The importance of organic carbon as a coadjutant in the transport of pollutants

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ABSTRACT

Dissolved organic carbon (DOC) is a physicochemical parameter widely used in the evaluation of surface water quality; however, its role as an agent of transport and transference of pollutants sometimes is still disregarded. The heterogeneous composition of DOC, predominantly composed of humin, humic and fulvic acids, renders it an inherent capacity to bind to organic and inorganic pollutants. This is an important feature when the knowledge of present and future conditions of aquatic environments is of concern. Some authors concluded that DOC is a controlling agent of mobility of metals, phosphorus, herbicides, and pesticides, among others. Nevertheless, some physical and chemical conditions in the water column and in the sediment can immobilize the contaminants and make the DOC less soluble, which will hamper the formation of DOC-pollutant complexes. This mini review is intended to present the importance of DOC quantification and some information on its association with water contaminants, which could render them unavailable for uptake.

Key words: aquatic systems, bed sediment, dissolved organic carbon, dynamics of pollutants, mini-review, organic matter

HIGHLIGHTS

- Dissolved organic carbon represents an important role in the dynamics of pollutants in water bodies.
- There is a close relationship between the DOC and a pollutant in surficial sediments and pore water.
- The heterogeneity of DOC composition turns it into a versatile ligand in aquatic systems.

GRAPHICAL ABSTRACT

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INTRODUCTION

Dissolved organic carbon (DOC) is composed of a wide variety of molecules. Its formation, besides chemical reactions, is associated with the transformation of organic matter in soils and surface waters as a result of metabolic reactions of microorganisms (Figure 1) (Kawasaki & Benner 2006; Condron et al. 2010; Malik & Gleixner 2013).

The determination of DOC concentrations provides approximate information on the total concentration of organic matter in water samples. DOC is a physicochemical parameter widely used in surface water quality assessment and represents an important role in the dynamics of pollutants in water bodies. The DOC available in aquatic systems can be derived from both autochthonous and allochthonous sources, the latter indicating either diffuse or point source pollution (Hughes et al. 2017). It is worth mentioning that the DOC presents an inherent capacity to link to pollutants in the water column, in the pore-water, and in the surficial sediments, which alters its availability, resulting in a constant transference between the interfaces in aquatic systems.

The understanding that the presence of DOC in the water column is associated with transport and transference of pollutants to sediments, and vice-versa, led researchers to consider this parameter for the assessment and evaluation of water pollution mainly in Europe, Canada, and the United States. Caron et al. (1985) observed in laboratory experiments that the addition of DOC to the aqueous phase caused a reduction in the adsorption of DDT onto particles in sediment. These authors stressed that the pollutant present in the water column existed as a dissolved DOC-DDT complex. This enabled the transport of the pollutant throughout the aquatic system.

In a modelling exercise studying the compartments water column, sediments, pore-water, and fish, Caron (1989) determined that 22% of the biphenyl TeCBP (2,2',4,4'-tetrachlorobiphenyl) was associated with organic matter in the pore-water. The author deduced that the highest concentration of DOC in this compartment indicated the possibility of transferring the contaminant from the pore-water to the water column by diffusion.

Results of studies carried out in the United States and in Sweden showed strong correlation between DOC and the concentration of mercury species (total and methyl) (Meili 1988; Zillioux et al. 1993; Hultberg et al. 1994; Watras & Bloom 1994; Krabbenhoft et al. 1995). Among the various studies developed in the United States and in Sweden from late 1980 to mid-1990, the results produced by Krabbenhoft et al. (1995) deserve particular attention. These authors reported that the seasonal increase in mercury species in the water column was concomitant with increases in DOC. During the survey period, they observed a variation in the concentration of total mercury from 0.9 to 6.3 ng L\(^{-1}\), whereas methylmercury varied from 0.21 to 0.33 ng L\(^{-1}\), in relation to the variation of DOC from 3.7 to 11.0 mg L\(^{-1}\).

Nonetheless, despite its importance in the transport and transference of pollutants, results on DOC have still been used only as an indicator of the presence of organic matter, and thus, have not been associated with other water quality parameters.

Figure 1 | Pathway of DOC formation (adapted from Kawasaki & Benner 2006; Condron et al. 2010; Malik & Gleixner 2013).
regardless of the limit of detection of the equipment/technique. For instance, some authors determined concentrations of DOC, suspended solids, nutrients (N and P), and metals during runoff events, whereas other authors presented results on the seasonality of DOC, pH, dissolved oxygen, ammonia nitrogen, and chemical oxygen demand (Barros et al. 2020; Li et al. 2020). However, results on the statistical significance of the interaction between DOC and other parameters were not presented.

Understanding the interaction between DOC and pollutants, especially toxic metals, is important to assess the availability of these elements in the water and in the water-sediment interface. This consideration is of particular importance due to the changes caused in the aquatic environment because of runoff and the consequent input of diffuse pollution (Bondareva & Fedorova 2020).

Based on the considerations presented before, this study reviews and presents the importance of DOC in the transport and transference of pollutants in surface aquatic systems.

**ORGANIC MATTER: COMPOSITION, CHEMISTRY, AND QUANTIFICATION**

Humic substances, composed predominantly of humin, humic and fulvic acids, are the major constituents of the organic matter present in most of the soils and sediments. These substances are the result of chemical and biochemical reactions and are present in organic soils and aquatic environments. The following functional groups result from these transformations: (i) nitrogen-containing, as primary amines (R-C = O-NH₂), secondary amines (R₁-C = O-NHR₂), and tertiary amines (R₂-C = O-NR₃); (ii) carbonyl, as aldehydes (R-CHO), and ketones (R₁-C = O-R₂); (iii) hydroxyl, as alcohols (R-OH); (iv) carbonyl, as carboxylic acids and acetates (R-CO₂⁻); (v) imines (R₁-C = NH-R₂); (vi) thioether (R₁-S-R₂); (vii) phosphonates (R-P(O)₂⁻) and (viii) organosulfonates (RSO₃⁻) (Souza & Santana 2014).

The humic and fulvic acids constitute the most studied humic substances, with average chemical formula in the soil as C₁₈⁶H₁₈₆O₈₉N₉S and C₁₃₅H₁₈₂O₉₅N₅S₂, respectively (Schnitzer 1983).

Over decades, researchers have proposed chemical structures for humic substances. Each proposed structure was characterized by similar functional groups with the presence of aliphatic and aromatic constituents. Their complexity increased as analytical methods and equipment used for the determination of chemical structures became more sophisticated (Stevenson 1994). However, more recently, it has been argued that humic substances should be understood as supramolecular associations derived from relatively small molecules which result from the degradation and decomposition of biological matter (Piccolo 2001).

The supramolecular structure is stabilized by weak dispersive forces, such as hydrophobic (van der Waals, π-π, CH-π) and hydrogen bonds. Thus, the intrinsic characteristics of the humic substances turn them into an effective agent for the control and sequestering of pollutants in soils and aquatic environments. Negatively charged groups of the humic substances react with positively charged organic and inorganic compounds. Reactions between nitrogen-containing pesticides or metals and humic substances could be cited as examples. Organic compounds with positively charged functional groups can also react with humic substances by cation exchange, for example, the herbicides atrazine and triazolam (Baldotto & Baldotto 2014).

The proportion of the organic matter in soils is estimated to vary from 65 to 75% as humic substances (Schnitzer 1983), whereas it has also been considered that 50% to 70% is referred to as the amount of humic acid in the composition of DOC in soils (Thurman 1985). The intimate relationship between the hydrological cycle and the biogeochemical cycles, the carbon cycle in particular, ensures that natural waters, ground and surface waters, contain organic substances. According to Hem (1989), the concentrations of DOC in surface waters vary from 3 mg L⁻¹, in semi-arid zones, to 19 mg L⁻¹, in subarctic zones. According to Thurman (1985), the humic substances represent between 5 and 10% of all ions in aquatic systems, and their anionic characteristic is responsible for the solubility in water.

The concentration of organic carbon in water samples is determined by the analyses of dissolved and total organic carbon, and the separation of phases is carried out by filtration in 0.45 μm membranes. The concentration of organic carbon is determined by a catalytic oxidation combustion technique at high temperature, in which all carbon species present are converted into CO₂ and measured by a non-dispersive infra-red (NDIR) sensor (LABEAM/UFPR, personal communication, 2021), as represented schematically in Figure 2. According to Mopper & Qian (2006), this method presents the following advantages: (i) high efficiency of organic matter oxidation; (ii) high accuracy; (iii) automated reading of the results. Nevertheless, the disadvantages that can be cited are: (i) lower precision of the analysis of blank samples; (ii) high sensitivity of the NDIR sensor to vibration, variation in the gas flow rate, and temperature.
In addition to the analysis used for quantification of DOC, spectroscopic techniques, such as fluorescence spectroscopy and visible ultraviolet spectroscopy (UV-Vis), have been used to identify the origin of the organic matter transported in aquatic systems. The UV-Vis produces information on aromaticity, distribution of molecular weight, origin, and reactivity, whereas the fluorescence is associated with quantitative and qualitative characterization of dissolved organic matter in natural waters (Chen & Yu 2021). Aiming at gathering reliable information on DOC characteristics and sources, both techniques are applied in parallel (Schnitzer 1983).

The spectroscopic techniques are important tools for the identification of the origin of the organic matter in water bodies, which can be allochthonous, i.e., produced outside the system and carried by runoff, or autochthonous. Another important role is related to the possibility of identification of natural processes of modification of the organic matter, which results in the classification of refractory pedogenic and composed of aromatic chains, or aliphatic aquagenic and composed of simpler aliphatic chains (Lee et al. 2019).

According to Abadi et al. (2012), spectroscopic techniques also present advantages and disadvantages. Among the advantages presented by UV-Vis spectroscopy, the capture of the entire spectrum of visible light; robust, accurate, and precise results; as well as fast sample processing can be cited. The disadvantages can be associated with a low concentration of the analytes, non-selectivity due to the high bandwidth of the visible light spectrum, the need for previous and adequate preparation of samples aiming at better selectivity, and sensitivity of results. Moreover, the maintenance of accurate calibration curves is an important factor to guarantee accurate and precise results. According to Nagata et al. (2001), the advantages associated with fluorescence spectroscopy are fast sample processing, high sensitivity, and high bandwidth of analysis. However, sample composition, homogenization, and concentration; temperature of the solution; pH, and salinity are factors that affect the fluorescence response (Carstea 2012). Other authors pointed out that the analysis of DOC by spectroscopic techniques is more economical than those carried out by conventional physicochemical methods (Monteiro et al. 2020).

Moreover, DOC quantification has also been carried out by mathematical modeling and satellite imagery. The use of both tools is dependent on organic carbon concentrations in periods of time that represent different conditions in the water body resulting from point source and non-point source inputs (Lv et al. 2019; Vitale & Guardo 2019; Chen et al. 2020; Cao & Tzortziou 2021; Rouhani et al. 2021). For example, the Soil and Water Assessment Tool (SWAT), a hydrosedimentological model, has recently had state variable equations added to its codes to calculate DOC transport in rivers. The codes inserted allow the calculation of DOC removed from soil layers by runoff and DOC transported into surface water (Du et al. 2019). These authors observed satisfactory results for DOC transport between terrestrial and aquatic environments.

However, depending on the sophistication needed to develop site-specific water quality models, the amount and quality of data available may be neither adequate nor sufficient (Cao & Tzortziou 2021). In turn, the use of satellite imagery also involves the conceptualization of mathematical equations. DOC concentrations will be estimated by equations that use colorimetric information on the dissolved matter, i.e., related to the optically active fraction of DOC (Chen et al. 2020). In both cases, it is likely that it will be necessary to produce additional data for the calibration of the models.

In summary, the DOC has been used conventionally for the understanding of the behavior, removal, and control of various pollutants. And last but not least, dissolved organic matter concentrations in aquatic systems can also be used to assess and predict water quality by modeling procedures based on the characteristics of the watershed.

**Dissolved Organic Carbon and the Transport of Pollutants**

As a transport agent in the aquatic system, DOC interacts with pollutants of distinctive properties depending on the physicochemical characteristics of the molecules and environment. The associations are carried out by sorption processes,
i.e., adsorption and desorption; deposition; resuspension; and complexation. The sorption processes are subdivided into: (i) hydrophobic sorption, which occurs between organic substances and minerals with organic coating; (ii) hydrogen bridges or exchange between weak ligands, in which two electronegative elements share a hydrogen atom; and (iii) cationic or anionic exchange, in which polarized ions or molecules are attracted to electrically charged surfaces (Landrum et al. 1984; Thurman 1985). Thus, it can be inferred that the DOC characteristics turn it into a versatile ligand.

Among the properties of DOC, the cation exchange capacity (CEC) is one of the most important. The CEC is related to the isoelectric point, which expresses the existence of cationic sites available to link with other elements. High values of CEC are related to organic matter due to the ionization of carboxylic groups in the pH of surface waters. The heterogeneity of the composition of DOC causes the molecules of organic matter to assume a polyelectrolytic behavior, which favors the association with various pollutants, hydrophilic or hydrophobic, dissolved or particulate (Thurman 1985; Santos & Paes 2016).

Thus, due to its physicochemical characteristics, the complexation between DOC and metals alters the physical speciation of the molecule and interferes with the partition between phases, which influences the toxicity and bioavailability of a specific metal (Meili 1988; Zillioux et al. 1993; Watras & Bloom 1994; Tomczak et al. 2019). According to Novotny (2002), this association results from the existence of two distinct mechanisms involving: (i) monovalent cations, with which there is an exchange between the carboxylic and the phenolic groups, and (ii) polyvalent cations, with which coordinated chemical bonds prevail.

Water quality can be related to either intensification or weakening of the interaction between DOC and pollutants. Thus, precipitation and deicing, related to diffuse pollution, and sewage and wastewater discharges, can be associated with alterations in the quality of surface waters. This would result in increased or decreased DOC concentrations, and consequently, would interfere with the capture or release of pollutants (Chen et al. 2021).

Over the years, due to the possibility of formation of DOC-metal complexes, various authors have confirmed the importance of DOC as an agent associated with the transport of these pollutants (Caron et al. 1985; Hultberg et al. 1994; Krabbenhoff et al. 1995; Hughes et al. 2017; O’Driscoll et al. 2018; Buyang et al. 2019; Barros et al. 2020; Bondareva & Fedorova 2020; Praise et al. 2020). For instance, Chakraborty et al. (2014) observed the formation of DOC-Hg in the water column, whereas Tomczak et al. (2019) observed in the water column a direct relationship between increasing concentrations of DOC and the concentrations of Mn, Cu, Cd, and Cr in the dissolved form, whereas the relationship was inverse regarding the particulate fraction.

Li et al. (2021) studied the coupled influence of DOC and pH on the adsorption of phosphate onto lanthanum-modified zeolite (LMZ) in a eutrophic shallow lake. The formation of the LMZ-PO$_4^{3-}$ complex was affected mainly by pH at low DOC concentrations and by DOC at high DOC concentrations. It was also observed that basic pH and high DOC concentrations increased the release of phosphate from the sediment into the water column. However, the presence of LMZ reduced the phosphate concentration in water due to the formation of the LMZ-P$_{\text{dissolved inorganic}}$ complex.

Another point that has to be taken into consideration when the eutrophication of lakes and reservoirs is of concern is the role of DOC in the regulation of these aquatic ecosystems (Wen et al. 2019). The concentration of colored DOC (CDOC) is an important characteristic of lakes and can be regarded as a limiting factor of algal growth, being the main light-absorbing constituent of surface waters. However, the CDOC macromolecules can be decomposed by photochemical degradation to simpler organic matter molecules and nutrients, which will provide conditions for the development of aquatic microbiota.

This, in turn, will affect the level of oxygen in the water column and will favor high CO$_2$ concentrations due to the growth of water macrophytes (McElamney et al. 2010; Weyhenmeyer et al. 2015). Other authors have pointed out the importance of understanding the relationship between DOC and eutrophication indicators, such as nitrogen, phosphorus, and chlorophyll-a (Wen et al. 2016; Wang et al. 2020).

The reduction of toxicity, bioavailability and bioaccumulation of organic pollutants can also be related to DOC in aquatic ecosystems. Results produced by Morin et al. (2021) showed a reduction in the concentration of the herbicides diuron (C$_{12}$H$_{14}$Cl$_2$N$_2$O), ikgarol (C$_{11}$H$_{19}$N$_5$S), and S-metolachlor (C$_{15}$H$_{22}$ClNO$_2$) associated with the addition of dissolved organic matter in the analyzed water. In turn, Wu et al. (2020) studied the phenoxy herbicide 4-chloro-2-methylphenoxyacetic acid (MCPA) and observed a complex interaction between the acidic hydrophobic portion of the organic matter and the herbicide via hydrophobic force, ligand exchange, and hydrogen bonding.

Since there is a strong association between DOC and various pollutants, the environmental conditions are of fundamental importance regarding the interactions between the DOC and a specific pollutant. Therefore, transport and transference of pollutants can be either intensified or reduced, which will result in alterations in the quality of surface waters.
THE DYNAMICS OF POLLUTANTS AND THE RELATIONSHIP WITH SEDIMENTS

Prior to addressing this matter, it is important to understand the suitable and unsuitable conditions related to the transport of pollutants by DOC. It is worth mentioning that surficial sediments and pore-water are relevant compartments in an aquatic system, in which the existence of a close relationship between the DOC and a pollutant is very likely. However, if the pollutant is strongly bound to the particles in the sediment, there is a low likelihood of being released to form a DOC-pollutant complex. This is particularly important to consider when the medium is anoxic, and both the pH and the pH\text{pzc} (point of zero charge) favor the conditions in which the particle-pollutant interaction will prevail. The relationship between the pH and the pH\text{pzc} is especially important since the pH\text{pzc} is defined as the pH value in which the potential determinant ions (H\textsuperscript{+} and OH\textsuperscript{−}) are equally adsorbed onto a surface (Pérez et al. 2017). Therefore, since the pH\text{pzc} of the sediment is determined, the ionization of surficial functional groups and their interactions with pollutants under a specific pH can be foreseen (Fiol & Villaescusa 2009).

The pollutants will be potentially trapped in the sediment, and in the case of remobilization, it will be an important source of further contamination (Lee et al. 2017). Therefore, the identification and quantification of contaminants in the sediment and in the pore-water may provide the means to understand the flux of pollution, as well as information on potential threats to biota by toxic substances, in particular metals (Melli 1988; Krabbenhoft et al. 1995; Barkay et al. 1997; Aguiar et al. 2020).

The association between pollutants and particles in the sediment is usually a result of physicochemical processes such as adsorption, precipitation of inorganic ions, and complexation between metals and organic matter (Poletto & Martinez 2011). Among them, adsorption is of particular importance. It constitutes a key role in the association between sediment and metals (Galunin et al. 2014), dyes (Dra et al. 2020), and herbicides (Hu et al. 2021), for instance. In the aquatic system, after particle reorganization and the formation of particle-pollutant complexes, the system will be prone to sedimentation or resuspension. These processes are reversible, even without external interferences. Nevertheless, some characteristics of the sediment and of the pore-water can unbalance the reactions, with a tendency to strengthen the association or disassociation with the pollutant.

Grain size, composition, age, CEC, and pH\text{pzc} are among the characteristics more likely to influence the process of association between the particle and the pollutant. However, to avoid misinterpretation of the results, these characteristics should not be assessed individually. For instance, due to their higher specific surface area and capacity of cation exchange, fractions of sediment with smaller grain sizes assist a more intense carriage of pollutants. Another important factor is that fine-grained particulate matter is prone to resuspension and thus remains in the water column over longer periods of time, which allows it to interact with DOC (Zhang et al. 2014; Buyang et al. 2019; Aguiar et al. 2020).

It is also important to mention that properties such as the oxi-reduction potential, the concentration of dissolved oxygen, and pH in the pore-water can cause changes in the sediment-pollutant association. Alterations in the water pH interfere with surficial characteristics of the sediment, altering the functional groups and hence modifying the adsorption processes. The ideal pH for the formation of stable complexes is dependent on the target pollutant and is deeply related to the amount of oxygen available and the pH\text{pzc} of the sediment (Dra et al. 2020; Hu et al. 2021). Moreover, when anoxic environments are of concern, an increased release of Fe and Mg oxides from the sediment to the water column has been observed, which results in a higher likelihood of linkage between these metals and DOC (Xie et al. 2015).

A sound evaluation of physical and chemical characteristics of aquatic environments, as well as a better understanding of the interaction between DOC and pollutants, should be the aim of monitoring plans designed for the assessment of aquatic environments with historic records of pollution. This should be focused mainly on those in which non-biodegradable contaminants have been discharged and those whose water is intended for public supply.

CONCLUSION

The heterogeneity of DOC composition and the CEC contribute to a larger extent to turn it into a versatile ligand in aquatic systems. Therefore, it is of fundamental importance that monitoring plans aim not only to quantify individual parameters but also to cover the association between the pollutant and DOC according to specific characteristics of the aquatic system.

Over the years, the importance of DOC-pollutant complex formation has been stressed. This association turns it into an important agent of transport and transference between the water column and the pore-water, and vice-versa, as particulate or dissolved matter. On the other hand, when public health and environmental safety are of concern, the potential mobilization of pollutants is of fundamental importance. It would be particularly important if the results could contribute to the understanding of the bioavailability of toxic metals and other contaminants in aquatic ecosystems.
However, the results of physicochemical parameters produced have still been based on an isolated focus. Moreover, it is noteworthy that the use of mathematical models has assisted in the determination of present and future concentrations of carbon, mainly when the water-sediment interface is taken into consideration. These models, when adequately conceived, could provide information on the quality of surface waters under various environmental conditions.

Thus, the acknowledgment of the importance of DOC as a constituent element of major importance in the transport and transference of pollutants in surface aquatic systems would result in a better understanding of the system as a whole.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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