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Review

Trends in Levels of Allochthonous Dissolved Organic Carbon in Natural Water: A Review of Potential Mechanisms under a Changing Climate

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Abstract: Over the past several decades, dissolved organic carbon (DOC) in inland natural water systems has been a popular research topic to a variety of scientific disciplines. Part of the attention has been due to observed changes in DOC concentrations in many of the water systems of the Northern Hemisphere. Shifts in DOC levels, and changes in its composition, are of concern due to its significance in aquatic ecosystem functioning and its potential and realized negative effects on waters that might be treated for drinking purposes. While it may not be possible to establish sound cause and effect relationships using a limited number of drivers, through long-term DOC monitoring studies and a variety of laboratory/field experiments, several explanations for increasing DOC trends have been proposed, including two key mechanisms: decreased atmospheric acid deposition and the increasing impact of climate change agents. The purpose of this review is three-fold: to outline frequently discussed conceptual mechanisms used to explain DOC increases (especially under a changing climate), to discuss the structure of DOC and the impact of higher levels of DOC on drinking water resources, and to provide renewed/sustained interest in DOC research that can encourage interdisciplinary collaboration. Understanding the cycling of carbon from terrestrial ecosystems into natural waters is necessary in the face of a variable and changing climate, as climate change-related mechanisms may become increasingly responsible for variations in the inputs of allochthonous DOC concentrations in water.

Keywords: allochthonous dissolved organic carbon; atmospheric acid deposition; climate change; phenolic compounds; drinking water

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1. Introduction

Dissolved organic carbon (DOC) is a complex mixture of aromatic and aliphatic carbon-rich compounds that are important natural components of aquatic ecosystems, modulating many basic biogeochemical and ecological processes [1]. Over the past few decades, several long-term studies have reported an apparent trend of increasing DOC concentrations in inland surface waters over large areas of the Northern Hemisphere. According to a comprehensive review, there remains some uncertainty as to the ubiquity of the trend in increasing DOC levels [2]. However, the review reports that it is clear that a number of studies purport to show an increasing trend in DOC levels over large regions located in the Northern Hemisphere [2], and under a changing climate, it is feasible that DOC changes may become more pronounced—making examination of the potential drivers worthy of attention. At sites where DOC has increased, waters have often become “colored” (brownish tint) or “darker” (more absorbing of radiant light) [3], resulting in changes in light penetration and availability to plants in aquatic ecosystems. DOC concentrations also impact the transport of nutrients as well as pollutants, like heavy metals, in ecosystems. Further, since natural water supplies are sometimes treated and used for drinking water, higher levels of DOC have been shown to contribute to an increased formation of potentially dangerous chemical by-products (the most publicized being the trihalomethanes (THMs)) upon traditional chlorine disinfection treatment. High DOC can also dictate an increased demand for pretreatment steps in the water disinfection process, effectively making water more costly to treat [4,5].

Several factors have been considered to explain the observed increases in surface water DOC, including changes in soil and surface water acidity (e.g., [6,7]) as a result of declining sulfur deposition (e.g., [8,9]), continued nitrogen deposition (e.g., [10]), climate change (e.g., [11,12]), changes in hydrology and precipitation (e.g., [13,14]), changes in land-use patterns (e.g., [15]), as well as combinations of some of these factors. Despite intensive research over a few decades, much remains unknown in regard to our understanding of the terrestrial cycling of carbon. While many studies suggest that changes in DOC are occurring over large regional areas and the potential mechanisms discussed here have the capability to influence these changes to varying degrees, it should be recognized that it may not be possible to establish sound cause and effect relationships using a limited number of drivers. Many drivers, in fact, can work to produce a variety of effects on DOC release from the terrestrial landscape to natural waters and these effects can even work in opposition to each other. Further, many drivers may be covariate and it may, therefore, be difficult to isolate specific effects on DOC, especially in ecosystems where small changes in DOC or in a particular driver are observed. Nonetheless, the drivers outlined in this review are important to consider in areas experiencing changes in allochthonous DOC inputs, but further research should take a critical approach when attempting to ascribe significant statistical relationships between a reduced number of drivers and changes in DOC.

It is also recognized that changes in DOC can vary significantly according to geographic region [16]. For example, arctic and subarctic regions will respond differently to the complex drivers of DOC change when compared to temperate and tropic regions. It is not within the scope of this review to cover in detail how each ecoregion will respond to changes in the carbon cycle and many of the published research articles we reviewed were performed in temperate and subarctic regions. To understand more about carbon cycling in the arctic and changes in arctic carbon stocks, the authors direct readers to a review by McGuire *et al.* [17]. A highly cited review in regard to carbon cycling in tropical forests is also available [18], as well as several articles highlighting organic-matter [19,20] and climate change [21] in the tropics.

Despite the complexity of this issue, much of the attention devoted to explaining the observed long-term changes in DOC has sometimes been reduced to two key hypotheses. The first attributes the increases in DOC in surface waters to a reduction in acidic deposition as a result of tougher air standards internationally [8]. Proponents of this hypothesis argue that the changes in DOC are representative of a return to pre-industrial DOC levels, prior to the addition of sulfate pollution in the atmosphere [8]. There appears to be supporting evidence in the trends of reduced acidity in many surface waters in the U.K. in conjunction with an increase in DOC levels [22], but in some regions not subject to intense acid-deposition, such as northern, high latitude regions, the sulfate reduction hypotheses alone may not be able to completely explain increasing levels of DOC [23].

The second hypothesis offered to explain the DOC increases in water observed in boreal regions and other regions with low acid-deposition, is climate change and all of its inherent consequences (e.g., increasing temperatures, unpredictable weather, increasing atmospheric CO_2, *etc.*) as the main driver for increases in DOC [11]. Increasing temperature and atmospheric CO_2 concentrations can result in greater primary production and the accumulation of degrading biomass to contribute to the ecosystem's DOC pool. Researchers have indicated this observed increase in DOC may be a result of a change in the way in which soils and inland waters store and respire carbon [11,24], potentially representing a systemic environmental change; essentially a response in the carbon cycle to enhanced atmospheric CO_2 concentrations. Other factors of climate change, like varied precipitation and associated droughts and hydrology changes can also affect DOC levels found in water, but their implications are complex and varied in the ways that they may impact DOC trends.

A purpose of this review is to highlight the atmospheric deposition and climate change paradigms used to explain observations of increasing DOC and to briefly discuss other possible drivers discussed in the literature, such as land-use. The topic of DOC increases has garnered much research over the last few decades, perhaps due to the implication of increasing costs for treating water, but also as a means to better understand the processes governing the terrestrial transport of carbon to natural waters [24] and the associated ecological consequences of increasing DOC. Understanding the mechanisms that govern DOC release to natural waters is important, as it can enhance the ability to model future changes in the chemistry and ecosystem functioning of aquatic environments, especially in the face of impending climate change.

2. Characterization of Natural Organic Matter in Water Systems

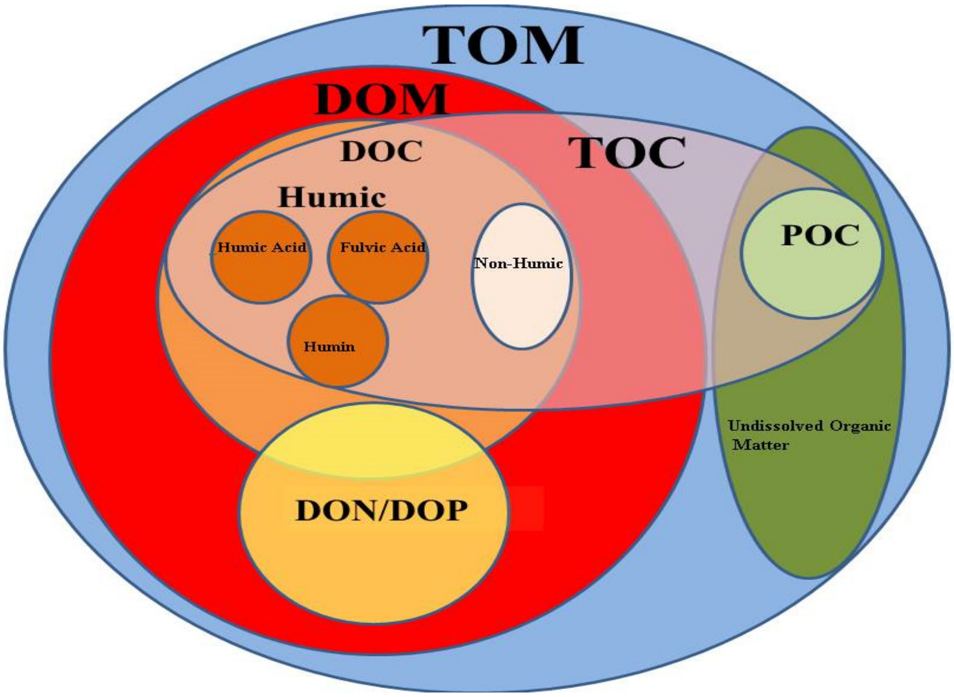
2.1. Natural Organic Matter Definition and Composition

There is a range of terminology that is used to describe organic matter found in water systems and the terms to discuss its different fractions are sometimes used ambiguously, while accounting for the variety of methods used in different studies to measure organic matter portions (for a quality review of this issue and a comprehensive study of terminology/methodology used in the literature, please see ref. [25]). For the purposes of this review, the following terminology will be used for the various forms of organic matter found in natural waters. The Venn diagram displayed in Figure 1 can help to categorize and visualize the forms of organic matter and related terminology in a simplified way.

Total (or Natural) Organic Matter (TOM) has approximately 50% carbon by weight, and the organic carbon species found in natural water are often referred to as Total Organic Carbon (TOC) [26]. TOC encompasses all molecular organic carbon species found in water (from small molecules like methane to macro-molecular structures such as lignins and proteins) [26]. Dissolved Organic Matter (DOM) is a term used generally when discussing dissolved organic substances, but the term is often used interchangeably with DOC in the literature, despite the fact that DOC makes up a fraction of the DOM profile. Physically, DOC is categorized as organic compounds that can pass through a 0.45 μm filter, though this is merely an operational definition [27]. Any particulates that do not filter through are designated particulate organic carbon (POC) [27].

DOC can be further divided, based on composition, into humic and non-humic fractions. Humic material contains both aromatic and aliphatic components with amide, carboxyl, ketone, and other functional groups [28]. The humic fraction can be further categorized into humic acids, fulvic acids, and humin. The criteria for inclusion into each of these three categories are based on solubility properties at specific pH levels [27]. Humic acids are soluble in water until pH < 2, and contain the highest molecular weight samples of the humics—in the range of 1500–5000 Da in natural waters [29]. Fulvic acids are soluble at all pH levels found in nature, and range in molecular weight between 600 and 1000 Da in natural waters [29], while humin is not soluble in water at any pH [27]. Further, fulvic acid characteristically has more carboxylic groups and oxygen atoms, while humic acid has more phenolic and aromatic groups with longer aliphatic chains [30]. Because humic acids have longer aliphatic chains, they tend to be more nonpolar than fulvic acids, making them less soluble in water [30]. Humics tend to have fairly broad absorption spectra, absorbing most intensely toward the blue region of the visible spectrum [31]. Though models of the molecular makeup of humic compounds are still debated, a representative model structure of a humic acid has been suggested in the literature (see ref. [32] for a representative image). More recent studies have increased the understanding of the composition of DOC beyond the classic categories of humic and fulvic acids using techniques such as nuclear magnetic resonance (NMR) [33], high performance liquid chromatography (HPLC) [34], and Fourier transform ion cyclotron resonance mass spectrometry (FTICRMS) [35]. FTICRMS, coupled with electrospray ionization (ESI), appears to be a promising method for resolving humic and fulvic acids at a molecular level. ESI-FTICRMS has been used, for example, to differentiate between autochthonous and allochthonous dissolved organic matter in marine environments [36], to assess changes in DOM brought about by its interaction with sunlight [37], and to compare and contrast humic and fulvic acids at nearly the molecular level [38,39].

Figure 1. Simplified Venn representation of the various forms of organic matter found in natural waters. Total Organic Matter (TOM), Total Organic Carbon (TOC), Dissolved Organic Matter (DOM), Dissolved Organic Carbon (DOC), Particulate Organic Carbon (POC), Dissolved Organic Nitrogen (DON), and Dissolved Organic Phosphorus (DOP) are represented. DOC can be further broken down to its humic (humic acid, fulvic acid, and humin) and non-humic material, while new analytical methods continue to reveal more molecular-level detail.



DOC is a complex material containing many molecules with a variety of functional groups—including phenolic compounds (which are of particular interest in this review). The phenolic components of DOC tend to be more recalcitrant to biodegradation [40], especially when compared to aliphatic compounds, and only certain microorganisms, including specialized fungi [41], seem to be able to decompose them [42]. As such, phenolic compounds have the potential to remain in the environment longer and some suggest the breakdown of lignin phenolic compounds may be a rate limiting step in the terrestrial carbon cycle [42,43]. In contrast, lignin phenols can be highly susceptible to photodegradation, and in areas that receive high levels of solar radiation, phenolic compounds have been shown to have faster rates of degradation [40]. Humic material can arise from the microbial breakdown of plants and organisms during the process of humification. The exact molecular mechanism of the humification process, though not fully understood, has been explained by lignin-based and polymerization/condensation-based processes [27]. Humic material can also be completely decomposed over time and ultimately returned to the atmosphere as CO_2.

The varied sources of humic material give rise to different spectroscopic properties. As an example, researchers have noted that humics from microbial-derived sources have less aromaticity than humics from terrestrial origins [44–46]. McKnight *et al.*, have proposed that samples with a Fluorescence index (FI) (fluorescence intensity at 450 nm/intensity at 500 nm, both measured at 370 nm excitation) of ~1.9 can be attributed to fulvic acid components of microbial origin [45]. In fact, SanClements *et al.*, showed that increasing DOC in U.S. lakes, which accompanied decreasing sulfate deposition, correlated with a decrease in FI [47]. Similar characteristic spectral responses are the basis for the classic fluorescence spectral classification schemes for DOC proposed by Coble [48,49]. Some studies have further used multidimensional fluorescence spectroscopy coupled with chemometric analyses to categorize modeled components with various types/origins of humic material [50–53].

2.2. DOC Sources and Production

Sobek *et al.*, report that DOC concentrations range from 0.1 to 322 mg/L, with a median concentration of 5.71 mg/L, for 7514 lakes studied in six continents [54]. A main source of DOC in natural waters is the leaching of degraded organic matter from the terrestrial landscape into freshwater systems. The breakdown of aquatic organisms and *in-situ* heterotrophic production can also contribute to DOC concentrations (referred to as autochthonous), but this review focuses on DOC that is exported from terrestrial sources (allochthonous), which is largely influenced by hydrology, temperature, and land-use/cover [55–58]. In a Swedish lake system, it has been estimated that less than 5% of aquatic DOC is autochthonous [59], while in others, particularly systems located in temperate ecoregions and those subject to extensive anthropogenic modification, autochthonous DOC production can exceed allochthonous inputs [55,60,61]. In soils, due to solubility dynamics, an increase of 0.5 pH units can lead to about a 50% corresponding increase in DOC release (though acidity can have an impact on microbial mediated production of DOC as well) [62] and increases in pH have also been shown to enhance the mobilization of DOC as a result of increased enzyme activities [63]. DOC mobilization can be reduced with increased ionic strength of the soil environment, though anions like sulfate, can compete with DOC for soil adsorption sites, thus partially increasing DOC mobility [64] Acidity and ionic strength are important players in the atmospheric chemical deposition mechanism for explaining DOC increases.

With terrestrial origins, allochthonous DOC production is principally described as the result of carbon assimilation via primary production in higher order plants, and is largely a function of the subsequent microbial degradation (or the leaching of plant litter in soils, which may be partially broken down) [64]. Greater amounts of primary production yield a higher accumulation of plant biomass that can become DOC. The plant material can introduce organic matter to its surroundings directly through root exudates, which can be further broken down to become DOC [64]. In addition to the mentioned biotic pathways (enzyme-catalyzed reactions), biomass can also be degraded abiotically (largely through photochemical processes), but often to a lesser extent than biotic processes [65], depending on regional climatic conditions. With plants, a portion of their biomass will be consumed by herbivores [66] whose subsequent death and degradation can be a secondary contribution to the net DOC. Another source of DOC production is through the release of organic matter via the breakdown of the microbial biomass itself [64]. The type of plant species producing the DOC is important in terms of the ultimate quantity that is produced; for example, coniferous dominated ecosystems produce about 50% more DOC than hardwood dominated ecosystems [64]. Likewise, the availability of inorganic nutrients during degradation, microbial environment acidity, and soil moisture (and its related conditions for dictating aerobic or anaerobic microbial degradation) can dictate the amount of DOC produced [67].

It is worth noting the importance of high latitude ecoregions on the bulk production of DOC. The subarctic and boreal regions have been subject to much attention in regard to DOC mobility/runoff into waterways in part because they are responsible for an estimated one-third (390–455 Gt C) of global soil carbon [68], representing 10%–15% of global terrestrial carbon [69], and the arctic delivers 25–36 $TgCyr^{-1}$ [70] to the Arctic Ocean, a quantity that is predicted to increase with a warmer climate. The subarctic is home to large stocks of peat, produced mainly by various species of *Sphagnum*, making it an important region for studies of global carbon sequestration and DOC production. Ultimately, peatlands can add to the global carbon budget in that they are areas where primary production can be greater than decomposition, resulting in a net carbon sink [68] and are therefore of particular significance in the broader context of climate change.

3. Changing DOC Concentrations in Natural Waters

DOC has shown changes in measured concentrations in natural water systems over the past few decades, with a large number of reports coming from North America and northern Europe [22,31,47]. At these sites, over the monitored timeframe (typically one to three decades), the DOC levels have largely been shown to be increasing, and in some cases, may have more than doubled. While the ubiquity of the observed changes in DOC is still up for debate, the vast majority of sites claimed data that show an agreement with the stated trend, though a few geographical areas report no increase and sometimes even a decrease in DOC concentration. Below we will discuss several notable examples of DOC trends in the literature. For a critical review with comprehensive analyses of analytical and data treatment methods of long-term (>10 years) DOC monitoring studies in the literature, readers are encouraged to see ref. [2]. In this review, our intent is to highlight the primary drivers responsible for changes in DOC and to emphasize the complexity of these drivers as they relate to changes in DOC.

A review of the literature indicates that the systematic monitoring of DOC in natural water systems was not pervasive much before the 1980s, though a few studies go back as far as the 1970s—and even the 1960s. DOC in natural waters has been measured in several countries, including parts of Northern Europe, United States, Canada, Korea [71] and Africa [20] and almost all studies report DOC to be increasing [8,9,11,12,14,31,72–95]. Natural waters in the U.K. have been among the most thoroughly studied, in part because of the monitoring conducted by the U.K. Acid Waters Monitoring Network (UKAWMN), which has been measuring the chemical, physical, and biological traits of 11 streams and 11 lakes since 1988 [22,31]. All of the 22 UKAWMN sites showed DOC concentration increases, with an average increase of 91% over a 15 year period [9]. In the U.S., general increases in DOC levels have been reported in the waters of the Adirondack and Catskill Mountain regions of New York State [8,75,81,84,85,96]. Monitored sites in Vermont and Maine showed a few areas of small to moderate rises in DOC levels, while Pennsylvania did not show general increases [8,84]. A study in Canada showed DOC levels increasing 30%–80% in parts of that country during a 20 year period [97]. Areas of Central Europe [98,99] and Siberia [100–102] have also shown marked increases in DOC levels of their natural waters. Models have also predicted DOC level increases in the natural waters of Japan, New Zealand, and portions of China [82].

As one of the most comprehensive intergovernmental studies [84] of DOC, another report of natural waters over a dispersed area (studying 189 water sites in six regions of Europe and six regions of the U.S.) showed some interesting long term trends. All of the European, and all but one of the U.S., regions showed increasing DOC trends in monitored natural water over a twelve year period [84]. The one area that did not show the increasing DOC trend was the Blue Ridge Mountain region of the U.S. [84]. And in another significant study, 68% of 315 varying size natural water sites in the U.K. displayed significant increases in DOC levels over one to four decades [91]. In an even larger study of 522 streams and lakes in North American and Europe, 88% of the surveyed sites showed increases in DOC concentration between the years 1990 and 2004 [8].

4. Mechanisms for Changing DOC Levels

There are several mechanisms that have been used to explain variations in DOC availability and production in freshwaters. Readers are encouraged to see the reviews in refs. [64,103] for discussions of the biogeochemistry and mechanisms potentially responsible for DOC concentration variations in water. As stated, a focus of this review is to explore the widely discussed mechanisms of decreased atmospheric acid deposition and climate change agents, specifically elevated atmospheric CO_2 and temperature, but related precipitation/hydrology and land-use will be introduced as well. Of particular interest here are the mechanisms that are, or will be, factors under a changing climate. Caution should be applied, however, when attempting to explain DOC changes using a reduced number of drivers as changes in DOC are controlled by a variety of complex, interrelated processes, many of which are not fully understood. Fitting schematic diagrams and tabulated information illustrating the complexity of these drivers at work in the terrestrial transport of carbon to inland waters can be found in two quality reviews [104,105].

4.1. Atmospheric Chemical Deposition-Related Increases in DOC

Though the impact of climate change agents are intriguing and are a focus here in subsequent sections of this review, some researchers believe that the impacts of climate change cannot explain the magnitude of reported DOC increases [8] at their study sites. Atmospheric chemical deposition (often referred to as “acid deposition”) has been postulated as the main driver responsible for the observed increase in DOC concentrations in natural waters at specific study sites [8,9,31,73–75,83,84,88,94,106–108]. One of the more cited papers on the topic reports that the observed increase in DOC levels is the result of decreases in anthropogenic sulfate, sea salt, and other chemical species in the atmosphere that deposit in the soil [8]. This inverse relationship is believed potentially to be able to account for the magnitude of DOC increase that elevated temperatures and increased atmospheric CO_2 levels alone are seemingly unable to approach, but due to the fact these drivers vary contemporaneously, it is difficult to rule out one driver over another.

As previously highlighted, measurements from 522 lakes and streams in the U.S., Canada, and northern Europe were used to show how increases in DOC concentrations during the time span of 1994–2004 correlate with reductions in atmospheric chemical deposition [8]. In fact, the argument could be made that the observed DOC increases are merely steps toward the DOC levels returning to pre-industrial levels, before anthropogenic sources began adding chemical pollutants to the atmosphere (beginning in about 1750, peaking in the 1970s, and decreasing ever since) [8]. The major chemical in the atmospheric chemical deposition model, sulfate deposition from air pollution, has decreased by about 50% between the years 1986 and 2001 in the U.K. [109] due to notably successful international air regulations. As a consequence, large-scale reductions in sulfate deposition have been observed in many countries.

Simultaneously, increases in nitrogen emissions over the past 150 years have resulted in increases in deposited atmospheric nitrogen (N), which has resulted in an accumulation of N in soils and greater fluxes of N in rivers and streams (in addition to N from agricultural runoff) [110]. It has been hypothesized that increased soil N will stimulate the microbial processing of DOM, resulting in a net decrease in DOC that is available for export to the fluvial network as it is potentially outgassed as CO_2 [10], though experiments designed to test this hypothesis have produced conflicting results [111–114], possibly indicating that N deposition alone is not responsible for changes in DOC [103]. One study points to the significance of nitrogen deposition in bogs, because bogs receive their nutrient supply almost exclusively through atmospheric deposition [114]. The authors of this study show that increased N deposition may result in increased DOC release and an enhancement of phenol oxidase activity in *Sphagnum* litter, promoting peatland carbon release through DOC export and increased outgassing to CO_2. More research into the interplay between C and N cycling is warranted, as much remains not fully understood, particularly the extent to which high N deposition rates will influence plant productivity and litter decomposition. Further, for the purposes of this review we chose to focus primarily on sulfur deposition as it is the more abundant atmospheric deposition chemical referenced in the literature for explaining DOC increases in freshwaters.

It has been observed in the aforementioned studies that sulfate deposition has become significantly reduced [84], while coastal areas in northern Europe recorded reductions in sea salt (a proposed secondary contributor to DOC increases) [115]. And though most of the 522 studied sites showed the inverse relationship between DOC and sulfate concentrations, some coastal areas showed increasing DOC that was not accompanied by significant decreases in sulfate—but these areas showed significant decreases in chlorine concentrations [8]. Models showed that more than 85% of the total anion effect on DOC was a function of anthropogenic sulfate reductions in most of the studied geographic sites [8]. In some areas, the total anion effect was dictated by chlorine to about the same extent as sulfate, and the two anions likely impact DOC concentrations in water by similar mechanisms [8].

The solubility of the bulk of humic matter in soils is largely dependent on acidity [116] and/or ionic strength [117], as increases in either will decrease DOC solubility in laboratory experiments [64]. Acid deposition, specifically by sulfuric acid will increase the acidity as well as increase the total anionic strength (predominantly, increased $[SO_4^{2-}]$) of the soil environment, while sea salt deposition also increases the total anionic strength (increased $[Cl^-]$). A net result of the greater deposition of these chemical species is the decreased solubility of DOC in soils, yielding less mobility to water catchments and resulting in lower DOC levels. Conversely, the observed trends in the reduction of atmospheric chemical deposition should lower soil acidity and anionic strength, allowing for greater solubility of DOC and accounting for the observed increases in DOC concentration in natural waters. Indeed, in a recent study using U.K.-wide upland soil pH datasets, a correlated relationship between DOC and acidity changes was observed [118], lending further support to the chemical deposition paradigm for explaining DOC increases in these systems.

Increasing DOC levels in natural waters can actually be accompanied by increasing organic acidity, as many of the components of DOC are acidic (like humic and fulvic acids). In fact, the presence of these organic acids may be counterbalancing the contributions of declining acidity due to acid deposition—slowing (buffering) recovery from the acidification of the natural waters [8].

Though the trend toward increases in DOC levels, and specifically the link with decreasing sulfate deposition, is compelling, there are a few datasets that show regional areas where DOC is not increasing, despite declining sulfate deposition [76,90,91]. Some argue that DOC concentrations were increasing in the 1960s (or earlier) when sulfate deposition was still increasing and that laboratory studies on the quantitative role of acidification on the mobility of DOC can be ambiguous [119]. In all, it is apparent that a causal relationship between DOC levels and reduced acid deposition may be difficult to establish, especially in areas where the magnitude of DOC changes are small, and that the exact mechanism for changing DOC may include a more complex combination of drivers.

4.2. Climate Change Driven Increases in DOC

Due largely to anthropogenic contributions resulting from the combustion of fossil fuels, the atmospheric concentration of CO_2 has increased by over 60 ppm since 1960 and could rise to about double its current concentration of about 400 ppm by the year 2050 according to IPCC estimates and interpretation of their various models [120,121]. Likewise, an average increase in the global temperature of 0.74 °C has been observed over the past 100 years, and the IPCC estimates that the global temperature could rise by about another 3 °C by the year 2100 (depending on the prediction model chosen) [121]. Many detrimental effects are predicted as a result of climate change, however, the impact of increasing levels of DOC in natural waters has not received as much attention in the IPCC report, perhaps in part because the complex dynamics of terrestrial carbon export are not yet fully understood [121] and available for prediction. Furthermore, net temperature increases are expected to be greatest and most rapid at mid and high latitudes, where the majority of the global peat stock is contained [122].

The various agents associated with climate change have been reported as possible causes for the observed increased DOC levels in several natural water systems [11,12,14,68,69,76,77,79,89,97,98, 100,101,123–129]. As precipitation and its associated hydrology changes are functions of our natural climate, they too have been proposed as dynamics that will change with climate change [121]. Further, hydrologic changes have also been postulated as mechanisms for the observed increases in DOC [92,130,131].

Much of the primary literature related to climate change and its presumed impact on DOC concentration in natural waters deals with increased levels of atmospheric CO_2 and temperature warming. As will be discussed in relation to DOC increases, temperature can play a role in microbial degradation rates and atmospheric CO_2 can increase primary production and root exudates. A secondary outcome of elevated levels of atmospheric CO_2 can be the shift in the population of one plant species to another, where the species taking over the environmental area might assimilate and turnover biomass to DOC more readily. Other drivers are significant in terms of regional observations in DOC, including land-use change and modified hydraulic flow-paths, which will be discussed in subsequent sections.

4.2.1. Increasing Atmospheric CO_2

Increases in plant biomass can accompany elevated atmospheric CO_2 concentrations above ambient levels. This increase is largely due to enhanced levels of primary productivity by plants, and related increases in root exudates [12,69]. In fact, CO_2 "enrichment"/"fertilization" is a technique that has been used by farmers/gardeners in the U.S. to increase their crop yields (strategic biomass) since the mid-1960s [132]. Several controlled laboratory experiments have demonstrated increased biomass accumulation and increased primary productivity under increased atmospheric CO_2. Since 1999, free-air CO_2 enrichment (FACE) technology has been applied to a variety of ecosystem studies; including deciduous, alpine, and evergreen forests; deserts; grasslands; and bogs [133]. FACE experiments have been crucial to our understanding and defining of the ecological processes and responses that occur under elevated atmospheric CO_2 concentrations, especially as it pertains to refining quantitative modeling, but FACE experiments are not always conducive to application to global ecosystem processes [133]. One of the major advantages of FACE experimentation, over laboratory microcosm experimentation, has been the ability to experiment in a larger temporal and spatial context, allowing for the creation of improved models of real-world ecosystems.

Through empirical studies, researchers have predicted an increase of about 20% DOC production when atmospheric CO_2 levels are at twice their recent ambient levels [134]. During a three year experiment of peat monolith samples, the concentration of CO_2 in solardomes was held constant at 372 ppm (matching that of the ambient air at the time) in control samples and at 607 ppm (ambient + 235 ppm) in elevated CO_2 samples [69]. At the end of the three year experiment, pulse isotope labeling studies were conducted on the control and elevated CO_2 samples by exposing them to $^{13}CO_2$ for five hours and monitoring the assimilation of the ^{13}C at various time intervals using collected leachate and plant tissue for analyses [69]. Under conditions of elevated CO_2 levels, measurements of DOC in leachate collections resulted in a 66% increase in concentration over measurements taken from the control samples, while the above and below ground biomass increased by 115% and 96%, respectively [69]. Likewise, $^{13}CO_2$ pulse labeling showed about a ten times increase in "new" (produced within 24 hours of the label exposure) labeled DOC (^{13}DOC, in this case) [69]. The pulse labeling experiments indicate increased exudation (from the roots of increased biomass) as the dominant driver of DOC production under elevated atmospheric CO_2, while microbial degradation still plays a role over the longer term of the isolated ecosystem. Also, the *Sphagnum* moss dominated peat samples shifted greatly toward vascular (lignified tissue) plants, which assimilated 49% more ^{13}C during isotope pulse labeling and led to higher overall DOC production [69].

In terms of allochthonous DOC, some is further broken down and fractions are even returned to the environment as outgassed CO_2, contributing to atmospheric CO_2 concentrations. If further decomposition of organic matter is inhibited, greater quantities of DOC could be released to runoff. In the case of experiments under elevated CO_2, a presence of greater amounts of phenolic compounds (which may further inhibit the breakdown of DOC) was found [89]. The phenolic content of DOC can be an important indicator in the climate change-related mechanisms and its presence is also of concern when water is chlorinated for drinking purposes (discussed in subsequent sections).

One of the more cited articles on the subject of the role of elevated atmospheric CO_2 levels reports increases in DOC concentrations of 14%, 49%, and 61% for bog, fen, and riparian peatlands samples, respectively, at an elevated atmospheric CO_2 concentration of (235 ppm + ambient = 607 ppm) over three years of the controlled study [12]. For clarification, this study [12] was conducted by the same researchers who performed the above experiment [69], and in a parallel timeframe, but on two additional peat types (one of the three peat samples discussed here was the sole sample type reported in the study above). Of course, variations in both estimated and measured DOC levels are expected with the different ecosystems that researchers might be studying (e.g., different forms of peatlands, pine *vs.* deciduous), nutrient availability needed to assist humification, soil moisture, and other variables. This study also showed the similar trend in the shifting of species composition of the isolated environment toward more vascular plants [12]. Fen and riparian peatland soils tend to be rich in the nutrients needed for humification, while bogs tend to be deficient in nutrients, including phosphorus and nitrogen [135]. This nutrient dependence points toward a mechanism of primary production enhancement accompanying elevated atmospheric CO_2 levels for the production of the DOC end product, as the nutrients are needed for primary production of biomass [12]. In soil types where nutrients are less available (like in bogs) [135], the amount of nutrients will be the limiting factor in primary production—showing less sensitivity to environmental stimuli (like increases in atmospheric CO_2 levels) [136].

To support the hypothesis that primary production is responsible for the DOC increases under increased atmospheric CO_2 levels, $^{13}CO_2$ was again used as a marker when it was exposed for five hours to the contained atmosphere of peat monoliths that had been under ambient and elevated (235 ppm + ambient) atmospheric CO_2 levels for about three years [12]. Through photosynthesis and translocation processes, the ^{13}C was traced to the DOC leachate from the monoliths [12]. Not only was more ^{13}C translocated into the sample's biomass (56% more in tissue studies) under elevated atmospheric CO_2 conditions, but the amount of DOC in the soil that was attributed to the "newer" assimilated ^{13}C throughput was an order of magnitude higher [12]. Again, the authors attributed this to the fact that primary production (and associated root exudates) appears to be more sensitive to elevated atmospheric CO_2 levels than microbial degradation [12], which will be discussed further in relation to temperature sensitivity.

Despite the presented data, some believe that elevated atmospheric CO_2 levels cannot account for the magnitude of the observed global trend in DOC concentration increases. The elevated atmospheric CO_2 level (about 607 ppm) used in the two related studies outlined above is much higher than the approximate 20 ppm in atmospheric CO_2 increase that has been measured during the timeframe in which the observed global DOC concentrations were increasing. This poses a challenge to arguments surrounding elevated atmospheric CO_2 levels being solely responsible for the magnitude of observed global DOC concentration increases in freshwaters. Opponents of the elevated atmospheric CO_2 mechanism state that, assuming a linear relationship between DOC increases and elevated atmospheric CO_2 levels, that the group's [12] data for bog, fen, and riparian peat sample would represent only 1.2%, 4.2%, and 5.2% DOC concentration increases, respectively—at the approximate 20 ppm increase in CO_2 concentration over the 20 years of the UKAWMN measurements [9]. It should be noted that bog, fen, and riparian peatlands dominate the U.K. ecosystems of the UKAWMN monitored waters [9]. This is perhaps one reason why the atmospheric chemical deposition theory has been mentioned as an additional or alternative theory to this atmospheric CO_2-controlled increase.

Many FACE experiments have been conducted in a variety of ecosystems. For example, a group at Duke University's Forest FACE experimental station has established an experiment that subjected an actual pine plantation (*Pinus taeda)* in North Carolina to elevated atmospheric CO_2 levels equal to some climate model projections for the year 2050 (about 550 ppm) for twelve years [127]. In a more recent example, a FACE study in the Swiss Alps looked at the effect of elevated atmospheric CO_2 concentrations on a forest near the timberline consisting mainly of a pine species (*Pinus uncinata)* and a deciduous tree species (*Larix decidua*) [137]. More than eight different hypotheses were tested during the most intensive period of FACE experimentation at various sites (1999–2011) and many proved difficult to support [133]. The most well supported hypotheses appear to be in relation to (1) an observed increase in net primary production per unit of leaf-area index (LAI); (2) an apparent closure of leaf stoma in response to elevated CO_2; (3) elevated CO_2 can apparently alter intra- and inter-specific competition for soil resources amongst forest trees, potentially signifying a change in species composition with elevated atmospheric carbon; (4) a weak increase in soil microbial activity under elevated CO_2; and (5) that elevated atmospheric CO_2 does not necessarily imply an increased ecosystem C storage [133], which may have implications for DOC levels within catchments. While FACE experiments have increased our understanding of some ecosystem responses to increased CO_2, many questions remain, but FACE experimentation has demonstrated how complex the interactions of C in an ecosystem are, how they may vary regionally, and how a multidisciplinary approach to DOC research is further warranted to fully understand the dynamics of carbon through ecosystems [133].

4.2.2. Increasing Temperature

Temperature rises are believed to increase DOC levels in natural waters, though the increase has been primarily attributed to improved activity by microorganisms, and specifically by enzyme activity (especially by phenol oxidase) [11]. Phenol oxidase is an enzyme that catalyzes the oxidation of phenolic compounds to quinines [138]—which may occur by extracellular enzyme hydrolysis or by microbial metabolism [12]. Controlled studies on peat samples showed direct increases in DOC production with warmer temperatures [11,129]. In one study, a 10 °C increase in sample environment yielded a 36% increase in phenol oxidase activity, a 33% increase in DOC concentration found in leachate, and a 72% increase in phenolic compounds found in leachate [11]. The presence of higher levels of phenolic compounds is significant, as they are known to inhibit the further breakdown of DOC [139]—making them more available for transport to natural waters [140], including those used as drinking water sources. Additionally, in a study of peat porewater DOC concentrations, warming with infrared lamps (temperature increase of 1.9 °C) produced DOC concentrations about 15% higher than those in controlled, non-heated peatland plots [129]. Further, DOC from the warmed plots degraded faster in lability experiments than the control plots and showed a decreased aromaticity using "specific UV absorbance" ($SUVA_{254}$ = Absorbance @ 254 nm/[DOC]), which suggests an associated increase in microbial activity [129].

Despite the above preliminary findings, the effect on DOC levels using the net global temperature increase estimated by IPCC (0.5–0.7 °C) over the past several decades falls short of explaining the observed DOC trends that have been monitored globally—and a 10 °C increase would likely be a more reasonable temperature rise required to explain the observed global DOC trends [12]. It should be noted that a 10 °C increase in the next century is not projected by any of the current IPCC models. For clarification, the 10 °C rise in temperature chosen in the experimental method of the early study [11] was likely chosen to correlate with the common biological activity coefficient, Q10 (the measure of biological activity over an applied 10 °C increase), not to necessarily match IPCC climate change scenarios. Also, these earlier temperature increase studies were performed on very nutrient rich peat samples that might be expected to be more sensitive to warming (with sufficient nutrient availability to accommodate enhanced microbial activity), but might not be fully representative of all the geographical areas that are producing the observed DOC increases [9]. Nevertheless, other peat soil sample types have been found to be even more sensitive to DOC production due to warming, with even greater increases in aerobic microbial conditions [130]. Though water saturated peat samples are known to produce DOC largely by anaerobic means, there are layers that degrade aerobically due to seasonal drying in the soil [9]. Aerobic degradation and possible future droughts predicted by climate change scenarios could have a synergistic impact on increases in DOC production in soils.

It is estimated that the global 0.5–0.7 °C temperature increase during the time when many DOC levels were actively being measured could potentially be responsible for a 10%–20% increase in DOC concentration in the areas and soil types that were monitored [9]. Still, researchers who make these estimates maintain that they measured a much larger average DOC increase (91%) over about 20 years on a large and geographically diverse data set from the U.K. [9]. Another study cites temperature as potentially being responsible for about 12% of the 78% total DOC increase in a U.K. peat catchment [79]. So, even though rising temperatures appear to be a plausible player in explaining DOC increases, scientists are looking for other mechanisms to account for the larger magnitude of observed increases.

4.2.3. Combined Effect of Increased Atmospheric CO_2 Concentration and Temperature

The combination of elevated CO_2 and temperatures, in conjunction with longer growing seasons, might show additive or synergistic increases in the DOC levels found in natural waters. Experimental investigations on the separate roles of these climate change agents show that they can have at least a partial effect on DOC concentrations in natural waters. Inasmuch as climate change predicted scenarios strongly indicate increases in both atmospheric CO_2 levels and temperature, the interaction of these two factors on natural water DOC concentrations is also of interest. Perhaps, the combined effect can account for both individual models' shortcomings in regard to the magnitude of observed DOC levels that they appear to entail.

In an extension of the studies discussed above (separate/isolated warming and elevated atmospheric CO_2 experiments), the same research group performed a parallel study, again on peat monoliths of riparian peatlands in solardomes and over a three year period [89]. Their data showed a 119% increase in DOC concentration in collected leachate when under a combination of elevated atmospheric CO_2 (again, ambient + 235 ppm CO_2) and temperature (ambient + 3 °C, for this experiment—as opposed to 10 °C discussed for the above experiments) conditions compared to samples kept under ambient (average 372 ppm CO_2 and seasonal average temperatures) conditions [89]. Separate samples kept in elevated atmospheric CO_2 and elevated temperature conditions alone produced 36% and 22% more DOC, respectively, than ambient control samples in collected leachate [89]. It is important to note that the additive effect of the isolated elevated conditions accounts for less than half of the DOC production under the combined condition. The synergistic increase in DOC concentrations for this study is indicative of the potential impact of climate change on DOC flux in natural waters worldwide.

In this same study, both above and below ground DOC concentrations were shown to increase synergistically with the combined treatment conditions [89]; above ground biomass increased by 284% and below ground biomass increased by 407% [89]. Peat Poly-β-Hydroxyalkanoate (PHA) is a microbial nutrient stress indicator that is used to assess competition for inorganic nutrients between the plants and the decomposition microbial agents [128], and was shown to increase 30% under elevated CO_2, 19% under elevated temperature, and 51% under the combined conditions [89]. This was suggestive of an approximate additive relationship in the combined conditions. Phenol oxidase is an enzyme often accredited with the storage and translocation of organic carbon [11]. In this experiment, phenol oxidase decreased by 58% under combined conditions in an apparent synergistic relationship [89]. β-Glucosidase plays a role in the breaking down of general organic substances [89,141] and was shown to decrease by 27% in a slightly synergistic relationship between increased CO_2 and temperature [89]. Similar to the rationale for monitoring PHA, phosphatase can be used to determine whether there has been competition for specific phosphorous nutrients [89]. Phosphatase was shown to increase by 24% under combined conditions, but decrease 9% under elevated temperature and increase 33% under increased CO_2, suggesting neither an additive or synergistic relationship [89]. Phenolic compounds in collected leachate almost doubled in separate elevated atmospheric CO_2 and temperature conditions, and nearly quadrupled in the combined conditions [89]. This finding again indicates that these compounds are more prevalent because of the synergistic reduction of phenol oxidase activity (which breaks down phenolic compounds like those found in lignins, humic acid, and fulvic acid) in the combined conditions [89]. The combined treatment also displayed an additive increase in general microbial nutrient stress, showing microbial competition with the plants, straining the microbes to find available inorganic nutrients—which can be a limiting factor to net DOC production [89]. The results of these chemical measurements led to the development of mechanisms that explain the increased DOC measurements in terms of additive and synergistic effects of elevated CO_2 and elevated temperatures.

The enzyme, phenol oxidase, is an interesting single molecule in the global carbon cycle and has been examined in the literature in detail in regard to its mechanism of carbon assimilation. Phenol oxidase has been labeled the delicate "enzyme latch to the global carbon stock" as it regulates the stability of some 455 Gt C supply in peatlands, and is largely responsible for preventing the release of large amounts of CO_2 back into the environment and could have serious impacts on climate change [142]. Peatlands hold 20%–30% of the world's soil carbon supply, and in anaerobic conditions (true of most water saturated peatlands), the microbial breakdown of phenolic compounds is restrained [142,143]. Under these conditions, phenolic compounds remain in the soil and become available for transport, as part of the net DOC profile, to aquatic systems. Consequently, phenolic compounds are known to inhibit other enzymes from further breaking down organic matter, adding to the net availability of DOC for transport [142]. Some researchers believe that this "enzyme latch" mechanism could be responsible for a portion of observed DOC increases [42,79,142,143]. However, in the presence of droughts (that could accompany climate change), the microbial conditions could become more aerobic, increasing the activity of phenol oxidase, and encouraging the further breakdown of phenolic compounds (and subsequently, other organic compounds) [142,143]. Under these more aerobic conditions, total DOC available for transport may be diminished, but the process could release vast amounts of CO_2 back into the atmosphere [143] with potentially harmful consequences. It is interesting to note that biosensors based on the enzyme interaction of phenol oxidase have been studied for use as phenol sensors in water treatment processes [144].

Along with greater biomass production that is seen with the climate change agents, the suppression of the further breakdown of DOC by phenolic compounds might be a strong accelerator of DOC levels toward current trends. In the study detailed above, there were also changes in plant species composition of the peat samples in the elevated atmospheric CO_2 (slight shift), temperature (moderate shift), and combined (extreme shift) conditions [89]. Some of these potential climate change induced shifts in species composition of an environmental area might also add to the observed global increases of DOC levels in natural waters, as some species exude DOC more readily [89].

Even though it is still a point of debate, while warming and elevated atmospheric CO_2 mechanisms alone appear to fall short in explaining observed DOC level trends, it is conceivable that the synergistic effect of the two conditions combined might approach quantitative explanations of DOC trends. It is also noteworthy that the experimental conditions used in some studies—namely, combined elevated temperature and atmospheric CO_2 levels—are within feasible ranges of IPCC estimates for climate change conditions that could be experienced within the next 50 years or so. Therefore, even opponents of this mechanism for explaining recently observed DOC concentration trends in natural waters should be cognizant of the notion that these could well be the factors driving DOC trends under a changing climate in the near future and beyond.

4.2.4. Changing Hydrology and Its Effect on DOC Concentrations

Many changes to the water cycle are predicted as global temperatures rise, as the water cycle is particularly sensitive to changes in the climate [24]. It is predicted that there will be alterations to precipitation (flooding and drought), discharge, modifications to terrestrial flow-paths of water, and transformations to the hydrologic connectively of the world's water catchments with a warmer climate [121]. Variations in the hydrology of catchments will result in changes to the way DOC is transported, affecting the quantity and composition upon delivery to inland and marine waters. Tranvik and Jasson [145] discussed the significance of hydrology on the transport of DOC from streams to the ocean and stated the ways in which warming might have affected DOC export over a decade ago. Here, we intend to provide several examples of how hydrology affects allochthonous DOC quantity and composition in natural waters. Readers seeking more information, particularly in regard to autochthonous DOC and hydrologic changes, should also consider the comprehensive review of hydrologic changes and DOC associated with climate change provided by Porcal *et al.* [103].

Precipitation is expected to increase, decrease, and/or become more variable with climate change. Increases in the frequency and severity of droughts have been predicted in some geographic regions, while in others, increases in precipitation are likely, with more severe storm events and floods expected [121]. Changes in the amount, frequency, and seasonal timing of hydrologic events are significant considerations in the prediction of future DOC, as precipitation can increase terrestrial primary production and enhance the export of DOC to natural waters [104,146]. In a study with experimentally controlled drought and rainfall, drought was accompanied by decreases in DOC and its phenolic components, and increased precipitation was accompanied by significant increases in allochthonous DOC and an even more pronounced increase in the phenolic content of allochthonous

DOC [42]. Similarly, DOC concentrations decreased in response to a simulated drought that was shown to impact the metabolic activity of biofilms in waters from an experimental wetland [147]. In a study of the effect of drought on litter and peat, drought was shown to be the dominant factor to explain decreases in DOC releases from both sources and the DOC that was released was less hydrophilic in character, suggesting more difficulty in its removal for water treatment purposes [148]. Additionally, in a study in Australia, a severe, decade-long drought was followed by extreme flood events that effected large areas and persisted for several months [149]. During the drought conditions of this study, organic material accumulated on land and in dry fluvial channels, but once this material was again inundated, DOC rapidly leached into the water column of a multitude of streams, rivers, and lakes, resulting in conditions favorable for rapid microbial metabolism and hypoxia [149]. These events, commonly referred to as blackwater events, have also been reported in Brazil [150] and the southern United States [151] and often result in large fish kills. Blackwater events provide insight into the potential water quality challenges under more variable precipitation conditions in the future [149].

Soils that are well-drained, a characteristic of many upland watersheds, tend to have greater proportions of degraded, microbially-derived organic matter than soils located in lowland areas, such as swamps and marshes, where the soil is poorly-drained [152]. This suggests that microorganisms that breakdown DOC and phenolic compounds do so most efficiently in aerobic (water table drawdown) conditions. Under aerobic conditions, phenol oxidase activity increases and organic matter and its constituent phenolic compounds are more readily degraded [128,143]. This hypothesis has been further tested in peatlands, where drought was shown to increase phenol oxidase activity and bacterial growth in a series of *in vitro* and mesocosm experiments, as well as field observations [143]. Conversely, in high flow or flood conditions (anaerobic), not only might there be higher levels of phenolic compounds [63], but they could be more readily swept away by access to water flow. This was true in peatlands previously experiencing drought, where the effect of high flow conditions resulted in a re-wetting of the peat and carried markedly high concentrations of carbon away, in addition to re-establishing the anoxic pre-drought conditions [143].

The amount of water discharged from fluvial networks is an important consideration, as it can alter both vertical and lateral hydraulic flow-paths in catchments. Multiple studies have indicated that in temperate streams, for example, much of the DOC that is exported occurs during high-flow conditions [153–155] and is largely governed by intra-annual variation in hydrologic regimes [61,156]. Additionally, the composition of DOC exported during high-flow or low-flow conditions has been shown to change and is thought to represent alterations to the flow-path of water due to precipitation. For example, under high-flow conditions, stream waters were shown to contain DOM with large C-to-N ratios, increased aromaticity, and ^{14}C values which indicated that DOM had a less degraded nature, all variables that suggest DOM originating from the upper soil horizons, indicative of a surficial flow-path [152,157]. In contrast, streams under low-flow conditions contained DOM with much older ^{14}C ages, small C-to-N ratios, and a decrease in aromaticity—all indicative of a microbially-processed DOM from lower soil horizons, suggestive of a deeper, ground-water flow-path. Additionally, watersheds with mixed land-use, different land cover types, and anthropogenically modified hydraulic flow-paths can contribute to the DOC quantity and quality in rivers and streams (land-use will be discussed further in a subsequent section).

Jencso *et al.*, highlight the importance of hydrologic connectivity of a watershed in the transport of solutes [158] such as DOC. Hydrologic connectivity is subject to seasonal variation, for example, low connectivity occurs during the winter, when flows over land, to streams, and to rivers are often frozen or otherwise disconnected [158]. In the spring and summer seasons, DOC found in rivers shows signs of more terrestrial inputs (*i.e.*, increased lignin phenols) [159], suggesting a more connected landscape where water carries solutes from all regions of a watershed. Further, the IPCC has predicted that runoff resulting from the thawing of permafrost in the arctic and subarctic areas and subsequent formation of new ponds and lakes will increase the availability of stored carbon stocks [121] through increased hydrologic connectivity [160]. As permafrost thaws, the hydrologic connectivity of arctic and subarctic regions will increase, resulting in greater export of allochthonous DOC to fluvial networks, and ultimately, to the ocean.

Changes in the hydrology experienced by various watersheds will be an important predictor of DOC composition and quantity in the future, especially in areas of high and mid latitudes [161], on both regional and global spatial scales and short and long-term temporal scales. Additionally, increases or decreases in the abundance of ponds, lakes, and man-made reservoirs/impoundments are expected to change the way DOC is exported [104] and processed on land differently in different geographic regions, so additional studies to understand the effect of precipitation, discharge, hydraulic flow-path and the hydrologic connectivity of a catchment are warranted, especially under a changing climate.

4.3. Land-Use and Its Effect on DOC Levels

Analysis of satellite imagery reveals that human land-use activities, such as clearing of forested areas for agriculture and residential land-use, are transforming a large proportion of the earth's surface [162]. Human land-use, including modifications to hydraulic flow-paths, alters biogeochemical cycling, directly affecting water quality, including DOC input to aquatic ecosystems [163–165]. For example, Yallop *et al.*, found that land management may be the most significant driver of humic DOC fluctuations for their study conducted in the U.K. [166] and Gough *et al.*, showed that significant differences in DOC concentration, quality, and THM formation potential are all influenced by land cover type [165]. Further, nutrient enrichment of agricultural land is currently a leading cause of degraded water quality in U.S. coastal waters [167]. Waters with excess nitrogen and phosphorus are impaired by direct effects, like eutrophication, as well as indirect effects, such as changes in temperature, pH, and light attenuation [163,168]. But much less attention has been given to drivers of terrestrial carbon cycling in regard to land-use, especially in terms of land management decisions, where DOC is often overlooked [58]. Further, little is understood about the impact climate change will have on the drivers of DOC in varied land-use catchments.

Researchers have learned about the influence of land-use and land management on stream biochemistry in regard to carbon by analyzing the fluorescence characteristics of DOM [169]. In a recent study, the character of riverine DOM in 34 watersheds in south-central Ontario, Canada was examined in relation to catchment land-use, with findings showing a relationship between agricultural land cover and the composition of DOM in water draining these areas [170]. Values for FI and β/α (a ratio used to estimate the contribution of recently produced DOC, β, to its more degraded form, α) increased as the amount of continuous crop cover increased in the different watersheds [170]. The authors suggest that this indicates a more microbially-derived DOM character [170]. Additionally, they found that there was a strong correlation between total dissolved nitrogen and the DOM composition [170]. It seems that the relationship between DOM composition and the high nitrogen availability associated with agricultural land-use disproportionately increases microbial respiration and changes the composition of DOM, such that it is composed of more microbially-derived moieties. This implies that there may be decreased DOM availability in systems downstream from agriculturally dominated watersheds and that DOM transport distances are decreased [170].

In a similar study, the hypothesis that the optical characteristics of DOM are influenced by microbial activity and land-use, specifically that increased agricultural land-use leads to higher microbial signature in the optical properties of DOM flowing downstream, was tested [55]. They found that the microbial activity increased for DOM in streams with a higher proportion of anthropogenic land-use and that the fluorescence characteristics associated with more labile components in DOM increased with more agricultural land-use [55]. The authors mentioned that their study period was particularly wet and that the increased soil moisture actually made their correlation between more labile, microbially derived DOM stronger [55], pointing, again, to the significance of hydrologic regimes in regional DOC studies.

The main points from these spectroscopic studies are that land-use altered the quantity and quality of DOM exported from human-influenced streams when compared to more natural streams and that DOM from agriculturally dominated watersheds was more labile and supported higher microbial activity when compared to DOM from forested watersheds [55,170]. It is fairly unclear whether land-use will magnify or buffer changes to DOC concentrations and composition in regard to predicted climate change variables, but it is clear that land-use can contribute to changes in DOC levels in natural waters. Therefore, continued studies from varied ecosystem types can contribute to the overall understanding of terrestrial carbon cycling and its prediction in the future.

5. The Impact of Increased DOC on Drinking Water Supply and Treatment

Regardless of the exact driver for the observed increases in water DOC levels, there are several environmental and health concerns associated with the trends, especially in regard to its impact on drinking water. Because increases in aquatic DOC concentration can intensify the “color” of natural waters, higher levels can block the sun’s radiation from penetrating to reach deeper ecosystems, even though some DOC is beneficial to blocking solar ultraviolet (UV) radiation from damaging aquatic life. DOC also plays a role in natural nutrient transport [171], which in the case of excessive concentrations of DOC, can also increase the bioavailability of pollutants like mercury in natural waters [172]. As discussed previously, higher levels of DOC, and thus, organic acidity, can also make natural waters more acidic.

Higher concentrations of DOC in water systems that are used for drinking water supplies are a considerable concern for the treatment and disinfection of drinking water [107,173–179]. When treated by the most common chlorination practices, drinking water produced from sources with elevated levels of DOC can produce potentially dangerous by-products; including chloroform, haloacetonitriles, and chloral hydrate—along with the infamous trihalomethane by-products (U.S. EPA maximum drinking water level of THM = 80 ppb [176,180]). Alternatives to traditional chlorination disinfection techniques, like ozonation, and pretreatment strategies, like coagulation/flocculation or filtering, might be necessary for the treatment of natural water that is high in DOC concentration. Since 2006, the U.S. EPA has imposed more rigid regulations on water treatment disinfection by-products through "Stage 2" of their "Disinfection and Disinfection By-product Rule" [181].

In addition to the EPA, disinfection by-products are regulated by the World Health Organization and the European Union [176]. The problem of DOC levels and drinking water treatment have been reported in the U.S. [175,176] Norway [14,173,182], Sweden [178], Australia [173], and the U.K. [31,179], among other locations. In the Central Valley of California, where 23 million people receive their drinking water from the Sacramento-San Joaquin River watershed, DOC levels are a major concern for their drinking water supply [176]. As such, Sacramento's drinking water treatment has been the source of much study [175–177,183].

Studies that are aimed at characterizing the chemical structure of DOC in different input water systems, in order to select the best treatment strategy, are important. In one study, natural water sources of drinking water supplies for Norwegian and Australian systems found differing potentials toward the formation of disinfection by-products upon chlorination related to the chemical characterization of their DOC profiles [173]. In particular, the phenolic/aromatic portion of some DOC profiles are believed to be reactive sites for by-product formation [173]. In fact, a phenolic component of natural DOC, meta-dihydroxybenzene (resorcinol), is thought to be one of the major precursors to the formation of THMs [4]. As well, β-diketones found in DOC are also believed to be THM precursors [184]. Also, methoxyphenol is believed to be one of the most chlorine reactive components of DOC [185]. The phenolic content of DOC may increase under predicted climate change conditions, making DOC levels an even greater concern for water resource managers and treatment facilities.

Using multidimensional fluorescence with parallel factor analysis (PARAFAC) and ^{13}C-NMR studies, quinones (diketones being oxidized-quinones), were shown to represent significant portions of the DOC fluorescence profile [33]. Likewise, phenolic portions of humic acids from the International Humic Substance Society (IHSS) were identified with fluorescence/PARAFAC and reagent-based phenol assays [53] and lignin phenols found in several large artic rivers have been attributed to a PARAFAC-derived component [160]. In kinetic studies of THM formation upon chlorination of natural waters, it was shown that resorcinol components make up 15%–30% of THM precursors in natural water and are likely fast reacting (formed within first hours) THM precursors [4], while other phenolic compounds are likely slow reacting (from hours to weeks) THM precursors [4]. A mechanism has been suggested that involves chlorination by electrophilic aromatic substitutions of phenol that causes ring cleavage, followed by an addition/elimination pathway [186].

Aromatic molecules absorb strongly at 254 nm, thus UV_{254} (observed absorbance at 254 nm) has been suggested as a standard for measuring DOC [20,187]. Specific UV_{254} ($SUVA_{254}$), is the absorbance at 254 nm, measured in inverse meters, divided by an average DOC concentration in milligrams per liter. $SUVA_{254}$ has been proposed as a predicting tool for the evaluation of the suitability of waters containing DOC for the different water treatment methods [188,189]. The variability in "color" of DOC-laden water from different sources is often linked to its aromatic/phenolic content [26]. In the disinfection study mentioned above, phenolic portions of DOC were correlated to THM formation—and the relationship between UV_{254} readings and measured THM concentrations were examined [4]. The relationship between phenolic components of DOC in natural waters and climate change agents has been discussed here in detail, and the inherent importance in monitoring drinking water sources for such components appears to be an area of importance for future studies.

The different sources of natural waters within a system will contain different concentrations and compositions of DOC and inherent phenolic moieties. In effect, two different sampled locations could have the same net quantity of DOC, but because of differences in the composition of the native DOC, they will have different potentials for forming disinfection by-products. Hydrologic factors, including water flow, mixing, and transport, are crucial to understanding the fate of DOC (and its phenolic content) from its source location to its end water supply location. Land-use, anthropogenic sources, and seasonal variations can all impact the composition of DOC and phenolic compounds in water. Additionally, whether a result of climate change or a natural climate function, changes in the water table levels, including severe occurrences of droughts and floods, have an impact on DOC and inherent phenolic compound levels.

In the presence of higher levels of DOC, water treatment facilities may be forced to pre-treat their water with filtration, carbon adsorption, coagulation, or chemical techniques prior to disinfection by chlorination. These costly pretreatment steps often remove much, but not all, of the THM precursors and one study suggests some pretreatment steps may even double the proportion of brominated THMs, a disinfection by-product that is considered to be more carcinogenic than chlorine-derived THMs [179]. Furthermore, less time consuming and more cost effective methods will be required to assist water treatment plants and regulating agencies in monitoring drinking water in regard to potential for forming disinfection by-products. It has been reported that coagulation can reduce THM formation by 40%–50%, depending on the water source [190,191] and different portions of the DOC profile are removed more efficiently than others [50,192]. Pre-oxidation with ozone or chlorine dioxide leads to lower yields of THM upon chlorination [4]. Some scientists suggest that controlling DOC at the geographic source may even be the most economical way to control disinfection by-product formation [176,193]. Sometimes, drinking water supplies, primarily from surface waters, are mixed with groundwater reserves in order to dilute DOC concentrations; however, this practice can be counterproductive if the groundwater also contains DOC (or even a high fraction of phenolic compounds). In groundwater mixing of water supplies, bromine can also be introduced to the system, thereby introducing the potential for formation of brominated disinfection by-products [191]. Readers are also encouraged to see the review by Ritson *et al.*, in regard to changing DOM with climate change and the potential effects on water treatment processes [105].

6. Conclusions

The intent here was to review the issues and research related to observed increases in allochthonous DOC concentrations in several natural water systems, with particular attention to the impact on water resources under a changing climate, in the hope of providing renewed/sustained interest in the study of carbon cycling across the terrestrial landscape and to encourage a multidisciplinary approach toward current research in regard to the drivers of increasing allochthonous DOC levels. Climate change agents such as increases in temperature, variations in precipitation, drought, and related hydrology issues are complex in the way that they impact DOC levels, and may lead to either increases or decreases in aquatic DOC. The experimental evidence that relates elevated CO_2 and temperatures associated with climate change to allochthonous DOC increases in water provides the basis of a plausible mechanism for the increased production, and decreased net degradation, of DOC that is subsequently available for transport to area water catchments. Though it can be inferred that climate change has contributed to the observed increases in the DOC levels of natural water systems over the past few decades, the contribution might be less substantial thus far, as estimates show that elevated temperature and atmospheric CO_2 levels could account for only 10%–20% and 1%–5% of the observed DOC concentration increases, respectively [9]. The experimental controls in the climate change-DOC studies [11,12,69,89,129] often exceed the levels of warming and atmospheric CO_2 coinciding with the current increases in DOC, which makes it difficult to translate the results on a broader scale. In fact, the experimental conditions of most of these experiments exceed the IPCC predicted model for the next 50–100 years. Further, it is possible that climate change-related mechanisms might become increasingly responsible for continued variations in the net DOC concentrations in freshwaters—even before the climatic levels reach those of the experimental conditions.

The atmospheric chemical deposition paradigm predicts that DOC levels might stabilize in the future as sulfate deposition trends reach a lowered steady-state. In short, the current trend of increasing DOC potentially represents a return to DOC levels similar to those of the pre-industrial environment [8,118]. If atmospheric chemical deposition is a key driver responsible for the observed increased DOC levels over recent decades, the prevalence of its role will likely wane with decreasing deposition. Under these conditions, climate change agents may become a dominant mechanism in regulating DOC production and flux. Regardless, the role of DOC levels in selecting appropriate drinking water treatment techniques is an area of paramount importance.

Though not as heavily examined in the primary literature, it is likely that a combination of the major conceptual mechanisms could be occurring. Such a combination has been cited as possible causes for the observed trends in DOC [79,98,130,182,194]. Some studies indirectly state that more than 85% of DOC increases in different geographical areas can be explained by decreases in anthropogenic sulfate deposition, leaving room for other factors (like those of climate change) to contribute [8]. At the core of differentiating the two key conceptual models (or accepting a combination of the two) is whether primary production of DOC and microbial activity (and perhaps the related role of phenolic compounds) or solubility dynamics are driving the observed DOC changes in natural waters. As stated in the introduction, we have simplified our interpretation of current research to a reduced number of drivers of changes in DOC concentration by placing emphasis on two main paradigms presented commonly in the literature. While these drivers may correlate well at specific study sites, the complexity of the processes that govern the release of allochthonous DOC to inland natural waters is immense and may not lend itself to the establishment of distinct cause and effect relationships between a specific driver and specific instances of changing DOC over the spatial and temporal scales included in this review. Future studies should take a critical approach when assigning causal relationships to correlations, especially to explain DOC changes of a lesser magnitude.

It is proposed that future work on this topic should focus, in part, on the analysis of the phenolic composition of DOC. Not only could such a focus potentially assist in deciphering the two main mechanisms for DOC increases, but because of increasing projected climate change conditions (as well as trends of reducing atmospheric chemical deposition), the climate change model (and its inherent projected increases on the phenolic content of DOC) could become the primary driver of DOC levels in the future, especially in areas not subjected to historic acid deposition, areas undergoing land-use change, areas subject to a changing hydrologic regime, and areas situated in mid-high latitudes [118,161]. Studies of the phenolic composition would also be prudent due to concerns related to the role of phenolic compounds in the current and future treatment of drinking water.

Understanding carbon transfer across the terrestrial landscape and into aquatic ecosystems is important, especially considering the unprecedented anthropogenic environmental changes we are experiencing in the biosphere, lithosphere, atmosphere, and hydrosphere and the threat to drinking water sources [152]. To understand the effect of a changing climate on DOC quantity and quality in natural waters and to be better able to predict future DOC changes, it is apparent that work from multiple scientific disciplines is required to unravel the complexity of this issue. The multidisciplinary approach requires a commitment of collaboration from different communities of scientific research that often operate in isolation from each other [152]. Training new scientists to think in a more multidisciplinary way toward the subject of carbon cycling across the terrestrial environment will require exposure to a broad field of subjects in an educational setting. Ultimately, multidisciplinary collaboration will require effective communication of experimental findings and proposed paradigms, as well as an increased exchange between soil and aquatic disciplines [152].

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Conflicts of Interest

The authors declare no conflict of interest.

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