbon (VOC) fraction in the rain samples collected at two sites in São Paulo state (Brazil) ranged from 0% to 56% of their total DOC content. Although these high-VOC concentrations may be derived from the large use of ethanol fuel in Brazil, our results showed that when using the high-temperature catalytic oxidation technique, it is essential to measure DOC rather than non-purgeable organic carbon to estimate organic carbon, since rainwater composition can be quite variable, both geographically and temporally.

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1. Introduction

The removal process of the atmospheric dissolved organic carbon (DOC) by rain prior to its oxidation to carbon dioxide is of great importance when evaluating the global carbon biogeochemical cycle. It has been estimated that the organic carbon fraction may account for 80% of the global flux of rainwater carbon (Willey et al., 2000) and it can be of greater bioavailability to the oceanic biota than that derived from river water (Avery et al., 2003).

In urban areas, vehicular emissions are an important source of carbon input to the atmosphere, which include volatile organic carbon (VOC) species carcinogenic to humans, as well as...
precursors for the formation of photo-oxidants (Vasconcellos et al., 2005; Guo et al., 2007). Different types of vehicular fuels may dominate the species of VOC found in the urban atmosphere (Colón et al., 2001), and therefore rain water DOC measurements should account for such water soluble volatile compounds. DOC concentrations in rainwater from urban areas or from places impacted with biomass burning can reach relatively high values (Willey et al., 2006; Williams et al., 1997; Lara et al., 2001), while in remote areas they can be as low as 10 μmol C L⁻¹ (Kieber et al., 2002). In deep seawater, DOC concentrations are about 30–40 μmol C L⁻¹ (Aminot and Kerouel, 2004). These low concentrations of organic carbon in natural waters enhance the importance of analytical accuracy and the care needed to avoid contamination through all the sampling and analytical steps. The samples’ contact with the atmosphere, the sampling bottles, and the careless handling during collection and analysis are a few examples of potential contamination for DOC in natural waters (Spyres et al., 2000). Sharp et al. (2002) reported an international effort to elaborate an intercalibration exercise to produce a certified reference material to assure the accuracy of the data for DOC in seawater samples in order to overcome the uncertainties towards the analytical methods used in the early to mid-1990s (Sharp, 1997).

As discussed by Thomas et al. (1995), problems in the analytical method, and more particularly blank problems, may explain most of the differences in DOC concentrations measured in seawater by various groups using high-temperature catalytic oxidation. The importance of better understanding the global carbon cycle demands an analytical effort to assure that the reported data represent the actual state in the study area.

This work aims to identify a simple and efficient method to decontaminate glassware used for DOC analysis, reports a rainwater storage study, and shows the importance of accounting for volatile organic compounds when choosing the analytical method to measure organic carbon species in rainwater.

2. Materials and methods

2.1. Sites description, sampling and sample treatment

The rain samples were collected in two Brazilian cities, Ribeirão Preto (RP; 21°10’42”S and 47°48’24”W) and Araraquara (A; 21°47’37”S and 48°10’52”W), located in São Paulo state, being 80 km apart, at approximately 313 km from the state capital (São Paulo City) and 350 km from the Atlantic coast. Ribeirão Preto has a population of 550,000, and Araraquara 196,000. The region is eminently agricultural, where sugar cane production and processing is dominant. Rainwater samples were collected based on events using a wet-only home-made automatic collector, placed at a height of 1.5 m at the “Universidade de São Paulo”, campus Ribeirão Preto, located in a very low-traffic suburban area. The rain sampler at the “Universidade Estadual Paulista”, campus Araraquara, was a wet only automatic precipitation sampler UNS 130/E—Eigenbrodt placed on a building roof at a height of ca. 15 m. The polyethylene funnel from the automatic collector was covered with aluminium foil, and the original drain and flasks were replaced by glass ones.

A glass funnel (23 cm diameter) was attached to an amber glass bottle by a moulded PTFE screw top, and the whole sampling system was replaced by a clean set after each rain event. For the large majority of the events (except for the night events), the samples were immediately collected, stored in a fridge (4°C) and filtered within a maximum of 24 h. The filtration was performed in a laminar flow hood following clean protocols during the whole procedure (Campos et al., 2002).

The filtration system consisted of a glass syringe, a stainless steel filtration unit (25 mm diameter; Millipore), and a 0.7-μm pore size glass fibre membrane (GF/F; Millipore-AP40) previously baked in a muffle furnace at 550°C for 5 h. The membrane filters were rinsed with ca. 20 mL of ultra-pure water (Milli-Q Simplicity system, Millipore) before use to remove possible contaminants. When the rain volume allowed, the first sample aliquot (5–20 mL) was used to rinse the membrane and subsequently the pre-cleaned amber storing flask.

2.2. Glassware contamination

To evaluate the efficiency of different procedures to eliminate DOC residues from glassware, a set of borosilicate beakers (25 mL) were contaminated with a 0.01 mol L⁻¹ citric acid solution (a model of organic carbon compound; Tue-Ngeun et al., 2005) prior to treatment. The contamination was performed by completely filling the beakers with the
citric acid solution, disposing of the solution after 24 h, and then letting the vessels to dry upside down on an aluminium foil. Typically, sets of three beakers were submitted to a specific cleaning procedure, after which, each of them was filled up to the top with ultra-pure water. The beakers were then capped with PVC film, stored in closed plastic containers and let to rest at room temperature for at least 24 h before measuring the residual DOC in the water. When the cleaning procedure consisted of submersing the beakers in a cleaning solution, the flasks were retrieved from the solution and immediately filled up with ultra-pure water, capped and let to rest as described above.

2.3. Methods and instrumental blank

Organic carbon was determined by high-temperature catalytic oxidation using a Shimadzu TOC 5000A total organic carbon analyzer. The standards for organic carbon were prepared from reagent grade potassium hydrogen phthalate in ultra-pure water, while the inorganic carbon standards were prepared from a mixture of anhydrous sodium carbonate and sodium hydrogen carbonate.

Although the methods used here are standard protocols, the analytical character of this work demands their description. Initially, a 200 μL sample aliquot was injected in the combustion tube to measure the total carbon (TC) concentration. TC is the sum of inorganic carbon (IC) and total organic carbon (TOC). The latter comprises particulate carbon (PC) and DOC, which, on its turn, includes the VOC species. In this work, TOC is equivalent to DOC because the rain samples were firstly filtered, and the synthetic compounds used were completely dissolved. After TC was determined, a new aliquot was acidified (H3PO4 25%, v/v) and purged with a CO2-free carrier gas to remove and measure the CO2 produced by the inorganic species. Although VOC is eliminated during the purging procedure, only CO2 can be detected by the infrared sensor and, therefore, measured. The difference between TC and IC allows for the calculation of the concentration of all the dissolved organic species, that is, of DOC.

In order to estimate if the rain samples had appreciable concentrations of VOC, a sample aliquot (typically 5 mL) was acidified (HCl 2.0 mol L⁻¹; pH 2) and purged during 10 min before an aliquot was introduced in the combustion tube. In this way, only the non-purgeable organic carbon (NPOC) that remained soluble in the sample was detected and measured. The difference between DOC and NPOC allowed for the estimation of VOC, also denominated purgeable organic carbon (POC).

Sample aliquots were injected three times in the instrument for each of the carbon species measured. The relative standard deviation was ≤2% for concentrations of 167 μmol C L⁻¹ (2 ppm), which is lower than those reported by other studies (e.g., Decesari et al., 2005). The instrumental variability was daily tested using hydrogen phthalate standard (250 μmol C L⁻¹) stored at 4 °C. When the variability was >7% new standards were prepared and a new analytical curve was built.

It is essential to report the protocol for blank estimation and data correction for the accurate determination of DOC concentrations in samples with a low organic carbon content (Spyres et al., 2000). The catalyst bed used was Pt supported on alumina or on quartz wool to improve sensitivity. In the case of the high-sensitivity catalyst, the instrumental blank (also called blank system or blank check) was performed by a special procedure allowed by the Shimadzu 5000A equipment. The programme is set to inject twice 2 mL of ultra-pure water into the system in order to remove any remaining carbon within the equipment. Then, a new aliquot of ultra-pure water is injected into the TC combustion tube to produce a “carbon free water” which is recovered in a pre-cleaned trap for analysis. This “carbon free water” is then re-injected into the system using the same volume and protocol as for the samples (200 μL), and after five injections the average area is recorded. This last procedure is repeated 10 times and the last mean value obtained is considered to be the “instrumental blank”. During this work, the instrumental blank was periodically checked and the obtained area was typically between 3% and 8% of the area of a 42 μmol L⁻¹ standard. This value was subtracted from those obtained for the samples. The analytical curve was shifted to zero to subtract the organic carbon present in the ultra-pure water used to prepare the standards.

3. Results and discussion

3.1. Study for glassware decontamination

In order to set a reference value to evaluate the decontamination procedures tested, ultra-pure
water freshly retrieved from the deionizer system was used as a blank control during the course of this study. At this point, the glassware decontamination procedure was not yet defined, and a rigorous handling care was not crucial.

In order to define the “maximum” contamination level, DOC concentrations were determined in five sets of beakers contaminated with citric acid, which were not submitted to any decontamination treatment. While the elevated average DOC residual concentration (Table 1, procedure “A”) shows the need to establish a vigorous treatment to efficiently clean the flasks, the relatively homogeneous contamination (RSD = 16.3%) allows for comparison among the different decontamination procedures.

The first commonly used cleaning procedure tested was to soak the contaminated beakers in a bath of sodium persulphate 10% for 1 h at 60 °C (Kaplan, 1994). The instrumental peaks produced were badly shaped with noticeably enlarged areas. This is probably because persulphate residues reacted with some organic material adsorbed on the catalyst, leading to its oxidation and the production of carbon dioxide. In this study, the residual DOC concentration was measurable in only two of the treated beakers (Table 1, procedure “B”).

Another type of treatment that is broadly used is baking the glassware for 5–6 h at 450–550 °C (Kaplan, 1994; Sharp et al., 2002). In this study, the average concentration for residual DOC was surprisingly high—six times higher than the control (Table 1, procedure “C”). Rinsing the contaminated beakers before baking them did not improve the results (Table 1, procedure “D”). Calcination appeared to be highly inefficient for heavily contaminated borosilicate glassware, since such a large DOC contamination is unlikely to happen during the cooling process and/or the resting time with ultra-pure water. The most efficient of the published methods tested here was soaking the beakers for 1 h in a nitric acid 10% (v/v) bath (Thomas et al., 1995; Sharp et al., 2002; Tue-Nguyen et al., 2005), although the decontamination achieved was not yet satisfactory when compared with the ultra-pure water used as control (Table 1; procedure “E”).

New decontamination procedures were tested in this work based on the Fenton and photo-Fenton processes which are well known for performing a rapid and efficient oxidation of organic matter due to the formation of hydroxyl radicals arising from the decomposition of hydrogen peroxide in the presence of Fe (II) (Pignatello et al., 2006; Nogueira et al., 2007). Initially, different sets of contaminated beakers were submerged for 1 h in freshly prepared solutions named “Fenton1” (0.5 mmol L⁻¹ Fe²⁺ (Fe(NH₄)₂(SO₄)₂·6H₂O) and 20 mmol L⁻¹ H₂O₂; pH 2.5) and “Fenton2” (1.0 mmol L⁻¹ Fe²⁺ and 100 mmol L⁻¹ H₂O₂; pH 2.5). The beakers were withdrawn from the cleaning solution and filled with ultra-pure water, which was analysed for residual DOC after resting for ca. 24 h. The increase in the concentration of Fe²⁺ and H₂O₂ solutions significantly improved the decontamination process, even when compared with the HNO₃ treatment (t-test; P = 0.05; Table 1, procedures “F and G”). The use of two germicide lamps (15 W each) above the Fenton2 solution for 30 min did not further decrease the final carbon residue (t-test; P = 0.05; Table 1, procedure “H”). Several other tests were performed using both Fenton solutions, such as: increasing the immersion time of the contaminated beakers, increasing the UV-irradiation time and rising the bath temperature to 60 °C. None of these procedures, including a bath with 100 mmol L⁻¹ H₂O₂ only, achieved DOC average concentrations better than 6.8 μmol C L⁻¹ (results not shown).

It is noteworthy that none of the treatments shown in Table 1 were able to reach the DOC background level found in the control ultra-pure water. This could be due to the cleaning solutions themselves, as the beakers were not rinsed after submersion in those media. At this point atmo-

<table>
<thead>
<tr>
<th>Procedure</th>
<th>DOC ± S.D. (μmol C L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultra-pure water—control</td>
<td>4.36 ± 1.83 (n = 10)</td>
</tr>
<tr>
<td>(A) No decontamination</td>
<td>156 ± 25.4 (n = 15)</td>
</tr>
<tr>
<td>(B) Persulphate bath 10%: 1 h, 60 °C</td>
<td>215 ± 16.3 (n = 2)</td>
</tr>
<tr>
<td>(C) Calcination: 5 h, 550 °C</td>
<td>27.7 ± 13.2 (n = 6)</td>
</tr>
<tr>
<td>(D) Calcination: 5 h, 550 °C, rinsing</td>
<td>22.5 ± 0.82 (n = 3)</td>
</tr>
<tr>
<td>(E) Nitric acid bath 10%: 1 h</td>
<td>11.2 ± 2.66 (n = 12)</td>
</tr>
<tr>
<td>(F) Fenton1 bath (1 h)</td>
<td>12.4 ± 5.65 (n = 9)</td>
</tr>
<tr>
<td>(G) Fenton2 bath (1 h)</td>
<td>6.83 ± 2.02 (n = 12)</td>
</tr>
<tr>
<td>(H) Fenton2 bath: UV 30 min</td>
<td>8.33 ± 0.80 (n = 3)</td>
</tr>
</tbody>
</table>

Ultra-pure water—stored in cleaned glass 1.03 ± 0.25 (n = 3) flask
Ultra-pure water—UV-irradiated prior storage <0.19

The “control” is the ultra-pure water freshly withdrawn from the deionizer system.

spheric contamination was also possible, as the experiments were performed in a common lab bench.

Having defined 1 h of submersion in the Fenton2 solution as the most efficient and simple treatment for glassware decontamination, this procedure was thereafter used for all the routine work in our laboratories followed by thoroughly rinsing the flasks with ultra-pure water. Any iron residues that may have remained in the storing flasks are probably too low to oxidize organic carbon from samples stored in amber flasks at low temperatures. When the samples’ volume allowed, the flasks were also rinsed with an aliquot of the filtered sample before storage.

3.2. Blank tests

To evaluate the possible DOC contamination from the lab atmosphere, six aliquots of ultra-pure water were transferred to pre-cleaned beakers capped with aluminium foil and were maintained on the lab bench for approximately 12–27 h. The DOC concentrations measured were within the values found for the control water showed in Table 1.

The DOC average concentration fell to 1.03 μmol C L⁻¹ (Table 1) when ultra-pure water was stored in a properly cleaned and sealed amber glass flask, having the aliquots retrieved in a laminar flow hood using clean protocols for trace analysis (Campos et al., 2002). Although this concentration is better than some reported values (e.g., 2.2 μmol C L⁻¹; Avery et al., 2006), it is still higher than desired (Sharp et al., 2002). Therefore, another aliquot of ultra-pure water was UV-irradiated in capped quartz tubes for 4 h using a home-made reactor (Campos et al., 2001) and stored. The DOC concentrations obtained were below the determined limit of detection of 0.19 μmol L⁻¹ (3 S.D.; Table 1), indicating the presence of residual carbon from the water purification system, which did not have a device for UV photo oxidation.

3.3. Storage study for preserving DOC in rainwater

Some authors adopt acidification as a method to preserve samples for DOC analysis, including the addition of H₃PO₄ and storage at 4 °C for up to 15 months (Wiebinga and de Baar, 1998; Lara et al., 2001). However, the drawbacks of acidifying the samples include the possibility of contamination, volatilization of dissolved carbon and hydrolysis of organic matter. Furthermore, the use of HgCl₂ should be avoided as it can deactivate the platinum catalyst (Spyres et al., 2000; Kaplan, 1994).

As the chemical characteristics of the DOC content can vary according to the type of sample and atmospheric inputs, a rainwater preservation study was conducted in order to assure the quality of the data reported. Rain samples freshly collected at the Araraquara site were filtered (0.7 μm), immediately analysed and then stored for further analysis.

Preliminary tests performed with potassium hydrogen phthalate standards (250 μmol C L⁻¹) stored at 4 °C showed that even in the presence of potential contaminants such as aqueous solutions of organic compounds, DOC concentrations remained constant for weeks by sealing the flasks mouth with a PTFE tape, an insert plug and a screw cap. Although those solutions were discarded, the flask sealing procedure was maintained, and thereafter clean protocols for trace analysis were used (Campos et al., 2002). No measurable contamination was observed in the blank tests and the storage study performed.

Fig. 1 shows the behaviour of DOC concentrations for several rainwater samples for up to 21 days of storage using the optimized cleaning procedure. For two of the samples an abrupt loss of DOC of ~60% was observed after 10–11 days of storage, while for the others the loss was much smaller and smoother with time, or even not significant up to 21 days (Fig. 1). The analytical variability for the samples that had a high enough volume to allow for the analysis of three sub-samples at each time interval was from 3% to 15%. Although it is expected some bacterial activity after filtration at 0.7 μm (Kaplan, 1994), for the type of samples analysed in this work DOC integrity can be maintained for at least 1 week at 4 °C, agreeing with the findings reported by Willey et al. (2000). It is unlikely that significant amounts of VOC could have been lost during the storage period at 4 °C or during the short period that the samples stayed at room temperature before analysis, but these possibilities cannot be completely dismissed.

3.4. Volatile organic carbon

In order to evaluate whether VOC could be an important component of organic carbon in the rain from the two sites studied, DOC as well as NPOC were measured in 16 rain samples (Table 2). The
estimated VOC concentrations were larger than the instrumental variability accepted (7%) for 11 samples, corresponding to 8–56% of the dissolved carbon present in the rainwater samples. There was no significant correlation between VOC concentrations and either the duration of the dry period preceding the rain event or the rain volume (t-test; \( P = 0.05 \)). However, it is worth noting that the two highest concentrations of VOC were present in the samples with the lowest volumes—14 and 20 mL—when typical rain volumes collected during the rainy season are about 300 mL. To identify the sources and the dominant aspects of the variability of the VOC species, a larger number of rain samples would be needed.

The vehicular source of VOC in Brazil is very peculiar, as ethanol has been used as a car fuel since the 1970s, and now accounts for 47.5% of all vehicular fuel used in the country (CETESB, 2006). Out of the 7.3 million vehicles registered in the metropolitan region of São Paulo, 65% run on gasohol (addition of \( \sim \) 22% ethanol to the petrol), 12.3% run exclusively on hydrated ethanol, and 6.1% are flex fuel, running on any proportion of ethanol and gasohol. The VOC profile in São Paulo’s air is dominated by ethanol with high concentrations of methanol and 1- and 2-propanol (Colón et al., 2001). Alcohol concentrations in São Paulo atmosphere are from 10 to 100 times higher than those found in Los Angeles, USA, while the \( C_4-C_9 \) \( n \)-aldehydes are 5–10 times higher (Colón et al., 2001). These organic species are very soluble in water and therefore could significantly contribute to the total concentration of DOC found in our rainwater samples.

In 2006, the vehicular fleet in the metropolitan region of São Paulo was responsible for 97% of the

<table>
<thead>
<tr>
<th>Date (local)</th>
<th>DOC (µmol C L(^{-1}))</th>
<th>NPOC</th>
<th>VOC (µmol C L(^{-1}))</th>
<th>VOC (% of total)</th>
</tr>
</thead>
<tbody>
<tr>
<td>29/30/01/06 (RP)</td>
<td>285</td>
<td>297</td>
<td>-12.0</td>
<td>(-4.2)</td>
</tr>
<tr>
<td>22/03/06 (A)</td>
<td>61.2</td>
<td>62.1</td>
<td>-0.90</td>
<td>(-1.5)</td>
</tr>
<tr>
<td>25/03/06 (A)</td>
<td>195</td>
<td>197</td>
<td>-2.60</td>
<td>(-1.3)</td>
</tr>
<tr>
<td>10/11/02/06 (RP)</td>
<td>141</td>
<td>139</td>
<td>1.30</td>
<td>(0.9)</td>
</tr>
<tr>
<td>21/03/06 (A)</td>
<td>160</td>
<td>153</td>
<td>7.50</td>
<td>(4.7)</td>
</tr>
<tr>
<td>30/01/06 (RP)</td>
<td>276</td>
<td>254</td>
<td>21.4</td>
<td>(7.8)</td>
</tr>
<tr>
<td>25/03/06 (A)</td>
<td>179</td>
<td>155</td>
<td>23.8</td>
<td>(13)</td>
</tr>
<tr>
<td>16/03/06 (RP)</td>
<td>433</td>
<td>370</td>
<td>62.3</td>
<td>(14)</td>
</tr>
<tr>
<td>30/01/06 (A)</td>
<td>180</td>
<td>147</td>
<td>33.2</td>
<td>(18)</td>
</tr>
<tr>
<td>15/16/02/06 (RP)</td>
<td>126</td>
<td>90.4</td>
<td>35.3</td>
<td>(28)</td>
</tr>
<tr>
<td>17/03/06 (RP)</td>
<td>327</td>
<td>233</td>
<td>93.5</td>
<td>(29)</td>
</tr>
<tr>
<td>16/03/06 (RP)</td>
<td>180</td>
<td>121</td>
<td>58.0</td>
<td>(32)</td>
</tr>
<tr>
<td>30/03/06 (A)</td>
<td>49.6</td>
<td>33.4</td>
<td>16.2</td>
<td>(33)</td>
</tr>
<tr>
<td>25/03/06 (RP)</td>
<td>101</td>
<td>61.9</td>
<td>39.5</td>
<td>(39)</td>
</tr>
<tr>
<td>21/03/06 (A)</td>
<td>167</td>
<td>89.9</td>
<td>77.5</td>
<td>(46)</td>
</tr>
<tr>
<td>07/02/06 (RP)</td>
<td>796</td>
<td>347</td>
<td>449</td>
<td>(56)</td>
</tr>
</tbody>
</table>

The percentage of VOC is expressed in brackets.

358 thousand metric tons of hydrocarbons emitted per year in the region, being 53% of those vehicles over 10 years old (CETESB, 2006). Assuming that Ribeirão Preto’s vehicular fleet is similar to that of São Paulo, its 256 thousand registered vehicles would emit ca. 12,178 t of hydrocarbon a year, which could at least partially explain the high concentrations of VOC carbon found in our rain samples. Furthermore, the residence time of VOC—on the order of days—(Avery et al., 2006) points to long-range transport from high-emission areas as a potential additional source of VOC in Ribeirão Preto.

Another important VOC source in the studied region is the incomplete sugar cane foliage burning practice (to facilitate manual harvesting) and the use of sugar cane crushing residues as fuel. These processes occur intensively during the sugar cane harvest period (mainly between April and October), and therefore do not coincide with the sampling period for the VOC estimation. However, the high-DOC concentrations found in the rain samples shown in Fig. 1 could at least be partially explained by the intense biomass burning activities in this region.

For seawater, the difference between DOC and NPOC may be negligible due to the small amount of VOC expected for such samples (<1% of TOC; Spyres et al., 2000). However, the results presented here show that it is essential to include VOC species when measuring DOC concentrations in rainwater samples, as their composition is known to vary greatly (e.g., Williams et al., 1997; Avery et al., 2001, 2003; Kieber et al., 2002).

4. Conclusions

The Fenton solution bath combines simplicity, low cost and high efficiency to decontaminate glassware for DOC analysis. Using the optimized protocol for cleaning the flasks, DOC concentration in ultra-pure water was found to be $1.03 \pm 0.25 \mu\text{mol CL}^{-1}$, falling to values below the limit of detection ($0.19 \mu\text{mol CL}^{-1}$) when the ultra-pure water was submitted to UV-irradiation prior to storage and analysis.

The storage tests at 4°C demonstrated that the DOC concentrations of the rain samples remained unaltered for at least 1 week, which has the advantage of avoiding the addition of preservatives and therefore potential contaminants. The blank tests and storage study demonstrated the good control over potential contaminants during sample analysis.

To report clearly how the instrumental blank was checked, as well as to detail the method used to determine DOC concentrations, is of great importance when dealing with samples with such a low content of organic carbon as rainwater. Our results showed that depending on the atmospheric chemical dynamics it may not be acceptable to report “DOC or TOC” concentrations in rainwater when using the procedure involving acidification and purging prior to analysis, that is, NPOC measurements.

The elevated VOC concentrations found in our rain samples could be due to the high emissions of hydrocarbons from the large use of ethanol and gasohol fuels compounded by the great number of vehicles running with obsolete technology. Although Brazil is at present the only country where the use of alcohol based fuels for automobiles is substantial, the appeal for reducing CO$_2$ emissions from fossil fuels is increasing the demand for alcohol-based fuels worldwide. In this context, it appears that not accounting for VOC in rain samples can lead to an important underestimation of the global rain DOC flux, which could be more significant in the near future.

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References


