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Scavenging of dissolved organic matter (DOM) by amorphous iron hydroxide particles $Fe(OH)_{3(s)}$

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Abstract

Scavenging of dissolved organic matter (DOM) by particulate metal oxides like $Fe(OH)_{3(s)}$ is one of three processes that can influence the concentration and composition of DOM in aquatic systems. The other two possible processes include photodegradation and biodegradation. In combination, these processes alter the concentration and composition of DOM systematically with increasing time, measured as hydrologic residence time (HRT). The objective of this research was to determine the change in $Fe(OH)_{3(s)}$-scavengable dissolved organic carbon (DOC) with increasing HRT (0–80 yr). In addition, DOC from allochthonous and autochthonous sources were included in this study. The susceptibility of DOC from surface waters to scavenging by $Fe(OH)_{3(s)}$ was found to decrease as a function of HRT, from approximately 90% to 79%. The lowest HRT system was operationally considered equivalent to allochthonous DOC, while autochthonous DOC was scavenged similarly to DOC from the 80 yr HRT system. These results indicate that scavenging of bulk DOC may be limited by metal loading in aquatic systems, and that the bulk of $Fe(OH)_{3(s)}$-reactive DOC is from allochthonous sources. In addition, all surface waters treated with $Fe(OH)_{3(s)}$ contained approximately 1 mg l^{-1} of DOC that was resistant to scavenging (SD = 0.50, n = 5), which suggests that a refractory fraction of DOC persists in surface waters.

Introduction

Most sediment–water research that involves organic matter (OM) focuses on the interaction between particles and nutrients or particulate-metal sorption processes (Urban et al., 1990; Aufdenkampe et al., 2001). This research provides a unique perspective to sediment–water research because the emphasis is on particulate interactions with dissolved organic matter (DOM). More specifically, this paper addresses the relationship between iron (Fe)-scavenging and concomitant variation in the composition of DOM.

DOM, measured and hereafter referred to as dissolved organic carbon (DOC), is important in the structure and function of aquatic ecosystems (Tipping et al., 1991; Curtis, 1998; Lean, 1998). The sources of DOC include leachate from terrestrial plants and soils (allochthonous DOC) and leachates and exudates from aquatic plants (autochthonous DOC). Allochthonous DOC provides the largest contribution of DOC to aquatic systems and is typically of a higher molecular weight, as compared to autochthonous DOC (Curtis, 1998; McKnight & Aiken, 1998; Engelhaupt & Bianchi, 2001; McKnight et al., 2001). However, DOC in aquatic systems can be transformed and fractionated by environmental processes including; photolysis, bacterial degradation and scavenging (Moran et al., 2000; Osburn et al., 2001; Aufdenkampe et al., 2001). Thus, the structural and functional role of DOC changes over time (Engstrom, 1987; Rasmussen et al., 1989; Meili, 1992).

We have conducted studies on the relationship between changes in DOC composition and environmental transformation and fractionation processes. As part of these studies it has been determined that DOC composition in aquatic systems is significantly correlated to metal complexation (Richards et al., 2001). Changes in the metal complexing function of DOC directly influence Fe-scavenging. Interaction between DOC and Fe is important in determining the rate of Fe-scavenging in surface waters because complexation of metals by DOC increases metal stability (Curtis, 1993). DOC has a high affinity for $Fe(OH)_{3(s)}$ and can be effectively scavenged by adsorption (Davis & Gloor, 1981; Gu et al., 1994, 1995). However, the capacity of DOC to complex trace metals generally appears to be in excess of metal concentration for many surface waters (Urban et al., 1990).

Here we report on systematic changes in the potential for interaction between DOC and synthetic $Fe(OH)_{3(s)}$. We collected surface water samples along a hydrologic flowpath of about 80 yr to attain a gradient of DOC from environmental loading and transformation/fractionation processes. Further, we include and compare samples of allochthonous and autochthonous DOC.

Site description

Samples were collected from a headwater creek (unnamed) and three downstream lakes (Duck, Wood and Kalamalka Lakes) in the Okanagan Lake watershed of the upper Columbia River (Southern Interior of British Columbia, Canada, Fig. 1). Cumulative hydrologic residence time (CHRT) increases along the flowpath because hydrology of the lake chains is discharge dominated, as the climate at the elevation of the lakes is semi-arid (Fig. 1). Thus, the lakes are analogous to batch reactors positioned in series.

The headwater creek sample, with a CHRT of less than 1 yr, is operationally considered as allochthonous DOC, being derived almost entirely from terrestrial sources. Autochthonous DOC was produced in an acrylic mesocosm (1 m^3) that was filled with DOC-free deionized water, amended with salts and nutrients and inoculated with plankton from Duck Lake that were filtered onto a glass fiber filter (Whatman GF/C). The mesocosm was not setup with the intention of accurately reproducing *in situ* conditions, but rather to maximize productivity of autochthonous DOC for comparison purposes. Reagent grade salts were added to simulate 1/10th of the concentrations of global average river water because it was determined in earlier investigations that full concentrations were unnecessarily high to simulate eutrophic conditions (Stuckner & Northcote, 1974; Wetzel, 1983). Nutrient ratios favored the growth of cyanobacteria and the dominant taxon was *Anabaena* sp. The mesocosm was stored outside in a locked compound for 4 months (from May to August), where it was exposed to natural lighting conditions. *In vivo* fluorescence and DOC concentration were measured weekly to monitor the growth of the plankton community and production of autochthonous DOC.

Methods

Synthetic $Fe(OH)_{3(s)}$

Amorphous iron hydroxide $Fe(OH)_{3(s)}$ was produced by mixing a 0.36 m solution of $FeCl_3$ in a 4 l Erlenmeyer flask and adjusting pH to 7 (Morel, 1983; Stumm & Morgen, 1995). The resulting floc was then thoroughly washed by diluting the mixture with deionized water (E-pure, Barnstead), stirring, settling and decanting the excess water. This process was repeated 10 times until the conductivity and dissolved organic carbon (DOC) concentration of the wash water was approximately equivalent to ultra pure water.

Sample treatment

Approximately 20 l of water was collected into 20 l polyethylene containers from each sample site and from the mesocosm in August 2001. Samples were filtered through GF/C Whatman glass fiber filters to remove particulates. Filtered samples were split into reference and experimental subsamples.

Scavenging of DOC by $Fe(OH)_{3(s)}$ was measured in 4 l of each experimental subsample with 0.5 l of concentrated $Fe(OH)_{3(s)}$ suspension (Gu et al., 1995). The mixtures were adjusted to pH 7 (with NaOH and HCl) and stirred for 10 min. Subsamples were then filtered through Whatman GF/C glass fiber filters, and stored in clean polyethylene bottles at 4 °C in the dark prior to analysis. We determined independently that DOC sorption to $Fe(OH)_{3(s)}$ was saturated at suspension concentrations of 1 g l^{-1} (Fig. 2), thus the treatment suspension densities (3 g l^{-1}) were sufficient to saturate the capacity for DOC scavenging.

DOC concentration was measured in reference and treated samples with a Shimadzu TOC-5000A Total Organic Carbon Analyzer. Dissolved inorganic carbon (DIC) was removed by acidifying samples ($pH < 2$) with select grade hydrochloric acid (2N HCl) and purging with oxygen for 7 min prior to analysis. The coefficient of variation for instrumental response was consistently less than 2% and the detection limit of the

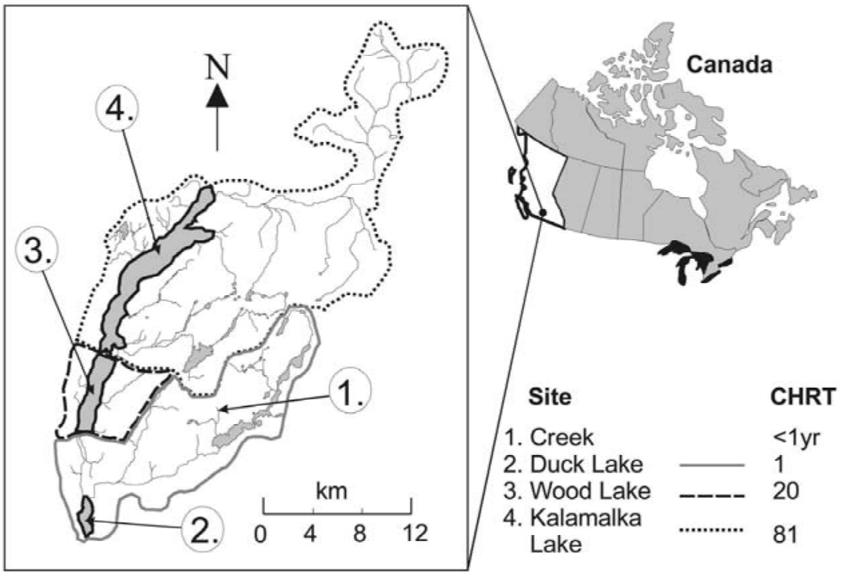

Figure 1. Map of the study area showing hydrologic flowpath (1 through 4), drainage basins and cumulative hydrologic resident time (CHRT) for each system that was sampled.

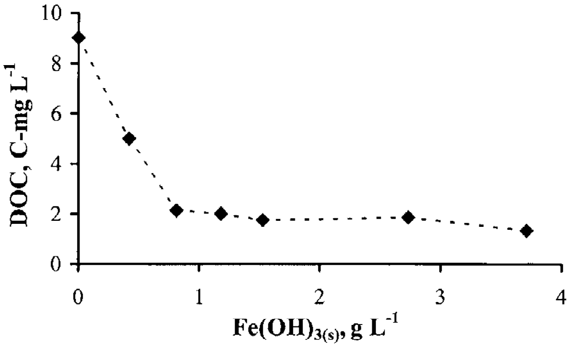

Figure 2. Sorption of dissolved organic carbon (DOC) and increasing amorphous iron hydroxide ($FeOH3_{(s)}$) concentration. Sample treatment concentration was 3 g l^{-1}.

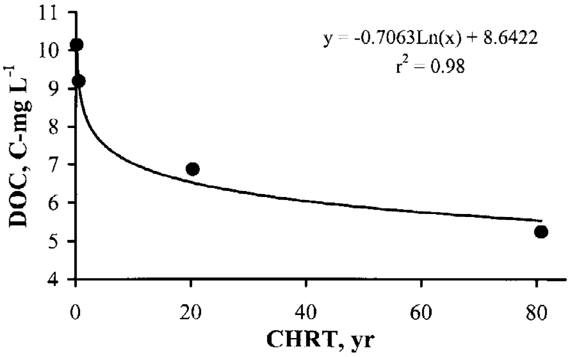

Figure 3. Concentration of dissolved organic carbon (DOC) and increasing cumulative hydrologic residence time (CHRT).

instrument was 0.05 C-mg l^{-1} at an injection volume of 250 μl.

Results and discussion

The concentration of dissolved organic carbon (DOC) decreased logarithmically from 10.1 to 5.2 C-mg l^{-1} with increasing cumulative hydrologic residence time (CHRT) among the surface waters sampled (Fig. 3). This pattern is consistent with observations elsewhere of DOC concentration dependence on hydrologic residence time (HRT) (Meili, 1992; Curtis & Adams, 1995; Curtis & Schindler, 1997). In all of the surface waters, more than three quarters of the DOC was scavenged by a 3 g l^{-1} $Fe(OH)_{3(s)}$ suspension. The proportion of $Fe(OH)_{3(s)}$-reactive DOC that was fractionated from each sample decreased from 90% to 76% and then to 79% with increasing CHRT (Fig. 4). The quantity of DOC scavenged also decreased with increasing CHRT because the effect of CHRT was greater on DOC concentration than it was on DOC scavenging (Fig. 4). These patterns of DOC fractionation indicate that a labile fraction of DOC, probably from allochthonous sources, is preferentially scavenged by $Fe(OH)_{3(s)}$. Preferential scavenging of allochthonous DOC is consistent with higher molecular weight molecules, as compared to autochthonous

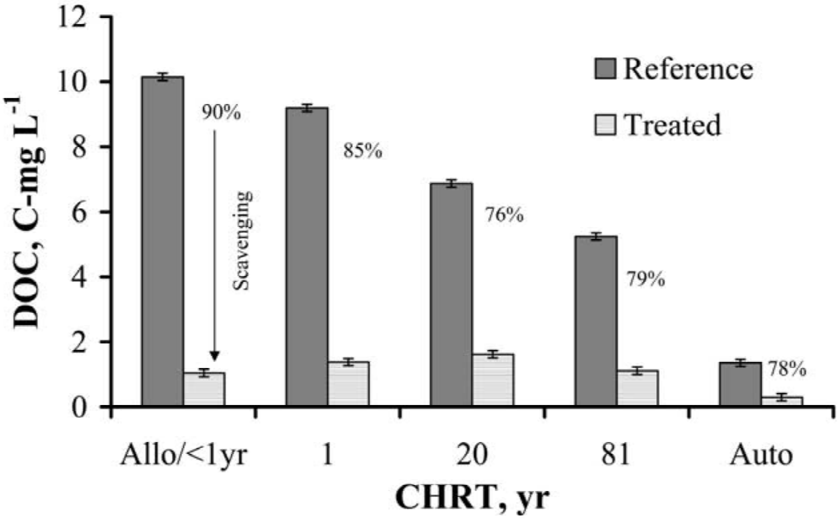

Figure 4. Concentration of dissolved organic carbon (DOC) for reference and $Fe(OH)_{3(s)}$ treated samples from the hydrologic flowpath (<1 – 81 yr) and for samples of allochthonous (Allo) and autochthonous (Auto) DOC. The difference between reference and treated samples is equal to the concentration of DOC lost to adsorptive fractionation by $Fe(OH)_{3(s)}$ (percent change from reference solution is shown).

DOC (Stewart & Wetzel, 1980; Davis & Gloor, 1981; McKnight et al., 1992; McKnight et al., 2001). The fraction of DOC that is not $Fe(OH)_{3(s)}$-reactive appears to be persistent in surface waters (approximately 1 C-mg l^{-1}, SD = 0.50, $n = 5$).

Concentrations of autochthonous DOC produced in the mesocosm were much lower than from surface waters, reaching a maximum concentration of only 1.36 C-mg l^{-1} after 4 months at levels of algal biomass corresponding to eutrophic conditions. In contrast to surface waters dominated by allochthonous DOC, only 78% of autochthonous DOC was scavenged by $Fe(OH)_{3(s)}$. Such low reactivity towards $Fe(OH)_{3(s)}$ is consistent with the relatively weak interaction between autochthonous-like DOC and other trace metals (Richards et al., 2001).

The relatively high proportional affinity of DOC for $Fe(OH)_{3(s)}$ in all surface waters suggests that most of the DOC is from allochthonous sources. This is supported by our observations that autochthonous DOC sorbs to $Fe(OH)_{3(s)}$ relatively poorly. Furthermore, recent studies suggest that autochthonous DOC loading is relatively small compared to allochthonous sources (Zumstein & Buffle, 1989; McKnight et al., 1994; Jonsson et al., 2001), which is consistent with low DOC production in the mesocosm even under a highly productive trophic state. Thus, autochthonous DOC appears to contribute little of the apparent $Fe(OH)_{3(s)}$-reactivity in surface waters relative to allochthonous DOC.

Differences between allochthonous and autochthonous DOC suggest that the small increases in the amount of $Fe(OH)_{3(s)}$-indifferent DOC with increasing CHRT, which increased from 1.05 to 1.63 C-mg l^{-1}, could be from a combination of two processes (Fig. 4). Firstly, $Fe(OH)_{3(s)}$-indifferent DOC could be a byproduct of transformed and fractionated allochthonous DOC (Waiser & Robarts, 2000), and secondly autochthonous DOC could accumulate over time due to a higher refractory fraction.

The observed CHRT dependence of DOC concentration and sorption potential on $Fe(OH)_{3(s)}$ is consistent with the dependence of other DOC qualitative properties on hydrologic residence time (HRT). For example, optical properties of DOC are HRT dependant for surface waters from different climatic and hydrologic regimes (Curtis & Adams, 1995; Curtis & Schindler, 1997; Curtis, 1998). Similarly, recent studies of trace metal complexation suggest similar dependencies on cumulative hydrologic residence time (CHRT) (Richards et al., 2001). Moreover, these studies suggest that the interaction of DOC with metals, including metal speciation in solution and scavenging of metals from solution, depend on the availability of a labile fraction of allochthonous DOC.

Conclusions

A large proportion of dissolved organic carbon (DOC) was $Fe(OH)_{3(s)}$-reactive suggesting that scavenging of DOC by $Fe(OH)_{3(s)}$ is limited in the majority of surface freshwaters by metal loading. Approximately 1 C-mg l^{-1} of DOC was resistant to scavenging, but this refractory fraction of DOC appears to be persistent in surface waters. The upper and lower extreme of $Fe(OH)_{3(s)}$-reactivity and DOC loading correspond to allochthonous and autochthonous sources of DOC respectively. Therefore, the bulk of $Fe(OH)_{3(s)}$-reactive DOC is likely from allochthonous sources, whereas autochthonous DOC may contribute to the persistence of refractory DOC in surface waters.

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