Water **2014**, *6*, 1360-1418; doi:10.3390/w6051360

OPEN ACCESS

water

ISSN 2073-4441

www.mdpi.com/journal/water

Review

Long-term Trends of Organic Carbon Concentrations in Freshwaters: Strengths and Weaknesses of Existing Evidence

Montserrat Filella [1,2,*] and Juan Carlos Rodríguez-Murillo [3]

[1] Institute F.-A. Forel, University of Geneva, Route de Suisse 10, Versoix CH-1290, Switzerland

[2] SCHEMA, Rue Principale 92, Rameldange L-6990, Luxembourg

[3] Museo Nacional de Ciencias Naturales, CSIC, Madrid E-28006, Spain; E-Mail: jcmurillo@ccma.csic.es

* Author to whom correspondence should be addressed; E-Mail: montserrat.filella@unige.ch; Tel.: +41-223-790-300; Fax: +41-223-790-329.

Received: 26 March 2014; in revised form: 25 April 2014 / Accepted: 4 May 2014 / Published: 20 May 2014

Abstract: Many articles published in the last few years start with the assumption that the past decades have seen an increase in dissolved organic carbon (DOC) concentrations in the rivers and lakes of the Northern Hemisphere. This study analyses whether the existing evidence supports this claim. With this aim, we have collected published studies where long series of organic carbon concentrations (*i.e.*, longer than 10 years) were analyzed for existing trends and have carefully evaluated the 63 articles found. Information has been collated in a comprehensive and comparable way, allowing readers to easily access it. The two main aspects considered in our analysis have been the analytical methods used and the data treatment methods applied. Both are sensitive issues because, on the one hand, the difficulties associated with correctly determining organic carbon concentrations in surface waters are well known, while, on the other, dealing with real environmental data (*i.e.*, lack of normality, censoring, missing values, *etc.*) is an extremely intricate matter. Other issues such as data reporting and the geographical location of the systems studied are also discussed. In conclusion, it is clear that organic carbon concentrations have increased in some surface waters in the Northern Hemisphere since the 1990s. However, due to a lack of data in many parts of the world, it is not known whether this phenomenon is general and, more importantly, in the areas for which such data do exist, the reporting and methodological problems in the published studies prevent any conclusion on the existence of a general temporal behavior of organic carbon from being drawn.

Keywords: organic carbon; DOC; dissolved organic carbon; temporal trends; time-series analysis; freshwaters; lakes; rivers

1. Introduction

Inland waters (ponds, lakes, wetlands, streams, rivers and reservoirs) occupy only a small fraction of the Earth's surface but have a disproportionate effect on the global carbon cycle. A large amount of the carbon taken up by terrestrial system ends up in inland waters. The resulting riverine export of terrestrial organic matter to the oceans is a key link between terrestrial and marine parts of the global carbon cycle. While the amount of carbon transported is small compared with the massive fluxes between atmosphere and land and oceans, overall it accounts for about half of the net ecosystem production [1,2]. Moreover, inland waters do not act merely as passive "pipes" for carbon transport; rather they are active components of the carbon cycle because organic carbon (OC) in freshwater bodies can also be buried in sediments or mineralized and released back into the atmosphere as carbon dioxide.

Over the past decades, it has become increasingly accepted that dissolved organic carbon (DOC) concentrations have been increasing in rivers and lakes of the Northern Hemisphere. If confirmed, DOC increase may have significant impacts, not only on the global carbon cycle, but also on freshwater food chains, the quality of drinking water and trace element and organic micropollutant circulation and ecotoxicity. The root causes of this increase remain unclear. Although a few review articles on the subject have been published [3–6], they largely uncritically accept the universality of DOC increase, collate published results and list suggested causes. They very seldom address issues related to the methodology used, quality of the results, *etc.* This critical study is an attempt to clarify the situation by analyzing published increasing trends and, in particular, the reliability of the analytical and data treatment methods used and, finally, to evaluate to what extent they are not the result of a belief system generated by a so-called "repetition cascade" (*i.e.*, repetition of claims) [7].

2. Methods

For literature searches we used the ISI Web of Science. Careful reading of published papers led to other references. Data considered in this study were restricted to studies published in peer-reviewed papers. Grey literature (*i.e.*, documentary material that is not commercially published, typical examples being technical reports and conference proceedings) was not included. Because of this choice, some presumably interesting results such as those of Monteith and Evans [8], Skjelkvåle [9], Stoddard *et al.* [10], Gruau and co-workers on French rivers [11,12] or Zobrist *et al.* [13] are not included. Although one might argue that taking account of some grey literature might be worthwhile, the facts are that its reliability is always difficult to assess due to the absence of peer-review control and that it is often difficult to access. These reasons finally prevailed. Note, however, that in many cases these data are either totally or partially published later in refereed articles, cases in point being Freeman *et al.* [14] and Evans *et al.* [15,16], who refer to Monteith and Evans [8], and Eikebrokk *et al.* [17] and Skjelkvåle *et al.* [18], who refer to Skjelkvåle [9].

Articles where changes in OC concentration have been studied over short periods of time (e.g., seasonal studies) or extensive comparisons among freshwater bodies in different climatic zones (e.g., [19]) that do not contain long time-series data have been excluded from this study. Since time scales that are too short do not allow long-term trends to be reliably detected, studies based on less than ≈ 10-year data series have not been included. On the other hand, studies where some surrogate parameter of OC (*i.e.*, color, absorbance, chemical oxygen demand) was measured instead of OC itself have been included. Finally, articles discussing trends in OC fluxes but not in OC concentrations have not been considered.

3. Results and Discussion

Sixty-three articles containing long-term OC concentration series have been identified. A few more studies reiterating previously published data or results (and giving the initial publication as a reference) are cited but not considered in the set. Publication dates span from 1989 to 2012. The key information contained in these studies has been collated in a systematic form in three tables. Table 1 collects information about geographical location, system characteristics, period covered, sampling frequency and data sources. Table 2 shows methodological –both analytical and statistical– information. Table 3 contains the trend results and, in order to facilitate the reading, some key information already provided in Tables 1 and 2. A significant effort has been made to give all key information in a simple and comparable way but this has not always been possible due to the disparate way in which ancillary and methodological information is sometimes given in the original articles.

3.1. Starting Considerations

3.1.1. Data Quality Traceability

Most of the long-series data come from government surveys and sometimes the published articles do not give either the characteristics of the water systems or the analytical methods used in detail. Where references are given, they sometimes refer to the grey literature, always difficult to access and assess, or to previous articles where the information is not always found. Since, in particular in the case of DOC concentrations, values depend heavily on the analytical procedure applied (see corresponding section), the reliability of the data and of the conclusions reached becomes, in practice, difficult to assess when sampling and methodological information is missing.

A point worth mentioning is that not all studies contain independent data. Rather, sometimes previously processed data are totally or partially reused in later studies. Regrettably, this is not always made clear in the articles in question (e.g., Dillon and co-workers publications on Canadian lakes, Worrall's on UK freshwaters). In some cases, such as in the many studies published by Worrall and co-workers based on UK data, tracking how the data sets are inter-related from the information given in the articles becomes really tricky. Connections between data sets are mentioned in Table 1 when clearly stated or when deduced after careful reading of the article but we are aware that we have probably not spotted all existing links.

A further factor that makes evaluating studies' reliability more difficult is the fact that very often non-transformed original data are not shown, even not in graphical form. When shown, it is mentioned in Table 2. Other types of data representation (e.g., month or annual means) are also mentioned.

Table 1. Published studies containing long-term organic carbon concentration temporal trends in freshwaters. System characteristics, sampling details and data sources.

Ref.	System						Period	Sampling frequency	Data source
	Type [a]	No.	Country	Details	General characteristics	Acid rain recovery? [b]			
[20]	river	1	Germany	River Elbe, km: 585–620; number of samples unknown Location on a map	Freshwater tidal zone; pre-oxygen minimum zone; salinity < 1	No	1985–2007	1985–1993: almost monthly 1994–2007: February, May–August, November	ARGE Elbe
[21]	lakes	30	Quebec, Canada	Located N of the St Lawrence River between Ottawa and Saguenay Rivers in Quebec Location on a map	Lake surface areas: 0.061–2.02 km^2 Max depth: 3–38 m Water retention time: 0.1–9 y (median: 1.8) Catchment areas: 0.42–6.96 km^2	Yes	1989–2006	Twice a year in spring and fall	Acid Rain Program of Environment Canada
[22]	stream	not clear	Wales, United Kingdom	Upper Hafren catchment, subcatchment of the Upper River Severn (Plynlimon) Location on a map	Catchment area: 1.17 km^2	NM	1990–2010	Weekly	Centre for Ecology and Hydrology (CEH) **Probably some data already included in [23]**
[24]	stream	1	Ontario, Canada	Plastic Lake catchment Location on a map	Small ephemeral stream	Yes	1987–1994, 1999–2009	Not given; probably information in [25]	Monitoring program, Ontario Ministry of Environment
[26]	rivers	11	Estonia	Large: Narva, Suur Emajõgi, Pärnu; small in N Estonia: Kasari, Vihterpalu, Keila, Vääna, Pudisoo, Valgejõgi; small in S Estonia: Väike Emajõgi, Võhandu Location on a map	Total catchment area: 57,619 km^2	NM	TOC: 1998–2007 COD: 1992–2007	6–12 times a year	Estonian national environmental monitoring programme

Table 1. *Cont.*

Ref.	System					Period	Sampling frequency	Data source
	Type [a]	No.	Country	Details	General characteristics	Acid rain recovery? [b]			
[27]	lakes	91	Canada	Atlantic Provinces: Newfoundland (NF) (14 sites), southwestern Nova Scotia (WNS) (45), eastern Nova Scotia (ENS) (23), southwestern New Brunswick (NB) (13) No list of sites given Approximate location on a map	–	Yes	NF, WNS: 1983–2007 ENS: 1990–2007 NB: 2000–2007	Semi–annually, during spring and fall overturn from May to October	Environment Canada monitoring at four Canadian Air and Precipitation Monitoring Network (CAPMoN)
[28]	lake	1	Switzerland	Lake Maggiore	Subalpine lake, recovered from eutrophic period in the late 1970's Lake surface area: 212 km^2 Max depth: 372 m	No	1980–2007	Monthly: Nov, Dec, Jan, Feb; fortnightly: other months	–
[29]	stream	6	United Kingdom	South Pennines: Trout Beck (Moor House) South Pennines: Lower Laithe, Keighley Moor, Agden, Broomhead, Langsett Location on a map	Peat–rich catchments	Yes	T' Beck: 1993–2006 L' Laithe: 1994–2006 K' Moor: 1979–2006 Agden, Broomhead, Langsett: 1961–2006	T' Beck: weakly Others: not clear	T' Beck: Environmental Change Network (ECN) **Data from T' Beck already published in [30,31]**
[32]	stream	1	USA	Bear Brook watershed, Maine	Low–alkalinity headwater stream	Yes	1988–1989, 1990–1995, 1996–2006	Weekly	–

Table 1. *Cont.*

Ref.	System						Period	Sampling frequency	Data source
	Type [a]	No.	Country	Details	General characteristics	Acid rain recovery? [b]			
[33]	moorland pools	4	Nether-lands	Achterste Goorven (AG), Groot Huisven, MiddelsteWolfsputven, Schaapsven Location in a map	No characteristics given	Yes	1978–2006	AG: 4 times/year (every season) The rest: once every 4 years	
[34]	lakes	55	Canada	Ontario: Dorset (8), ELA (4), Turkey (TLW) (5); Nova Scotia: Kejimkujik (26), Yarmouth (11) No list, approximate location on a map	Summary of lake characteristics in the article	Yes	1981–2003	Ontario: 5–24 times a year, from May to October Nova Scotia: 1 spring, 1 autumn	Different sources **Includes, at least, [35] data**
[36]	streams	2	Czech Republic	Lysina, Pluhuv Bor No map	Lysina: acidic, catchment 0.273 km^2 Pluhuv Bor: well-buffered catchment 0.216 km^2	Yes	1993–2007	Weekly	–
[37]	reservoirs streams	11 4	Czech Republic	Ore Mountains (Krušné hory) List of names, location on a map	Catchments: 8–74 km^2	Yes	reservoirs: 1969–2006 streams: (1969, 1974, 1983)–2006	Median sampling: 34 days	Ohre River and Labe River Authorities
[38]	streams	8	Finland	Forested headwater catchments, eastern Finland: Murtopuro, Liuhapuro, Suoputo, Kivipuro, Välipuro, Porkkavaara, Kangaslampi, Korsukorpi No map	Catchments: 0.29–4.94 km^2	Yes	2: 1979–2006 3: 1979–1982, 1996–2005 3: 1992–2006	Variable, described in the article	–

Table 1. *Cont.*

Ref.	System						Period	Sampling frequency	Data source
	Type [a]	No.	Country	Details	General characteristics	Acid rain recovery? [b]			
[39]	streams	3	Canada	Streams: Mersey, Moose Pit Brook, Pine Marten Brook (Southwestern Nova Scotia) Location on a map	Catchments: 297 km^2 (Mersey), 17 km^2 (Moose Pit Brook), 1.3 km^2 (Pine Marten Brook)	Yes	Mersey: 1980–2005 Moose Pit: 1983–2005 Pine Marten: 1991–2005	Weekly	–
[40]	streams	6	Scotland, United Kingdom	Loch Ard (3 sites: Burns 2, 10, 11), Allt a'Mharcaidh, Sourhope (Alderhope and Rowantree Bruns) Location on a map	Catchments: 0.44–10 km^2	Yes	Burn 2: 1989–2002 Burns 10, 11: 1988–2003 Allt a'Mharcaidh: 1987–2002 Sourhope: 1995–2006	At least fortnightly	UK Acid Waters Monitoring Network (AWMN) and Environmental Change Network (ECN) **Loch Ard data in [41,42]**
[43]	streams	7	Ontario, Canada	Harp Lake (6 catchments), Plastic Lake (1 catchment) No map	Headwater catchments: 0.097–1.905 km^2	Yes	1980–2002	Weekly or fortnightly, more frequently during periods of high discharge Total: 1530 (PC), 2200 (HP)	Ontario Ministry of Environment Dorset Environmental Science Centre (DESC)
[44]	streams	7	Ontario, Canada	Same data as [43] No map	Same data as [43]	Yes	1980–2002	See [43]	**Same data as [43]**
[45]	stream	1	Ontario, Canada	Plastic Lake (PC1) No map	Wetland dominated catchment: 0.234 km^2	Yes	1980–2001	See [43]	**This catchment is included in [43]**

Table 1. *Cont.*

Ref.	System						Period	Sampling frequency	Data source
	Type [a]	No.	Country	Details	General characteristics	Acid rain recovery? [b]			
[46]	rivers	21	Sweden	No list, no map	Catchments: 210–26,800 km^2	Yes	TOC: 1987–2004 A, COD: 1970–2004	TOC: not given A, COD: monthly	Rivers included in national or regional monitoring programs (not detailed)
[47]	lake stream	1 1	Finland	Valkea–Kotinen, lake and catchment outflow Location on a map	Headwater catchment: 0.30 km^2 Mean depth: 3 m Volumen: 77,000 m^3	Yes	1990–2003	Not given	**Lake already studied in [48], same results**
[49]	lakes	12	Ontario, Canada	Boreal Shield lakes: 5 near Sudbury (very acidified), 7 near Dorset (less affected) Location on a map	Lake area: 0.058–0.936 km^2 Max depth: 8.0–38.0 m	Yes	Sudbury: (1981, 1982, 1987)–2003 Dorset: 1978/9–2003	Monthly or more frequently during ice–free season	–
[50]	river	1	Finland	Simojoki river, Finnish Lapland Location on a map	Catchment: 3160 km^2	Yes	1962–2005	1962–1981: 4 samples per year 1982–2005: 10–18 samples per year	Regional environment center
[51]	lakes and streams	522 (6 regions)	North America and northern Europe	No list, incomplete map	Remote systems	Yes	1990–2004	Not given	Data collated from several regional and national monitoring initiatives on acid–sensitive terrain **Probably some data already considered in other studies**
[41]	streams	2	Scotland, United Kingdom	Loch Ard: Burn 10 (0.9 km^2) and Burn 11 (1.4 km^2) Location on a map	Small afforested catchments	Yes	1983–2006	Weekly until 2003, thereafter fortnightly	**Loch Ard data in [42]**

Table 1. *Cont.*

Ref.	System						Period	Sampling frequency	Data source
	Type [a]	No.	Country	Details	General characteristics	Acid rain recovery? [b]			
[52]	streams	3	Norway	Birkenes (B), Storgama (S), Langtjern (L) No map	Severely acidified systems; forested, undisturbed Catchment area: 0.41–0.8 km^2	Yes	1985–2003	B: daily S, L: >1992 weekly; <1992 daily	Norwegian program for monitoring long–range transported air pollutants
[53]	lakes and rivers	117	United Kingdom	No list, no map		Yes	1977–2002	HMS data: some weekly, most monthly	Harmonised Monitoring Scheme database (HMS) **198 sites from [54] also considered**
[55]	lakes streams	12 5	USA	Adirondack lakes (AL) and Catskill streams (CS), New York List of systems in a table, location on a map	CS streams chosen in the most sensitive to acidification areas; AL lakes: only drainage lakes with retention time < 6 months	Yes	1992–2001	Lakes: monthly Streams: variable	Adirondack lakes: selected from the 52 in the Adirondack Long–Term Monitoring (ALTM)
[15]	lakes streams	11 11	United Kingdom	List of sites in a table, no map	Located in the main acid-sensitive regions of the UK, mostly moorland	Yes	1988–2003	Lakes: quarterly Streams: monthly	**Same data as in [16]**
[48]	lakes streams	13 2	Finland	List of systems in a table, location on a map	Small forest lakes and forest streams Lake area: 0.024–1.62 km^2 Depth: 4.7–19.5 m Catchment area: 0.28–4.36 km	Yes	1987–2003	ICP lakes: 1 sample winter and summer, 2 spring, and fall IM: 8–12 samples per year	10 lakes Regional Monitoring Network of Lake acidification (RMLA), 3 lakes ICP Integrated Monitoring program (ICP UM)

Table 1. *Cont.*

Ref.	System						Period	Sampling frequency	Data source
	Type [a]	No.	Country	Details	General characteristics	Acid rain recovery? [b]			
[31]	stream	1 (2 sampling sites)	United Kingdom	River Tees (Moor House): Trout Beck and Cottage Hill Sike Location on a map	Blanket peat catchment	NM	1994–2001	Weekly	**Trout Beck data already published in [30]**
[56]	lakes	7	Ontario, Canada	Dorset region: 7 lakes (Blue Chalk, Chub, Crosson, Dickie, Harp, Plastic, Red Chalk) and their 20 subcatchments Location on a map	Forested, oligotrophic and mesotrophic lakes Lake area: 0.3214–0.9360 km^2 Mean depth: 7.9–14.2 m Catchment area: 0.955–5.324 km^2	Yes	1978–1998	1 to 4 week intervals	–
[16]	lakes streams	11 11	United Kingdom	List of sites, no map	Located in the main acid-sensitive regions of the UK, mostly moorland	Yes	1988–2003	Lakes: quarterly Streams: monthly	UK Acid Waters Monitoring Network (AWMN)
[57]	river	1 (6 stations)	USA	Hudson River (New York), sampling points: km 146 and 5 stations km 63 to 222 Location on a map	Total catchment: 21,034 km^2	NM	1988–2003	Fortnightly (km 146), every 2 months (longitudinal series) in other points	–
[23]	streams	3 (6 sampling sites)	Wales, United Kingdom	Upper River Severn catchments (Plynlimon): Upper Hafren, Upper Hore, Lower Hafren, Lower Hore, Nant Tanllwyth, South2Hore No map	Catchments: 3580 km^2 (Hafren), 3172 (Hore), 0.916 (Tanllwyth)	Yes	(1983, 1984, 1988, 1990, 1991)–2002	Weakly or fortnightly	Centre for Ecology and Hydrology (CEH)

Table 1. *Cont.*

Ref.	System						Period	Sampling frequency	Data source
	Type [a]	No.	Country	Details	General characteristics	Acid rain recovery? [b]			
[18]	sites	189	Europe and North America	Europe: Alps (6), East Central Europe (20), Northern Nordic (7), Southern Nordic (19), UK/Ireland (9), West Central Europe (12) N. America: Maine/Atlantic Canada (18), Vermont/Quebec (15), Adirondacks (48), Appalachian Plateau (9), Upper Midwest (23), Virginia Blue Ridge (3) List of sites in [9], approximate location on a map	Regions defined based on similar acid-sensitivity and rates of deposition	Yes	1990–2001	Variable	International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP) **Probably some data already considered in other studies**
[58]	rivers	16	Finland	List of rivers in a table, location on a map	Vegetation: from boreal taiga to sub–arctic vegetation Mean annual discharge ($m^3 s^{-1}$): 3 > 100, 5 20–100, 8 < 20	NM	1975–2000, shorter for 5 rivers	Monthly	Finnish Environmental Institute (FEI) or regional environment centres
[59]	lake	1	Norway	Lake Elvåga in Østmarka area Location on a map	Forest area bordering Oslo city district Lake area: 1 km^2 Samples from 40 m depth	Yes	From: – 1976 (color) – 1982 ($COD_)$ – 1988 (DOC) to 2002	No information	Oslo Water and Sewage Works

Table 1. *Cont.*

Ref.	System						Period	Sampling frequency	Data source
	Type [a]	No.	Country	Details	General characteristics	Acid rain recovery? [b]			
[47]	lakes supply reservoirs streams and rivers	29 8 161	United Kingdom	List of sites in a table, location on a map	Catchments: 400 m^2–2120 km^2	Many sites, yes	variable–2000; some from 1962, most 10 years long	Variable	Sites from: Freshwater Laboratory; Scottish EPA; North Pennines; UKAWMN; CEH; Yorkshire Water reservoirs; ECN– Forestry Commission Data in [37] included
[30]	stream	1	United Kingdom	River Tees (Trout Beck) Location on a map	Blanket peat catchment Catchment: 11.4 km^2	NM	1992–2000	Weekly	UK Environmental Change Network (ECN)
[60]	rivers	2	United Kingdom	Rivers Tees (Broken Scar), Coquet (Warkworth) Location on a map	Rivers draining upland peat, low flood waves (2 days)	NM	Tees: 1970–2000 Coquet: 1962–2001	See [61]	**Same data as in [61]**
[62]	lakes	52 (48 not limed)	USA	Adirondack Lakes, New York List of lakes in a table, no map	Watersheds largely forested, with hardwood or mixed vegetation Lake area: 0.008–5.125 km^2 Max depth: 1.2–32.0 m	Yes	1982–2000 (17 lakes), 1992–2000 (52 lakes)	Monthly	Adirondack Long–Term Monitoring (ALTM) program lakes **Some data in [63]**
[64]	lakes	163	Finland	No list, location on a map	Forested catchments. All acid sensitive. Small (median area: 0.1 km^2), headwater or seepage lakes	Yes	1990–1999	Each autumn	Finnish acidification monitoring lake network (RMLA)

Table 1. *Cont.*

Ref.	System						Period	Sampling frequency	Data source
	Type [a]	No.	Country	Details	General characteristics	Acid rain recovery? [b]			
[65]	stream	1	Czech Republic	Malše River, no map	Upland stream Catchment area: 438 km^2	No	1969–2000	Daily	Waterworks Pořešín (Water Supply and Sewage South Bohemia)
[35]	lakes	9	Ontario, Canada	Lakes: Blue Chalk, Chub, Crosson, Dickie, Harp, Heney, Plastic, Red Chalk (two basins), located 150 km N of Toronto Location on a map	Oligotrophic Lake area: 0.13–0.94 km^2 Max depth: 6–38 m Renewal time: 1.1–7.7 y Catchment area: 0.93–5.89 km^2	Yes	1978–1998	5–24 times per year during the ice–free period	–
[66]	lakes	705	Canada	No list of sites, incomplete map Quebec, 33 lakes Ontario, 662 lakes		Yes	Quebec: 1990–1997 Ontario: 1990–1999	No information	Many different sources, detailed in the article; most Ontario lakes from the Canadian Wildlife Service (CWS)
[67]	lakes	8	Ontario, Canada	Lakes: Bell, David, George, Johnnie, Killarney, Nellie, OSA, Ruth–Roy in Killarney Park, near Sudbury Location on a map	Strongly affected by acidification	Yes	1988–2001	Annually in midsummer	Several sources given, not clear which one corresponds to OC data
[41]	lake streams	1 8 (one with 7 sites)	Scotland, United Kingdom	Loch Ard: 2 streams: Corrie burn (1 site), Burns (7 sites) Loch Grannoch: 6 streams and 1 loch	Loch Grannoch catchment area: 15.45 km^2	Yes	Loch Ard: 1977–2000 Loch Grannoch: 1978–present	Loch Ard: weekly or fortnightly Loch Grannoch: variable	–

Table 1. *Cont.*

Ref.	System						Period	Sampling frequency	Data source
	Type [a]	No.	Country	Details	General characteristics	Acid rain recovery? [b]			
[61]	rivers	3	United Kingdom	Rivers Tees (Broken Scar), Wear (Wearhead), Coquet (Warkworth) Location on a map	Rivers draining upland peat	NM	Tees: 1970–2000 Wear: 1969–1998 Coquet: 1962–2000	Tees: daily Wear: variable Coquet: initially daily, then weekly	–
[14]	lakes streams	11 11	United Kingdom	No list, no map	Freshwater draining upland catchments (peatlands)	Yes	1989–2000	Lakes: quarterly Streams: monthly	UK Acid Waters Monitoring Network (AWMN)
[68]	lakes	4	Ontario, Canada	Lakes Nellie, OSA, George and Bell in Killarney Park Location on a map	All acidification recovery sites Lake surface area: 1.885–3.474 km^2 Max depth: 26.8–54.9 m	Yes	1969–1999	Not given	Killarney Park is a Canadian EMAN (Ecological Monitoring and Assessment Network) site
[69]	lakes streams	21 16	Scotland, United Kingdom	Classified in four geographical areas List in a table, location on a map	Moorland and forested sites	Yes	(1972–1988)–2000	Variable, described in detail in the article	Freshwater Laboratory
[70]	"ICP Waters" sites	98	Europe and North America	No list, no map	Only acidification sensitive sites included	Yes	1989–1998	At least 2 periods per year	International Cooperative Programme (ICP) on Assessment and Monitoring of Acidification of Rivers and Lakes
[71]	lakes	344	Scandinavia	163 Finland, 100 Norway, 81 Sweden No list, map	Finland and Norway: headwater or seepage lakes, no pollution Sweden: forested areas, no pollution	Yes	1990–1999	Once annually (autumn)	National Monitoring Programs of Norway, Finland and Sweden (subset from the 5690 lakes in the Northern European lake survey of 1995)

Table 1. *Cont.*

Ref.	System						Period	Sampling frequency	Data source
	Type [a]	No.	Country	Details	General characteristics	Acid rain recovery? [b]			
[72]	rivers	9	Latvia	Rivers Venta, Tebra, Lielupe, Iecava, Misa, Daugava, Dubna, Gauja, Tuliya Location on a map	Drainage area: 33–70,600 km^2	NM	1977–1995	Monthly	Latvian Hydrometeorological Agency
[73]	lakes	161	Ontario, Canada	Sudbury region No list, no map	Acid stressed lakes Lake surface area: 0.001–3.50 km^2 Depth: 0.6–22.2 m	Yes	1983–1995	Annually	–
[74]	lakes	51 but only 37 used for OC trend analysis	Quebec, Canada	N of St. Lawrence River between Ottawa River and Baie Comeau; divided in 7 chemically homogeneous regions No list, location on a map	Headwater lakes Lake area: 0.13–0.57 km^2 Mean depth: 10.2–28.0 m Renewal time: 12.7–63.6 months Values quoted are region means	Yes (those not affected, excluded)	(1983, 1986, 1989)–1993	17: 6 times a year 20: twice a year 14: once a year	Environment Canada
[75]	lakes streams	3 4	Ontario, Canada	Experimental Lakes Area, lakes number 239, 240, 302S and inflowing streams and lake outflows; NW Ontario Location on a map	Lake area: 0.543, 0.442, 0.109 km^2 Mean depth: 10.9, 6.0, 5.1 m Renewal time: 4–26, <1–6, 4–12 y Lake 302S artificially acidified to pH 4.5	Yes	239: 1972–1990 240: summers 1972, 1975–1978, 1984–1990; all winters, except 1972–1974 and 1976–1981 302: 1981–1990 Inflow streams: 1970–1990	Lakes: monthly or more frequently during the ice–free season and 2–4 times in winter Streams: weekly	Experimental Lakes Area (ELA)

Table 1. *Cont.*

Ref.	System						Period	Sampling frequency	Data source
	Type [a]	No.	Country	Details	General characteristics	Acid rain recovery? [b]			
[63]	lakes	17	USA	Adirondack Lakes, New York List of lakes in a table, no map	15 drainage lakes, 2 seepage lakes Lake surface area: 0.01–5.035 km^2 Max depth: 4–24 m Retention time: 0.03–2.5 y	Yes	1982–1991	Monthly	Adirondack Long–Term Monitoring (ALTM) program lakes
[76]	lake rivers	1 7	Sweden	Lake Öjaren Rivers: Ore Älv, Ljusnan, West Dalälven, Hedströmmen, Alsterälven, Nissan, Lyckebyän Location on a map	Lake surface area: 20 km^2, max depth 9 m River catchments: 365–8493 km^2	Yes	Lake: 1960–1988 River Alsterälven: 1966–1987	Lake: 6 times per year Rivers: monthly	Surface–water monitoring program of the Swedish Environmental Protection Board
[77]	lakes rivers	283 18	Sweden	List of rivers in a table Location on a map	Lake median size: 2 km^2 River drainage area: 25–10,797 km^2; mean discharge: 4.0–146.3 m^3s^{-1}	NM	Lakes: 1972–1987 Rivers: 1972–1986 (some 1965)	Lakes: lower than in rivers Rivers: monthly	Databases: – Lakes –Long Term Variation (LLTV) – Running Waters Data Base (RWDB)
[78]	lakes	4	Sweden	Lakes Oxsjön (OX), Hammardammen (HA), Innaren (IN), Värmen (VAAll in South Sweden No map	Forest lakes Lake surface area: 0.90–16.4 km^2 Max depth: 2–19 m Catchment area: 10.2–200 km^2	Yes	OX: 1967–1982 HA: 1972–1988 IN: 1970's–1980's VA: 1976–1986	OX: 3–4 per year (vegetative season) HA: daily IN: 37 times in 1970's; 25, 1980's VA: 4 per year	–
[79]	stream	1	United Kingdom	Raw waters arriving at Chellow Heights treatment works, Upper Nidderdale, North Yorkshire Location on a map	Much of the water from Angram and Scar House reservoirs		1979–1987	From daily to less than weekly	Yorkshire Water

Notes: [a] The distinction between streams and rivers is not always well-defined, the denomination used by the authors has been kept; [b] NM = not mentioned.

Table 2. Published studies containing long-term organic carbon concentration temporal trends in freshwaters. Methodological information.

Ref.	Filtration	OC quantification method	Original data plotted?	OC range [a] / mg C L^{-1}	Types of OC	Lake sampling	Data transformation	Statistical treatment
[20]	Filtered (0.45 µm cellulose nitrate filters)	TOC, DOC: >1997: HTC (DIN 38409-H3-1) <1997: no documentation POC: probably by difference	Mean annual [TOC], [POC], [DOC] *vs.* time shown				Mean annual values shown, not clear how many sampling points have been averaged	No mathematical treatment
[21]	Not mentioned	DOC, UV–persulfate oxidation followed by IR	Mean [DOC] *vs.* time shown for all lakes	Mean range: 2.05–8.38		Integrated 0–5 m samples collected from the middle of the lake; when <1 m deep, drawn 1 m from the bottom to the surface	No, original data used	Trends: SMK Slope: magnitude of linear trend with DETECT software (reference given)
[22]	No information	DOC, no information	No	Median: 2.1			Probably all data used	Trends: Integrated Random Walk analysis
[24]	No information	DOC, no information	Mean monthly [DOC] *vs.* time shown				Monthly means used in calculations Discharge–weighted means	Trends: SMK, partial MK with different covariates (rainfall, T, discharge) Slope: not given, probably Sen
[26]	Not mentioned	>1998, TOC HTC (ISO 8245) Correlations TOC–COD established, not given and not used	Data for [COD] in five streams shown Data available in internet		COD ($KMnO_4$) (ISO 15705)		Probably all measured values used in calculations	Trends: MK (for COD only)
[27]	Not mentioned	TOC, see [39]	No				Biannual values, treated by geographical zones	Trends: SMK

Table 2. *Cont.*

Ref.	Filtration	OC quantification method	Original data plotted?	OC range [a] / mg C L^{-1}	Types of OC	Lake sampling	Data transformation	Statistical treatment
[28]	Filtered (precombusted GF/C filters, Whatman)	DOC: HTC (Shimadzu 5000A) POC: CHN elemental analyzer (Carlo Erba)	Data for [DOC] and [POC] shown			One sample at the deepest point Epilimnion: sampler that collects 5–L integrated samples Hypolimnion: thermocline (50 m depth) and at 50 m intervals down to the bottom; integrated sample by pooling volumes of each sample proportional to the thickness of the layer		Trends: MK
[29]	<1984, unfiltered in Agden, Broomhead, Langsett but A corrected: $A_{true}=1.06+0.63A_{apparent}$ [80]	Not measured [DOC] = 0.044*Hazen + 3.89 (r2 = 0.93, $p < 0.001$; 181 water samples, 2005; [81]) 1979–1989, Agden, Broomhead, Langsett, Keighley Moor: A (400 nm) Hazen = 11.77 × A_{400} established in Broomhead [80]	No		Color (Hazen units) A (400 nm)		Monthly and annual means	Trends: MK (annual observations); SMK (monthly observations) Slope: Sen
[32]	Not mentioned	DOC, not mentioned	No				Mean monthly concentrations	Trends: SMK Slope: Sen
[33]	Not mentioned	DOC, not mentioned	Yearly [DOC] median values *vs.* time shown for one system				For one system: yearly median values; normalised by log transformation	Trends: Spearman rank correlationstrends

Table 2. *Cont.*

Ref.	Filtration	OC quantification method	Original data plotted?	OC range [a] / mg C L^{-1}	Types of OC	Lake sampling	Data transformation	Statistical treatment
[34]	Not mentioned	DOC, references given	Annual [DOC] Z–scores *vs.* time shown Lakes in the same zone grouped	Dorset: 1.8–5.1 ELA: 3.0–6.7 TLW: 3.6–4.8 NS: 2.1–16.2		When [DOC] measured for different thermal layers, whole–lake [DOC] calculated by adding up total OC mass in each layer and dividing by lake volume; no information about how many lakes in this situation	1– Mean annual ice–free values 2– Z–scores (21–yr mean used) 3– Trends calculated by zones after combination of all lakes within a zone and within temporally coherent zones	Regional and global temporal coherence: Pearson's correlation coefficient Trends: visual Slope: LR
[36]	Unfiltered samples [DOC] = [TOC] since [POC] < 5% [DOC] [82] and "sample inlets of TOC analyzers exclude most particles"	1993–1997: HTC Dohrmann Carbon Analyzer 1998–2004: Shimadzu TOC5000 2005– 2007: Tekmar–Dohrman Apollo 9000	[DOC] *vs.* time data shown	L: 18.8, PB: 20.2 (mean discharge–weighted [TOC])			Two calculations: one based on weekly samples and one on annual discharge–weighted mean concentrations (based on a Nov–Oct water year)	Trends: LR
[37]	Unfiltered samples	Not measured "We refer to COD as the DOM concentrations" DOC/TOC correlations in [46,65] shown	Median "DOM (measured as COD)" *vs.* time shown	Median reservoirs: 2.1–6.2 Median streams: 3.4–9	COD ($KMnO_4$)	No information	Monthly concentrations used in calculations (probably original data since median sampling period: 34 days)	Trends: SMK Slope: Sen

Table 2. *Cont.*

Ref.	Filtration	OC quantification method	Original data plotted?	OC range [a] / mg C L^{-1}	Types of OC	Lake sampling	Data transformation	Statistical treatment
[38]	Not mentioned but probably unfiltered since TOC acronym is used in the paper	UV–persulfate oxidation or HTC Missing data 1978–1991 obtained from COD: [TOC] = 1.1218 + 0.6435 × COD (r^2 = 0.93; period and number of points used not given)	Mean annual [TOC] *vs.* time shown for all systems Probably wrong units		COD ($KMnO_4$)		Mean annual and seasonal [TOC] calculated by averaging weekly or biweekly values Missing winter data interpolated for annual mean calculation	Trends: SMK
[39]	Unfiltered [TOC] = [DOC] based on "our experience in these waters showed that POM < 5%"	<1994, UV–persulfate wet oxidation >1995: HTC (Shimadzu) Non HTC values corrected according to [83]	[TOC] *vs.* time data shown	5.4–10.0			Trends: weekly data Slope: monthly values	Trends: SMK Slope: not mentioned
[40]	Filtered (0.45 μm)	DOC, no information	All stream data plotted	Site means: 2.19–11.31			Trends: probably measured [DOC]	LR (95%) Periodicity of the mean monthly [DOC] for each data set was determined by deconstructing the time series using a Discrete Fourier Transform

Table 2. *Cont.*

Ref.	Filtration	OC quantification method	Original data plotted?	OC range [a] / mg C L^{-1}	Types of OC	Lake sampling	Data transformation	Statistical treatment
[43]	Not mentioned	Oxidation: UV in acidic persulfate media; colorimetry with phenolphthalein Same method as in [56]	Annual volume–weighted monthly averaged [DOC] and Z–scores *vs.* time shown	Average annual: 2.3–10.7			Monthly volume–weighted [DOC] calculated by dividing total mass exported by total discharge Z–scores (22–yr mean used)	Trends: partial MK with monthly discharge as covariate Comparison with average [DOC] 5 first years (1980–1984)
[44]	See [43]	See [43]	Same as in [43] presented otherwise	See [43]			Annual average and annual volume–weighted annual [DOC]	Trends: MK Slope: Sen
[45]	Not mentioned	Same as [43]	No	Average annual volume–weighted: 9.8			Annual volume–weighted [DOC]; see [43]	Same as [43]
[46]	[TOC], COD: unfiltered samples since "differ by <10%, and usually <5% ([84–86])" A: filtered (0.45 μm)	TOC, oxidative combustion (no details given) COD and A/TOC correlations shown but not used: [TOC] = 0.51 + 0.84 × COD (r^2 = 0.88) [TOC]=3.4 + 2.1 × A (r^2 = 0.67)	One LOESS of median Z–scores shown	Mean TOC range: 2.4–17.1	A (420 nm, 5 cm cuvette) COD ($KMnO_4$)		One median (all systems) Z–score for LOWESS (no details about calculation of Z–scores)	Slope: Sen but no values given LOWESS smoothing "for illustrative purposes", span = 0.75

Table 2. *Cont.*

Ref.	Filtration	OC quantification method	Original data plotted?	OC range [a] / mg C L^{-1}	Types of OC	Lake sampling	Data transformation	Statistical treatment
[47]	No information	DOC, no information	Lake outflow and catchment outflow [DOC] *vs.* time data shown:	17 ("the water are humic")		Sampling point not clear	Probably annual average used	Trends: MK Slope: Sen
[49]	Unfiltered but Dorset samples: 80 µm mesh	Same method as in [43–45,56]	Data for all lakes plotted but probably all are annual mean [DOC] *vs.* time	≤6		Composite samples taken either through the epilimnion and metalimnion or volume–weighted samples accounting for bathymetry taken through the whole water column	Annual ice–free season averages	Trends: MK
[50]	Unfiltered samples [TOC] = [DOC] because "differences between TOC and DOC are very small [86]"	Not measured Correlation from [87]: [TOC] = 0.675 × COD + 1.94	[TOC] *vs.* time data shown		COD ($KMnO_4$)		Concentrations flow adjusted using rank correlation between mean monthly concentrations and mean monthly flows	Trends: "multivariate extension" of MK, first for each month and then combined 30 point moving average
[51]	No information	DOC, no information	No			No information	"Sites with median [DOC] < 1 mg L^{-1} excluded"	Trends: MK Slope: Sen
[41]	Filtered (0.45 µm polycarbonate membrane filters)	DOC: "OC analyzer by oxidation"	[DOC] *vs.* time data shown	Mean: B10: 7.3; B11: 11.4				No mathematical treatment

Table 2. *Cont.*

Ref.	Filtration	OC quantification method	Original data plotted?	OC range [a] / mg C L^{-1}	Types of OC	Lake sampling	Data transformation	Statistical treatment
[52]	Unfiltered [DOC] = [TOC] because "[TOC] = 90%–95% [DOC]: in these catchments"	TOC, method not given	Weekly [TOC] *vs.* time data shown	Mean annual: 11.6 (L), 5.3 (B), 4.9 (S)			Samples with [TOC] > 18 not included Annual mean values weighted by month	Trends: MK, SMK Slope: Sen
[53]	Not mentioned	Methods of analysis vary between regions and over the years; none detailed When [DOC] not available: [DOC] = 0.379 × $Color^{0.83}$ (n = 477, r^2 = 0.72; from 44 sites, used in 2 sites) [DOC] = 10.09 × $\log_e (COD)^2$ – 7.19 (n = 489, (r^2 = 0.47, used in 42 sites)	6–year moving average values *vs.* time shown for some systems		Color (Hazen units) COD	No information	All records "corrected to a monthly time step"	Trends: SMK Moving averages shown in two figures but not commented
[55]	No information	DOC, no information	No			Lake water collected at the lake outlet	Months were chosen as seasons	Trends: SMK Trend test applied to residuals of a flow–concentration model (hyperbolic or log regression fit)

Table 2. *Cont.*

Ref.	Filtration	OC quantification method	Original data plotted?	OC range [a] / mg C L^{-1}	Types of OC	Lake sampling	Data transformation	Statistical treatment
[15]	No information	DOC, no information	Median [DOC] (for 10 lakes and 8 streams) *vs.* time shown			No information		Comparison median [DOC] 5 first years with median [DOC] last 5 years (Mann–Whitney test)
[48]	Unfiltered samples [DOC]=[TOC] since [DOC] = 94% [TOC] in Finnish lakes [86]	<1990: COD used to reconstruct [TOC], no correlation given >1990: UV persulfate oxidation or HTC	All lake data plotted	Mean lake value range: 1.5–11.3	COD ($KMnO_4$)	Middle of the lake, 1m depth	Trends in annual and individual months evaluated	Trends: SMK Slope: Sen
[31]	No information	No information	[DOC] *vs.* time data shown					No mathematical treatment
[56]	Unfiltered, prefiltered: 80 μm polyester mesh	DOC: oxidation: UV in acidic persulfate media; colorimetry with phenolphthalein	3–year running mean normalised with long–term mean	1.80–5.23		No information		Calculation of 3–year running means normalised with long–term mean
[16]	No information	DOC, no information	All data plotted			No information		Trends: SMK Slope: Sen
[57]	Filtered (glass fibber filters; no size given)	1988–1993: persulfate digestion (ASTRO 2001) 1994–2003: HTC (Shimadzu 5000) Intercalibration for 1 year	Mean annual [DOC] *vs.* time plotted for 3 stations	≈4				Trends: probably LR

Table 2. *Cont.*

Ref.	Filtration	OC quantification method	Original data plotted?	OC range [a] / mg C L^{-1}	Types of OC	Lake sampling	Data transformation	Statistical treatment
[23]	GFC filters (filtered in the field)	HTC (TOCsin II Aqueous Carbon Analyzer)	[DOC] *vs.* time data shown for 3 streams	Moorlands and forest: 1.5 (up to 14 in small streams)			Raw data and residuals after flow and season filter	Slope: LR, SMK (probably Sen)
[18][c]	No information, probably in [9]	No information, probably in [9]	No			No information		Trends: calculation of confidence limits about the median value in the slope distribution and testing for zero inclusion Slope: LR
[58]	Not mentioned	TOC, oxidation to CO_2 and IR detection (no details on type of oxidation)	No				Trends studied in March, May, August and October	Trends: SMK
[59]	Not mentioned	>1986: UV–persulfate oxidation (Astro 1859) >1996: HTC (Astro 2100) >1999: HTC (Shimadzu 5000)	Color, [COD] and [DOC] *vs.* time data shown for a water treatment plant inlet		Color (Pt units) COD ($KMnO_4$)	40 m depth		Apparently, no mathematical treatment
[47]	No information	DOC, no information	Probably monthly mean data, not original data, for Great Dun Fell, Upper Hafron, Warkworth			No information	All monitoring records converted to a monthly time step; then annual average [DOC]	Trends: SMK Slope: probably Sen

Table 2. *Cont.*

Ref.	Filtration	OC quantification method	Original data plotted?	OC range [a] / mg C L^{-1}	Types of OC	Lake sampling	Data transformation	Statistical treatment
[30]	No information	DOC, no information	Weekly [DOC] *vs.* time data shown for the Moor House catchment outlet					Trends: SMK
[60]	See [61]	See [61]	Monthly average color *vs.* time shown for Coquet and Tees (in this case, same figure as in [61]). Annual median data also shown		See [61]			Trends: SMK
[62]	No information	DOC, no information	[DOC] *vs.* time data shown for Big Moose	38 lakes < 500 μM		No information		Trends: SMK
[64]	No information	TOC, no information	No			Samples taken either from the middle of the lake (1 m depth) or at the outlet		Trends: MK Slope: LR
[65]	Not mentioned	Not measured Calibration DOC–COD: [DOC] = 1.4 + 0.67 × COD (n = 235, r^2 = 0.88, p < 0.001) from measurements 1995–1998 but not used; trend results given in COD values	Monthly mean COD *vs.* time shown		COD ($KMnO_4$)		SMK applied to "monthly average blocks of data"	Trends: SMK Slope: Sen

Table 2. *Cont.*

Ref.	Filtration	OC quantification method	Original data plotted?	OC range [a] / mg C L^{-1}	Types of OC	Lake sampling	Data transformation	Statistical treatment
[35]	Not mentioned	DOC: UV radiation in acid persulfate media; colorimetry with phenolphthalein	Average [DOC] and Z–scores *vs.* time for the ice–free season shown	Mean lake value range: 1.8–5.1		Samples collected at the deepest location in the lake either from the upper 5 m of the water column during the spring and fall overturns or from the entire water column during stratification. In this case, samples collected every 2 m were volume–weighted for each thermal layer and then volume weighted to give a single value for each sampling date	Calculation of: – mean [DOC] of all sampling dates for each ice–free season – mean annual ice–free [DOC] standardised to Z–scores (21–yr mean used)	No mathematical treatment; visual inspection figure
[66]	No information	DOC, no information	No					"Non–parametric test procedures" considering seasonality and autocorrelation
[67]	No information	DOC, no information	No				Probably original (annual) data used in the calculations	Trends: SMK (autocorrelation considered)
[41]	No information	DOC, no information Correlation DOC–A: [DOC] = 0.58 + 16.4 × A (r^2 = 0.89, n = 586) for one stream (same figure) but never used	[DOC] *vs.* time data shown only for one stream in Loch Ard area	1.3–36.8	A (250 nm)	No information		Trends: SMK and permutation based LR

Table 2. *Cont.*

Ref.	Filtration	OC quantification method	Original data plotted?	OC range [a] / mg C L^{-1}	Types of OC	Lake sampling	Data transformation	Statistical treatment
[61]	No filtration	Not measured Calibration DOC–color: [DOC] = 1.09 + 0.051 × Color from measurements 20 June 2000 but not used; trend results based on color values	Monthly average water color for River Tees and annual average color *vs.* time for all rivers shown		Color (Hazen units)		Probably monthly average values used	Trends: visual Slope: LR
[14]	No information	DOC, no information	Median [DOC] Z–scores for lakes and rivers *vs.* time shown			No information	Z–score calculated from quarterly data for lakes and monthly data for rivers	Trends: SMK
[68]	–	Not measured	Data shown for 4 lakes		Secchi disk depth			LR
[69]	No information	DOC, no information	No			No information		Trends: SMK and permutation based LR
[70]	No information	DOC, no information	No			No information		Trends: SMK (autocorrelation considered) Slope: Sen
[71]	Not mentioned	TOC, no information	No	Colored dots on a map (0.1–100 scale)		Norway, Finland: sampling at the outlet after autumn circulation period; Sweden: "sampled in the middle of the lake"	Probably original (annual) data used in the calculations	Trends: MK Slope: Sen
[72]	Not mentioned	Not measured	Color data for River Lielupe and [COD] data for River Gauja shown		Color (Pt scale) COD ($K_2Cr_2O_7$)		Original (monthly) data used in the calculations	Trends: MK, SMK Slope: Sen

Table 2. *Cont.*

Ref.	Filtration	OC quantification method	Original data plotted?	OC range [a] / mg C L^{-1}	Types of OC	Lake sampling	Data transformation	Statistical treatment
[73]	Not mentioned	DOC, no information	No	DOC range: 0.53–16.70		No information		Trends: MK Slope: LR
[74]	Not mentioned	DOC: "determined by autoanalyzer"	[DOC] *vs.* time data shown for Truite Rouge and Eclair lakes	Range of region' means: 253.1–564.5 µM		Integrated 0–5 m lakewater samples collected with a sampling iron		Trends: MK, SMK, Spearman /Lettenmaier, Hirsch and Slack tests (autocorrelation considered) Slope: LR
[75]	Filtered (precombusted Whatman GF/F filters)	DOC digestion: acid persulfate by autoclaving (1971–75), UV irradiation (1975–85), heating to 102 °C (>1986) CO_2 measurement: GC: thermal conductivity detector (1971–75), specific conductance after Ba stripping (1976–85), IR (>1986) Method changes intercalibrated; no details	Mean annual [DOC] *vs.* time shown for all lakes			Measurements "at several depths in the water column of each lake"; no information about treatment of these values		No mathematical treatment; probably visual inspection of figure
[63]	Not mentioned	DOC: UV persulfate oxidation, CO_2 detection by IR	[DOC] *vs.* time data shown for Constable and Arbutus ponds	Mean lake value range: 192–1132 µM	–	Sampling at the outlet of drainage lakes (15) and at the surface of seepage lakes (2)	Original (monthly) data used in the calculations	Trends: SMK (autocorrelation considered) Slope: Sen

Table 2. *Cont.*

Ref.	Filtration	OC quantification method	Original data plotted?	OC range [a] / mg C L^{-1}	Types of OC	Lake sampling	Data transformation	Statistical treatment
[76]	Filtered (0.45 μm)	Not measured	A (Alsterälven) and color (Lake Öjaren) annual means *vs.* time shown		Rivers: A (420 nm, 5 cm cuvette) Lake: color (Pt scale)	No information		Visual
[77]	Rivers: filtered (0.45 μm) Lakes: no information	Not measured	A *vs.* time shown for River Botorpsström and A annual means *vs.* time for rivers Botorpsström and Ätran		Rivers: A (420 nm, 5 cm cuvette) Lakes: color (Pt scale)	No information		Value comparison
[78]	Not mentioned	Not measured	Color annual means *vs.* time for lakes Oxsjön and Hammardammen shown		Color (Pt scale)	No information		Comparison of values from initial and final years
[79]	Filtered (0.45 μm Millipore membrane filters)	Not measured	A monthly mean averages and 12–month running means *vs.* time shown		A (400 nm)		Original data averaged to monthly values	12–month running means

Note: [a] All OC concentration values in the table are in mg C L^{-1} except when stated otherwise.

Table 3. Published long-term temporal trends in organic carbon concentrations in freshwaters.[a]

Ref.	Type of system	No.	Measured parameter [b]	Temporal trend? [c]	Trend magnitude [d] / mgC L^{-1} y^{-1}	Comments	Period	Location
[20]	river	1	TOC, DOC	DOC "decreased from around 1000 to around 500 μmol L^{-1}" in the late 1980s, constant after 1996; no stats	-	Relative % of DOC and POC changed	1985–2007	Germany
[21]	lakes	30	DOC	22: ss increasing ($p < 0.05$) 8: no trend	Range: 0.01–0.14 (individual values given)	Trend not related to initial (1989) or mean [DOC]	1989–2006	Quebec, Canada
[22]	stream	not clear	DOC	Increase, no stats	-		1990–2010	Wales, United Kingdom
[24]	stream	1	DOC	ss increase ($p = 0.023$)	0.02		1987–1994, 1999–2009	Ontario, Canada
[26]	rivers	11	COD	5 (out of 6 small rivers) N Estonia: ss increase (at least $p < 0.05$) Pärnu: increase ($0.05 < p < 0.1$) 4 S Estonia: no trend	-	COD slopes	1992–2007	Estonia
[27]	lakes	91	TOC	ss increase: $p > 99\%$: NB ($n = 13$) (2000–2007) p 95%: NF ($n = 14$) (2000–2007), WNS ($n = 45$) (1983–2007, 1990–2007, 2000–2007), ENS ($n = 23$) (2000–2007) p 90%: NF (1983–2007) no trend: NF (1990–2007), ENS (1990–2007)	-		Newfoundland (NF), W Nova Scotia (WNS): 1983–2007 E Nova Scotia (ENS): 1990–2007 New Brunswick (NB): 2000–2007	Canada
[28]	lake	1	DOC, POC	DOC: ss decrease, epilimnion and hypolimnion ($p < 0.0001$) POC: no trends	-	[DOC] halved in 20 y (from 119 to 57 μmol L^{-1}) but it was discontinuous (peaks 1996–1999)	1980–2007	Switzerland

Table 3. *Cont.*

Ref.	Type of system	No.	Measured parameter [b]	Temporal trend? [c]	Trend magnitude [d] / mgC L^{-1} y^{-1}	Comments	Period	Location
[29]	streams	6	DOC estimated from color and A (400 nm)	ss increases, $p < 0.001$	Trout Beck: 0.06 L. Laithe: 0.09 K. Moor: 0.32 Agden: 0.20 B'head: 0.30 Langsett: 0.33	Authors qualify this DOC as "humic DOC"	T' Beck: 1993–2006 L' Laithe: 1994–2006 K' Moor: 1979–2006 Agden, Broomhead, Langsett: 1961–2006	United Kingdom
[32]	stream	1	DOC	"DOC concentrations have not varied substantially or systematically"	-		1988–2006	USA
[33]	moorland ponds	4	DOC	Achterste Goorven: increase, $p < 0.05$ ($n = 29$) Schaapsven: increase, $p < 0.01$ ($n = 8$) Groot Huisven, Wolfsputven: no trends	-		1978–2006	Netherlands
[34]	lakes	55	DOC	Cyclic pattern: decrease, increase, decrease Only one region with ss increase: ELA (4 lakes) ($p = 0.015$)	ELA: 0.03	Synchronous within regions, not synchronous across regions except in Nova Scotia	1981–2003	Ontario, Canada
[36]	streams	2	TOC	ss increase ($p < 0.001$)	Weekly samples: Lysina: 0.42, Pluhuv Bor: 0.43 Annual discharge-weighted mean concentrations: Lysina: 0.62, Pluhuv Bor: 0.93	Lysina: 64% increase, Pluhuv Bor: 65%, taking as reference mean 1993–1994	1993–2007	Czech Republic

Table 3. *Cont.*

Ref.	Type of system	No.	Measured parameter [b]	Temporal trend? [c]	Trend magnitude [d] / mgC L^{-1} y^{-1}	Comments	Period	Location
[37]	reservoirs streams	7 4	COD	Reservoirs: 5 ss increase, ($p < 0.001$, except Karmenicka: $p < 0.01$), 2 no trend Streams: all ss increase, ($p < 0.001$, except Cerna voda: $p < 0.05$)	-	COD slopes COD increase positively correlated with average [COD] ($R^2 = 0.79$, $p < 0.001$)	reservoirs: 1969–2006 streams: (1969, 1974, 1983)–2006	Czech Republic
[38]	streams	8	TOC, 1978–1991 estimated from COD	7: increase ($p < 0.05$) 1: no trend	-	Annual trends became detectable when there was at least one season with ss increase	2: 1979–2006 3: 1979–1982, 1996–2005 3: 1992–2006	Finland
[39]	streams	3	TOC	Uncorrected. Mersey (1980–2005), Moose Pit (1983–2005), Pine Marten (1991–2005): no trend Uncorrected. Mersey (1980–1994): ss decrease ($p = 0.06$), Moose Pit (1983–1994): ss decrease ($p = 0.05$) Uncorrected. Mersey, Moose Pit, Pine Marten (1995–2005): no trend Corrected. Mersey (1980–2005): ss decrease ($p = 0.04$), Moose Pit (1983–2005): ss decrease ($p = 0.008$), Pine Marten (1991–2005): no trend	Corrected (all period): Mersey: −0.1, Moose Pit: −0.25 Uncorrected (<1994): Mersey: −0.25, Moose Pit: −0.58	Values < 1994 corrected for differences in OC method response	Mersey: 1980–2005 Moose Pit: 1983–2005 Pine Marten: 1991–2005	Canada
[40] [e]	streams	6	DOC	Loch Ard (3), Allt a'Mharcaidh (1): increase ($p < 0.001$) Sourhope (2): no trend	Loch Ard, Burn 2: 0.28 Loch Ard, Burn 10: 0.22 Loch Ard, Burn 11: 0.79 Allt a'Mharcaidh: 0.15	Marked seasonal pattern (particularly in Loch Ard), with an increasing amplitude in latter years	Burn 2: 1989–2002 Burn 10, 11: 1988–2003 Allt a'Mharcaidh: 1987–2002 Sourhope: 1995–2006	Scotland, United Kingdom

Table 3. *Cont.*

Ref.	Type of system	No.	Measured parameter [b]	Temporal trend? [c]	Trend magnitude [d] / mgC L^{-1} y^{-1}	Comments	Period	Location
[43]	streams	7	DOC	6 wetland-dominated streams: ss increase ($p < 0.05$) 1 upland-dominated stream: no trend	-	Wetland-dominated streams: 18%–43% increase, reference mean 1980–1984 Increases mainly due to high concentrations in last 4 years	1980–2001	Ontario, Canada
[44]	streams	7	DOC	6 wetland-dominated streams: ss increase (HP3, HP5, HP6, PC1: $p < 0.01$; HP4, HP6A: $p < 0.05$) 1 upland-dominated system (HP3A): no trend	HP3: 0.12 HP4: 0.046 HP4: 0.15 HP5: 0.10 HP6: 0.10 HP6A: 0.094 PC1: 0.12	**Same data as in [43,45]** Different results when using annual average or volume-weighted concentrations. Here volume-weighted shown	1980–2001	Ontario, Canada
[45]	stream	1	DOC	ss increase ($p < 0.01$)	0.12	**Same data as [43,44]** Varying depending on season	1980–2001	Ontario, Canada
[46]	rivers	21	TOC, A, COD	TOC increase "smaller (than A, COD) and negligible for some rivers", no stats Several periodic reversals in the direction of the trends	-	Median annual TOC increase: 0.27% Simultaneous behavior of TOC, A and COD Synchronicity among rivers	TOC (21 rivers): 1987–2004 A, COD (28 rivers): 1970–2004	Sweden
[47]	lake stream	1 1	DOC	Lake: ss increase ($p < 0.01$) Stream: no trend	0.19	**Same system studied in [48]** where slope = 0.18 mg C L^{-1} y^{-1} for 1987–2003	1990–2003	Finland
[49]	lakes	12	DOC	Sudbury lakes (5): all ss increase ($p < 0.05$) Dorset lakes (7): 3 ss increase ($p < 0.05$)	-		Sudbury: (1981, 1982, 1987)–2003 Dorset: 1978/9–2003	Ontario, Canada

Table 3. *Cont.*

Ref.	Type of system	No.	Measured parameter [b]	Temporal trend? [c]	Trend magnitude [d] / mgC L^{-1} y^{-1}	Comments	Period	Location
[50]	river	1	TOC estimated from COD values	No trend ($p > 0.05$)	-	DON increased ss ($p < 0.01$) (1982–2005) "Increases of DOC occurred earlier (1970s–1980s) but could not be quantified (low sampling frequency)"	1962–2005	Finland
[51]	lakes and streams	522 (6 regions)	DOC	363: increase, no stats 139: decrease, no stats "88% of ss trends ($p < 0.05$) were positive" but nowhere is said how many ss trends found	Values represented in a figure and in histograms per region	Upward ss slopes more frequent below 62° latitude in the UK and in NE USA Atlantic Canada little evidence of increasing DOC		North America and northern Europe
[41]	streams	2	DOC	Increase, no stats	-	Increasing amplitude of seasonalvariations leading to a long-term increase	1983–2006	Scotland, United Kingdom
[52] [f]	streams	3	TOC	All ss increase: Langtjern ($p < 0.008$), Birkenes ($p < 0.002$), Storgama ($p < 0.001$)	Langtjern: 0.13 Birkenes: 0.06 Storgama: 0.09	All period increases (trend divised by mean TOC): Langtjern: 14%, Birkenes: 22%, Storgama: 36%	1985–2003	Norway
[53]	lakes and rivers	117	DOC; in some cases, DOC deduced from color (2 sites) or COD values (42 sites)	1977–2002 (54 sites): 12 increase, 23 decrease, 19 no trend; no stats 1977–1986 (51 sites): 7 increase, 16 decrease, 27 no trend; no stats 1993–2002 (94 sites): 5 increase, 56 decrease, 33 no trend; no stats	1977–2002: $-0.04 - 0.02$ [j] 1993–2002: $-0.19 - 0.08$ [j]	198 sites from [47] also considered	1977–2002	United Kingdom

Table 3. *Cont.*

Ref.	Type of system	No.	Measured parameter [b]	Temporal trend? [c]	Trend magnitude [d] / mgC L^{-1} y^{-1}	Comments	Period	Location
[55]	lakes streams	12 5	DOC	75% lakes: ss increase ($p < 0.05$) 80% streams: ss increase ($p < 0.05$)	Lake mean: *0.091* [g] Stream mean: *0.056* [g]	Trends nss counted as a trend of 0 when calculating mean trend values	1992–2001	USA
[15]	lakes streams	11 11	DOC	In all: ss increase (Mann-Whitney), most $p < 0.001$	-	Average increase last first 5 years compared to 5 last years: lakes: 63%, streams: 71% Same results as [16] expressed otherwise	1988–2003	United Kingdom
[48]	lakes streams	13 2	TOC, <1990 deduced from COD	6 lakes: ss increase ($p < 0.001$) 3 lakes: ss increase ($p < 0.05$) 1 lake: ss increase ($p < 0.1$) 3 lakes: no trends 1 stream: ss increase ($p < 0.0001$)	Lakes: 0.10, 0.08, 0.14, 0.22, 0.18, 0.03, 0.11, 0.12, 0.04, 0.12 Stream: 0.35	Lakes with ss increase include both clear water and humic lakes Poor correlation (r = 0.30, $p = 0.33$) between annual TOC increase and initial [TOC]	1987–2003	Finland
[31]	stream	1 (2 sampling sites)	DOC	Trout Beck: "almost step change from 1995 to 1997 with little subsequent decline in values", no stats Cottage Hill Sike: similar but "with more evidence of a decline after 1997", no stats	-	Trout Beck, same data as in [30] but different conclusions	1994–2001	United Kingdom
[56]	lakes	7	DOC	Oscilations (3-year running means)	-	Oscillations in annual water discharge and total DOC load were similar in the 7 lakes; annual [DOC] variations were similar but less accentuated	1978–1998	Ontario, Canada

Table 3. *Cont.*

Ref.	Type of system	No.	Measured parameter [b]	Temporal trend? [c]	Trend magnitude [d] / mgC L^{-1} y^{-1}	Comments	Period	Location
[16]	lakes streams	11 11	DOC	All sites: ss increases, no stats	Range: 0.06–0.51	In all sites, annual [DOC] correlated to mean [DOC] for first 5 years ($r^2 = 0.71$) All period, 91% increase relative to 1988–1993 mean	1988–2003	United Kingdom
[57]	river	1 (6 stations)	DOC	All sites: ss increase ($p < 0.001$)	-	"DOC concentrations have doubled from 1988 to 2003" "Net change between 3 and 4 mg C L^{-1}" Decrease in downstream decline	1988–2003	USA
[23]	streams	3 (6 sampling sites)	DOC	"significant upwards trend" (p: 0.000–0.023)	0.056, 0.058, 0.055, 0.047, 0.051, 0.045, 0.146, 0.055, 0.019	Data filtered for season, air T, flow: residual trend for 1983–1993 and levelling off from 1983 onwards (streams draining forest)	(1983, 1984, 1988, 1990, 1991)–2002	United Kingdom
[18] [h]	sites	189 (12 regions)	DOC	6 regions ($n = 121$): ss increase ($p < 0.05$) 4 regions ($n = 59$): no trends 1 region (Virginia Blue Ridge) ($n = 3$): ss decrease ($p < 0.05$) 1 region (Alps) ($n = 6$): insufficient data	0.05, 0.08, 0.13, 0.06, 0.06, 0.06, −0.04	Europe: ss increase in Nordic countries and UK, nss in central Europe N. America: ss increase in Vermont/Quebec, Adirondacks, Upper Midwest; nss Maine/Atlantic Canada, Appalachian	1990–2001	Europe and North America
[58]	rivers	16	TOC	10: ss decrease ($p < 0.05$) at least once during March, May, Aug, Oct	-	Some ss decrease observed in: 8 rivers only for 1 period, 1 for 2 and 1 for 3; in total: in 13 of the 64 periods considered	1975–2000	Finland
[59]	lake	1	DOC, color, COD	DOC, COD increased since 1990 (no stats) Color increased 1976–2002 (no stats) but not continuously	-	After 2000, color declined (more than 40%), COD and DOC 11%–13%	From 1976 (color), 1982 (COD), 1989 (DOC) to 2002	Norway

Table 3. *Cont.*

Ref.	Type of system	No.	Measured parameter [b]	Temporal trend? [c]	Trend magnitude [d] / mgC L^{-1} y^{-1}	Comments	Period	Location
[47]	lakes supply reservoirs streams and rivers	29 8 161	DOC	153: ss increase ($p < 0.05$) 45: no trends	Mean all sites: 0.17		Variable–2000; some from 1962, most 10 years long	United Kingdom
[30]	stream	1	DOC	Increase, no stats	0.62 (annual median increase)		1992–2000	United Kingdom
[60]	river	2	Color	Increase, no stats	-	Tees median: 1.83 Hazen units y^{-1} (≈ 0.11 mg C L^{-1} y^{-1}) Coquet median: 0.52 Hazen units y^{-1} (≈ 0.026 mg C L^{-1} y^{-1}) Although this study uses exactly the same data set as [61], results for Coquet River differ; no reason given	Tees: 1970–2000 Coquet: 1962–2001	United Kingdom
[62]	lakes	52	DOC	1982–2000 (16 not limed): 7 ss increase, 1 ss decrease ($p < 0.1$) 1992–2000 (48 not limed): 7 ss increase, 41 no trend ($p < 0.1$)	Mean rate of DOC increase 1982–2000: *0.079* [g]	1982–2000: "the rate of DOC increase more rapid at higher lake [DOC]"	1982–2000 (17 lakes) 1992–2000 (52 lakes)	USA
[64]	lakes	163	TOC	0%–10% of lakes in different regions: ss increase ($p < 0.05$) Most: no trend	Values in a figure		1990–1999	Finland

Table 3. *Cont.*

Ref.	Type of system	No.	Measured parameter [b]	Temporal trend? [c]	Trend magnitude [d] / mgC L^{-1} y^{-1}	Comments	Period	Location
[65]	stream	1	COD	1969–2000: ss increase ($p < 0.05$) 1969–1984: ss decrease ($p < 0.01$) 1983–2000: ss increase ($p < 0.01$)	-	COD slopes	1969–2000	Czech Republic
[35]	lakes	9	DOC	"Common pattern: concentrations were higher between 1978 and 1982 and from 1990 to 1997"	-		1978–1998	Ontario, Canada
[66]	lakes	705	DOC	Quebec ($n = 43$): 14% increase, 10% decrease, 76% no trend ($p < 0.10$) Ontario ($n = 662$): 4% increase, 5% decrease, 91% no trend ($p < 0.05$) Subset Ontario no CWS ($n = 54$): 22% increase, 4% decrease, no 74% trend ($p < 0.05$)	-		Quebec: 1990–1997 Ontario: 1990–1999	Canada
[67]	lakes	8	DOC	1 (Johnnie): ss increase ($p < 0.05$) 7: no trend	-		1988–2001	Ontario, Canada
[41]	lake streams	1 8 (one with 7 sites)	DOC	All sites: ss increase, no stats	-		Loch Ard: 1977–2000 Loch Grannoch: 1978-present	Scotland, United Kingdom
[61]	rivers	3	Color	Tees: ss increase, no stats Wear: no trend, no stats Coquet: ss increase, no stats	-	Tees increase: 51 Hazen units (29 years), 1.75 Hazen units y^{-1} (≈0.1 mg C L^{-1} y^{-1}) Coquet increase: 29 Hazen units (39 years), 61% "Annual averages for the 3 sites show a clear common phase"	Tees: 1970–2000 Wear: 1969–1998 Coquet: 1962–2000	United Kingdom

Table 3. *Cont.*

Ref.	Type of system	No.	Measured parameter [b]	Temporal trend? [c]	Trend magnitude [d] / mgC L^{-1} y^{-1}	Comments	Period	Location
[14]	lakes streams	11 11	DOC	20: ss increase ($p < 0.05$)	-	Annual average increases (5.4%) proportional to mean [DOC] ($R^2 = 0.81$, $p < 0.001$)	1989–2000	United Kingdom
[68]	lakes	4	Secchi disk depth	Nellie, OSA: ss Secchi depth increase ($p < 0.05$) George: decrease, no stats Bell Lake: nss change ($p > 0.05$)	-	George: −0.1 m yr^{-1}	1969–1999	Ontario, Canada
[69]	lakes streams	21 16	DOC	36: ss increase, no stats	Median annual trend values in a figure	Site with the lowest DOC, the only one with nss increase Greatest annual DOC changes in sites with most highly colored waters	(1972–1988)–2000	Scotland, United Kingdom
[70]	"ICP Waters" sites	98	DOC	Northern Nordic Countries ($n = 6$): no trend Nordic Countries/UK ($n = 24$): ss increase ($p < 0.001$) Central Europe ($n = 34$): no trend Eastern North America ($n = 22$): ss increase ($p < 0.01$) Midwestern North America ($n = 9$): ss increase ($p < 0.001$)	- 4.8×10^{-4} [i] - 3.6×10^{-4} [i] 1.2×10^{-4} [i]		1989–1996	Europe and North America
[71]	lakes	344	TOC	42 (12%): ss increase ($p < 0.05$) 4: ss decrease ($p < 0.05$) 87%: no trend	Values in a figure	Lakes with increases located in SE Norway, S Sweden and in a few cases S Finland	1990–1999	Scandinavia
[72]	rivers	9	Color, COD	Color: 4: ss decrease ($p < 0.05$); 2: ss increase ($p < 0.05$); 3: no trend COD: 7: ss decrease ($p < 0.05$); 1: ss decrease ($p < 0.1$); 1: no trend	-	Color (in Pt scale) and COD slopes	1977–1995	Latvia

Table 3. *Cont.*

Ref.	Type of system	No.	Measured parameter [b]	Temporal trend? [c]	Trend magnitude [d] / mgC L^{-1} y^{-1}	Comments	Period	Location
[73]	lakes	155	DOC	3%: ss increase, no stats 5%: ss decrease, no stats 92%: no trend	Median: −0.11 Range: −0.75 to 0.42 [j]		1983–1995	Ontario, Canada
[74]	lakes	37	DOC	17: ss increase (p = 0.1) 1: ss decrease (p = 0.1) 19: no trend	-	Net changes (1985–1993) by region: R1 (n = 6): +1.7 μM C R2 (n = 8): +66.6 μM C R3 (n = 8): +81.6 μM C R4 (n = 5): − R5 (n = 4): − R6 (n = 6): +55.8 μM C	(1983, 1986, 1989)–1993	Quebec, Canada
[75]	lakes streams	3 4	DOC	Lakes: decrease, no stats Streams: increase, no stats		Lakes: "DOC concentrations declined by 15%–25%" Streams: "average concentrations increased by 30%–80%"	Early 70's–1990, depending on system	Ontario, Canada
[63]	lakes	17	DOC	4: ss decrease (p < 0.1) 13: no trend	*−0.072* [i] (Constable), *−0.108* [i] (Windfall), *−0.144* [i] (Heart), *−0.156* [i] (Squash)		1982–1992	USA
[76]	lake rivers	1 7	Lake: color Rivers: A(420 nm)	Linear decrease from the end of the 1960's to the beginning of the 1970's, followed by an almost linear increase up to 1988			Lake: 1960–1988 River Alsterälven: 1968–1987	Sweden

Table 3. *Cont.*

Ref.	Type of system	No.	Measured parameter [b]	Temporal trend? [c]	Trend magnitude [d] / mgC L^{-1} y^{-1}	Comments	Period	Location
[77]	lakes rivers	283 18	Lakes: color Rivers: A(420 nm)	Lakes: increase, no stats Rivers: ss increase in 17 (95% level)		Lakes: average increase: 20 mg Pt L^{-1}, marked increase (≈100%) in large areas of N and S Sweden Rivers: relative increase: 12%–150%; largest increases in the smallest drainage areas; increase appears to be a part of long-term variations (oscillations); no distinct geographical distribution pattern	Lakes: 1972–1987 Rivers: 1972–1986 (some 1965)	Sweden
[78]	lakes	4	Color	Increase, no stats		Oxsjön: 10 to 20 mg Pt L^{-1} Hammardammen: <30 to >40 Innaren: 0–10 to 11–20 Värmen: 20 to 50	Oxsjön: 1967–1982 Hammardammen: 1972–1988 Innaren: 1970's–1980's Värmen: 1976–1986	Sweden
[79]	stream	1	A(400 nm)	No long-term trend, no stats		Short term increases in 1980, 1985, 1987 Tendency towards more extreme values	1979–1987	United Kingdom

Notes: [a] Complementary information in Tables 1 and 2; [b] In general, the DOC/TOC term used by the authors has been kept except when the term DOC had been used in studies where it is clear that samples were unfiltered; [c] ss = statistically significant, nss = not statistically significant. Non statistically increases and decreases are considered "no trends"; [d] Values only given when trend statistically significant, except when mixed in the original publication (in this case, a cautionary note is added). When value in italics, original value in other units; [e] [88] includes data from two streams (Loch Ard Burn 2 and Allt a'Mharcaidh) but refers to this study for DOC long term trend values; [f] Data from one of the catchments (Langtjern) further treated in [89] by empirical regression analysis and a process-based model; [g] Original units: μmol C L^{-1} y^{-1}; [h] [17] show exactly the same results. They cite [9] as a source; [i] Original units: μeq C L^{-1} y^{-1}; [j] Probably slopes for non statistically significant trends included.

3.1.2. Limited Geographical Location

Not many long series of reliable OC data exist. An exception is data collected in association with the follow up of a given problem. This is the case of extensive surveys in northern US and European countries related to acid deposition effects. As a consequence, and as Table 1 shows, many of the published studies on OC trends have been obtained in systems affected by acid rain. This means that (i) these systems are located geographically in a limited zone of the planet and that, as a consequence, they are often climatically similar; (ii) the type of organic matter present in the water bodies is similar (*i.e.*, the bodies are mostly rich in humic-type compounds with limited concentrations of other types of organic matter linked to productivity [90,91]). Published studies are distributed as follows: United Kingdom (19, most in Scotland and northern England), Canada (15, mostly in Ontario and Quebec), USA (5, all in the East Coast), Scandinavian countries (13), Czech Republic (3), Estonia (1), Germany (1), Latvia (1), Netherlands (1), Switzerland (1). Three studies [18,51,71] cover a large number of systems over Europa and North America but located in the same climatic zones as the smaller size studies mentioned. Apart from the limited geographical covering of the existing studies, the fact that these OC concentrations have been measured in systems recovering from a strong chemical disturbance such as acid rain means that the main trends observed will be directly related to the chemical changes in water composition associated with the main system modification (either acidification or recovery), eliminating, or at least greatly reducing, any possibility of detecting trends linked to global climatic changes.

3.2. Analytical Aspects

Organic carbon concentration is a particularly "difficult" parameter because it is highly dependent on the measurement method used. For this reason, it is essential to know, and to understand, this aspect of published studies in order to be able to evaluate the validity and meaning of their conclusions. Methodological information concerning analytical aspects is gathered in Table 2. It includes filtration and information about the analytical method used to determine OC or any other surrogate parameter considered.

3.2.1. On TOC, POC and DOC

The simplest classification of the total organic carbon (TOC) pool includes TOC, to be split into particulate organic carbon (POC) and dissolved organic carbon (DOC), both fractions being obtained by filtration through a filter with a nominal pore size of 0.45 (usual in freshwaters) or 0.22 μm (more common in oceanography). Astonishingly, in a majority of the studies (42%–67% of the total) filtration is not even mentioned. This can never be justified. When filtration is mentioned, the pore size (0.45 μm) is given in only six articles and the type of filters without pore size in four further ones. In nine articles it is explicitly said that water was unfiltered and in six of them unfiltered OC is measured and called DOC on the basis that POC only accounts for 5%–10% of TOC in the waters studied. This might be reasonable in humic-type waters, such as the ones existing in higher latitude zones where most of the studies have been performed, but it cannot be assumed in water systems in other climatic

zones. The fact that DOC and POC may evolve differently over time [20,28] also needs to be taken into account when considering temporal trends, even in low-POC containing waters.

3.2.2. Organic Carbon Concentration Measurements

OC measurements have never been straightforward. Progress in the measurement of OC concentrations has been led mainly by oceanographers who developed and introduced the high-temperature catalytic oxidation (HTC) method for low OC concentration measurements in the late 1980s [92]. After some problems due to inappropriate blank estimates in the first publications that forced their authors to withdraw their data [93], the HTC technique imposed itself as the technique of choice in the field, for both seawater and freshwater. However, when considering long-term series of OC data, it is unavoidable that a significant part of the data has been obtained by other techniques, mainly through the wet oxidation method (WCO), based on the chemical oxidation of organic compounds by persulfate, combined or not with photo-oxidation using ultraviolet light. What are the implications? First, as pointed out by Dafner and Wangersky [94], when using older DOC data, one should be aware that values are likely to be in the right neighborhood but with a greater variability than we would now accept. A typical range of error of the DOC measurements by a recent HTC apparatus is 1%–2% as a relative value, which corresponds to approximately 1/10 the error of the WCO method [95]. However, what it is less clear is whether both methods, irrespective of their inherent variability, produce (and previously produced!) similar results. To our knowledge, definitive large scale intercomparison tests have never been performed, although different authors conducted comparisons with variable results, ranging from no significant difference [96], low underestimation (3%–6%, [97]) or high underestimation (20%–24%, [83]) by the WCO method. Matters become even more complicated when we consider that, even within a single method, there are response variations over time. For instance, a progressive increase in DOC concentrations has been observed along with the use of progressively stronger oxidants in the WCO method [98].

Another method, used only by Dillon and co-workers [35,43–45,49,56] in Canadian lakes employs colorimetry with phenolphthalein as a detection method after UV oxidation of OC to CO_2 in acidic persulfate media. How this method compares with the usual infrared detection of CO_2 in WCO and HTC methods is unknown.

In the case of the time series considered here, two further questions arise. One, with no clear answer, is whether it is valid to compare results from different studies when obtained using different analytical methods for OC measurement. The second is how the fact of using data obtained with different methods within the same study series is dealt with and what effects this has on the trends reported. Sometimes authors mention that the methods used have been intercalibrated for a period of time (e.g., [39,57,75]) but not all authors report intercalibration (e.g., [36,38,48,59] do not). It is worth mentioning the case of [39] who studied OC trends with and without correcting old wet persulfate data and obtained quite different results (Table 3).

A much more controversial issue is the use of surrogate parameters such as color (expressed in so-called Hazen or Pt units, equivalent to the platinum concentration in a standard solution of platinum/cobalt chloride salts of the same absorbance/color), absorbance (250, 400, or 420 nm) or COD (chemical oxygen demand). This is highly controversial for two reasons. The first one is

methodological, concerning how the link is made with "real" OC concentrations. The second reason concerns the validity of the hypothesis underlying all these studies: that OC and the surrogate parameter evolve in the same way with time.

Concerning methodological issues, some studies follow tendencies directly in the surrogate parameter as such [26,60,61,65,72,77] but a common practice is to establish an empirical correlation between the parameter values and OC concentrations using data simultaneously measured over a short period of time [29,38,48,50,53,61] and discuss tendencies, causes, *etc.* in terms of OC concentrations. Often these correlations are just used to explain the period where OC concentrations have been directly measured (Table 3). When given, correlations used are provided in Table 2. In one case [53], the authors use correlations established in other studies on the assumption that they will also apply to their systems. This approach is difficult to justify. Even extrapolating synchronous data between close systems seems questionable. For instance, Pärn and Mander showed that TOC and COD for rivers in Estonia, a small country, showed different Spearman's correlation coefficients depending on the area considered (much higher in the North than in the South) [26].

Definitively more open to discussion is the underlying hypothesis that both OC and the measured parameter will change over the years in the same way. Consider, for instance, that Apsite and Klavins [72] showed that statistically significant increasing trends obtained when considering color became statistically significant decreasing trends when considering COD. The surrogate parameters used such as color, absorbance, *etc.* only respond to a fraction of the organic matter present in the system, usually the fraction more refractory to degradation fraction, often known as humic substances [99,100]. Surprisingly, this fact is rarely acknowledged in the studies considered, with rare exceptions such as [29]. Probably, in many of the systems considered in the studies evaluated here, these types of substances account for the bulk of the OC present (see Section 3.1.2) and, thus, the hypothesis that both change in the same direction, and in the same magnitude, might be applicable. Nevertheless, this remains unproved and the few studies where, directly or indirectly, the question of the quality of the organic matter present has been addressed, do not seem to support this hypothesis. For instance, Dawson *et al.* [88] showed a significant change in the relationship between UV absorbance and DOC over 22 years at two upland moorland catchments in Scotland; despite increases in long-term DOC concentrations, their analysis suggests that the proportion of hydrophobic material declined. Erlandsson *et al.* [46] have reported on Swedish rivers where DOC and absorbance (420 nm) were measured between 1987 and 2004 and found that there was a significant increase in the absorbance/DOC ratio in 19 of the 21 rivers considered. They also found an increase in the COD/TOC ratio that corroborated that changes in the quality of the organic matter had occurred. Worrall and Burt [53] examined a seven-year record of daily coagulant/color records in a water treatment plant (Broken Scar, Scotland) and found that the DOC entering the water works was becoming increasingly difficult to remove by coagulation, suggesting that DOC was becoming more hydrophilic in this catchment. They also suggested that there was no reason to believe that the relationship between DOC and color had not shifted over the course of the study; although color showed no significant trend, it is possible that the DOC from the catchment was becoming less colored so that DOC could be increasing without a significant increase in color. Lepistö *et al.* [50] calculate the C/N ratio (although not directly: OC by assuming a relationship between DOC and COD published in 1993 and organic nitrogen by difference between total and inorganic N) and found that this C/N ratio decreased during the study

period (1962–2005), again pointing to a change in the type of organic matter. Temporal changes in the type of organic matter have also been recently shown in stored samples from lakes in the northeastern United States [101].

Finally, it should be added that in about 40% of the studies considered (Table 2), there is no information about the method used for OC quantification and that, rigorously, in these cases it is impossible to go further in the evaluation of the results obtained.

3.2.3. Other Data Quality Issues

Most of the available lake and river time series data are from national and local monitoring programs and it is often not possible to assess the quality of such data on the basis of the contents of the articles (e.g., reproducibility, use of certified reference materials, sampling procedures, *etc.*). With regard to trace elements, it was shown many years ago that much of the dissolved trace element work published by these programs was incorrect due to problems of contamination during sampling and analysis [102–104]. It is unknown whether this type of problem might have also affected OC measurements.

An additional aspect that needs to be considered is that data used in the trend studies are often monitoring data for regulatory purposes and that the fact that the objectives of this type of measurement differ from those of research-oriented studies is not without consequences. For instance, since the main concern of regulatory monitoring is simply to ascertain that some limit values are not exceeded, often not very sensitive techniques are used. The use of censored data (*i.e.*, sets of data where some of the data are known to be "less than" some threshold) always introduces a bias in the magnitude of possible trends observed. The existence of this type of constraint has rarely, if ever, been mentioned in this field.

3.2.4. Bias Towards Studying Systems "Where Something Happens"

In addition to the well-known fact that citation practices confer on negative values an inherent quality of not spreading easily through the literature [7], authors rarely choose to study systems "where nothing happens" and often do not report results where the expected effects are not observed. Obviously, this has the automatic consequence of producing a bias in existing results and in the corresponding accepted belief. Although it is inherent to this type of problem that proving that it exists is well-nigh impossible, it is worth mentioning that it is highly probable that this behavior affects the subject considered here, leading to an overrepresentation of systems showing OC increasing trends.

3.3. Data Treatment Aspects

The second issue that needs to be considered is related to the way experimental data are treated. This information is set out in Table 2. Different aspects need to be discussed: data censoring, data transformation prior to their treatment and methods applied to detect temporal trends and to quantify them.

3.3.1. Data Censoring

It is impossible to know when data has been censored because it is rarely mentioned explicitly in the studies considered (*i.e.*, OC concentration detection limits and the number of values below these). Thus, it is impossible to assess the effect that data censoring might have in the conclusions reached. The only two cases found where explicit mention is made of "manual" censoring practices suggest a lack of understanding of the implications. A highly cited study [51] states: "sites with median concentrations of <1 mg/L were excluded from our analysis" and this in order to restrict their analysis "to sites where DOC concentrations were sufficient to allow reliable quantification of trends". By doing this, the authors plainly ignored that values ≤ 1 mg C L^{-1} are common in many systems. It also suggests a bias towards favoring systems with high DOC concentrations, which usually means northern humic-type ones. Since some authors [14,37,48,62,69] observed that trends are correlated with initial concentration levels, it is clear that, in practice, not considering low concentrations introduces a bias towards the measurement of higher trends. On the other end of the spectrum, de Wit *et al.* [52] wrote: "samples with exceptionally high TOC concentrations (>18 mg C L^{-1}) were excluded from the dataset" because "TOC in these samples had been modified by in-stream processes rather than being products of soil processes", reasoning difficult to understand when studying OC behavior in natural systems.

3.3.2. Data Transformations

When looking for trends and thus dealing with large data sets, different approaches are possible: use all data in the time series considered, sample a subset of the observations (*i.e.*, plainly eliminate values), use mean values (e.g., monthly, yearly, *etc.*) calculated from measured ones. Using a subset or averaging is often done simply to ensure some regularity in the temporal distribution of the data in the series (sometimes required for the statistical methods applied). In the case of the time series considered here, the frequency of sampling is highly variable between studies and sometimes even within the same study (Table 1); very often original data are not used when applying data treatment methods but rather monthly or annual means are used instead. Since averaging is not an innocuous procedure [105], the exact procedure used, including sampling frequency and method of calculation of mean values, needs to be described in detail. Unfortunately, this information is very often omitted from the articles. In fact, this is one of the more difficult aspects to trace in the articles considered.

The way mean values are calculated in rivers influences the results obtained as shown by Eimers *et al.* [44]. These authors compared the effect of using volume-weighted and arithmetic means at seven headwater streams in Canada, obtaining different results. On average, annual measured DOC concentrations were 13%–34% higher than volume-weighted values and, although DOC increases were found in both cases, slopes were much larger in the measured data. Hruška *et al.* [36] also found differences in the magnitude of the trends observed (but not in the significance level) when using these two types of mean value calculation procedure.

The question merits some further discussion in the case of lakes. Depending on the size of the system (*i.e.*, depth), many boreal and temperate lakes physically stratify in summer. Physical stratification drives chemical stratification and this needs to be taken into account when sampling.

Again, in the studies considered here, information about how lake sampling has been performed is sometimes lacking (as is unfortunately the case in the studies covering a high number of systems like in [18,51,71]). When sampling methods are described, different strategies, not necessarily leading to comparable results, have been followed (Table 2). In general, only one value (obtained in very different ways, e.g., sampling at one fixed depth, integrated sampling, value averaging) per date is considered. This strategy simplifies calculations but, firstly, leads to non comparable results and, secondly, when OC is measured at only one point, it does not take into account that OC concentrations may evolve differently in surface waters than at depth and, when averaged or integrated, information is lost while possible existing trends might become less clear.

Data have sometimes been normalized using Z-scores [14,34,35,43,46]. Z-scores are calculated by subtracting from all values the mean over the period under study and dividing by the standard deviation. They have mostly been used for comparing systems with different levels of OC concentrations.

3.3.3. Trend Detection and Quantification

Since many water variables are not normally distributed, it is not generally appropriate to analyze them for temporal trends using parametric methods such as linear regression [106]. Accordingly, non-parametric methods have been largely used in the studies reviewed here. The non-parametric test for trends most frequently applied is the Kendall test (or Mann-Kendall, MK) [107,108]. The MK test compares every pair of values of the variable, and calculates the sign of the difference. The signs (indicating whether the second observation in each pair-wise comparison is higher, lower or equal than the first) for all pair-wise comparisons are summed and a Z-statistic calculated as the sum of signs divided by the standard deviation of the sum of signs. The statistical significance of any trend is indicated by the corresponding p-value. Unfortunately, the significance associated with the detection of a trend is not always given (Table 3).

There are many cases where concentrations in surface waters show strong seasonal patterns. This is often the case of OC. Ideally, seasonal variations must be removed in order to better discern any trend in the studied variable over time. The seasonal Kendall test (SMK) [106] accounts for seasonality by computing the MK test on each of the seasons separately and then combining the results. The SMK has been used in many OC trend studies (Table 2). The existence of seasonality can be tested by applying the Kruskal-Wallis statistic test but authors usually apply SMK without any previous test, presumably deducing seasonality visually or assuming that it probably exists. An alternative way of treating the effect of seasonality is applying trend tests (*i.e.*, MK) to annual mean values. This approach has also been used. Although it eliminates seasonal effects and a part of the random variation of data, it has the drawback of reducing the information content.

The MK test does not estimate the magnitude of trends (slopes) but it has become usual to associate slopes calculated according to the method of Sen [109,110] when a trend is detected. The method of Sen is a nonparametric method where the slope is approximated as the median value of all the pairwise slopes in the time series. However, a non negligible number of studies applied linear regression even after having used the MK method to find the existence of trends.

The MK test is known to be well adapted to censored data (when only one censoring threshold exists; although note that the magnitude of the Sen slope is likely to be in error when using censored data), the presence of outliers and missing values. Limitations of the MK test are that there must be no serial correlation for the resulting p-values to be correct, and that data must be monotonic. A few of authors mention the use of modifications of the MK method that account for autocorrelation [63,67,70,74]; the most usual modification is the one proposed by Hirsch and Slack [111]. It is not excluded that others account for autocorrelation without mentioning it.

Monotonicity is potentially a serious problem in OC trend studies. In practice, monotonicity as such has rarely been statistically tested and data are generally assumed to be monotonic. However, cyclical patterns have been observed by some authors [34,35,46,56,65,77] either by looking at the graphical representation of the data or when applying smoothing methods such as the calculation of moving averages (also called running averages). Although not exempt from problems [105], calculation of moving averages provides a robust description of a data pattern and, although it has been seldom applied to OC data series, where it has been, cyclical patterns have appeared. Cyclical behavior has been observed in many parameters affected by climatic variations [112] and therefore is not astonishing that OC data show it, but it is worrying is that such behavior might have gone undetected in cases where monotonicity has been assumed. Obviously, for cyclicity to be apparent, long temporal series are needed.

It is common in hydrology to attempt to eliminate flow-related variability by adjusting water concentrations to flow (e.g., with LOWESS) and applying a trend test to the residuals. To our knowledge, this procedure has only been used by Burns *et al.* [55], after hyperbolic or log regression fit of the data. Other authors mention the use of the partial MK test with discharge or other parameters as covariates [24,40].

Some authors estimate the magnitude of the trends by comparing initial and final values either in absolute terms or as a percentage. In principle, this should be avoided because, even if the mean of some initial and final years are used, the value remains very much dependent on initial and final conditions. Sometimes, even increases observed over a given period are extrapolated beyond it (e.g., Worrall *et al.* [30] found a 53.4% increase over 8 years (1993–2000) but in the abstract talk about a 78% increase since 1970, "the period over which increase has been observed for the catchment as a whole").

4. Conclusions

Careful analysis of the 63 studies listed in Table 3 has revealed the existence of a number of problems both in the way results have been published (*i.e.*, key information is missing from the articles, making it difficult to judge the reliability of the results; the degree of independence between published studies is fuzzy in some cases) and in the way OC analysis was performed (*i.e.*, different, and not necessarily comparable, methods have been used along the years). In general, data treatment looks to be more problem free from the methodological point of view even if, sometimes, it is difficult to follow some methodological aspects such as, for instance, how authors pass from measured data to the numbers actually used in data treatment. This is not a trivial question because, as Stevenson and co-workers recently showed for temperature [105], different types of climatic patterns and anomalies

are captured depending on which of various local and global methods are used. The failure to consider the possible existence of cyclicity, concomitant on the widespread assumption of data monotonicity, may also be a major flaw in OC studies that merits further consideration.

Can the initial question that motivated our study be answered in spite of these limitations? In brief, can we reasonably state that "there is a common trend of increasing concentrations of DOC in streams and lakes"? First, we think that it is clear to any reader that, because of the limited geographical coverage of the existing studies, if any general increasing OC trend did exist, our statement would need to be restricted to some northern zones of the North Hemisphere. Nearly no data exist for many areas of US and Europe temperate zones and none for the rest of the world.

That said, it would nevertheless be tempting to pool together observed trends and "play statistics" with them. However, this would have little sense for many reasons. First, in general: (i) studies cover very different temporal periods; (ii) the number of systems included in each individual study is very different, ranging from one intermittent stream [88] to a major comparison of 705 systems [66]; 33 of the published studies cover less than 10 systems and only 9 more than 100. Curiously, if all trends were pooled together, the existence of four earlier studies [64,66,71,73] covering a huge number of lakes in Canada and Scandinavia (1324 in total), where about 90% of the systems in each study showed no statistically significant trend, would probably give an overwhelming majority for the "non trend" category.

Secondly, how many of the 63 studies contain results that can be considered "usable"? A fast screening shows that not many. If studies that contain the same results published more than once by the same authors are eliminated from the initial 63 studies, 60 remain. Unfortunately, as explained above, there is no way of accounting for the interdependence of other published data. If we consider only studies which contain statistically significant results supported by a p value (irrespective of being increases, decreases or no trends), we are left with 37. And, if we fix the limit of significance at $p < 0.05$, then only 34 of the initial 63 studies remain. It is worth mentioning here that judging this aspect is sometimes a bit tricky. For instance, in an important study covering 522 systems [51] there is no way of assessing the number of systems with significant trends (except trying to digitize some small figures appearing in the supporting information file) because the paper states than: "Upward slopes ($n = 363$) outnumbered downward slopes ($n = 139$), and 88% of significant trends ($p < 0.05$) were positive" without saying how many significant trends had been found. If of the remaining 34 studies, we consider only studies where OC has been measured as such (even leaving studies where correlations with surrogate parameters have been used for some periods of missing data), 27 studies remain. Finally, if we do not consider the studies where absolutely no information is given about the analytical methods used, we are left with no more than 11. This last filter really reveals the limitations imposed by the lack of adequately reporting.

In conclusion, it is clear that OC concentrations have increased in some surface waters in the Northern Hemisphere since the 1990s. However, it cannot be proved that it is a general phenomenon because of the lack of data –temporal series– in many parts of the world and, as this study discusses, in the areas for which such series exist, the reporting and methodological problems in the published studies prevent so far reaching a conclusion about the existence of a general temporal behavior of OC concentrations.

5. Recommendations for Future Work

Apart from the many different "technical" questions discussed along the different parts of this critical review, and that can be easily gleaned from the text, the main lesson to be learned from the situation described is the urgent need to improve the way both analytical and data treatment methods are reported.

Obviously, since this type of studies use already existing data, there is no room for improvement of their quality. The quality and types of data varies widely making it hard to analyze and harder still to use to detect temporal trends. However, it is possible, and extremely necessary, that raw data quality is carefully evaluated and that all details are given concerning analytical procedures used, data censoring, *etc.* Current publishing possibilities also make it feasible to make raw data easily available to all readers (e.g., through Supporting Information files, web-accessible files, *etc.*) facilitating appraisal and reuse.

Concerning data treatment, apart from the need to apply non-parametric methods –which are already widely used by this research community– there is no "best method" to recommend. However, methods used and any data pre-treatment applied should be, again, carefully detailed. Now that organic carbon concentrations have been determined for some systems for more than 30 years, systematic testing for cyclicity should be strongly encouraged in order to detect any possible climate-driven trend.

Finally, better citing practices will be welcome. Careful reading of the introduction of the 63 papers considered show a worrying repetition of the "accepted belief" that organic carbon concentration increases are widespread and a few papers are repeatedly cited. Citation "is not simply an impartial scholarly method for joining related published knowledge" [7]. Authors should probably be less guided by inertia when making the choice of which results to cite and which to ignore.

Acknowledgement

We thank the librarians of the old Center for Environmental Sciences (CCMA-CSIC) and of the National Museum of Natural History (MNCN-CSIC) for their help.

Authors Contributions

Montserrat Filella conceived the subject of the article and wrote it. Juan Carlos Rodríguez-Murillo contributed to gathering information and writing the article.

Abbreviations

A:	absorbance
COD:	chemical oxygen demand
DOC:	dissolved organic carbon
DOM:	dissolved organic matter
GC:	gas chromatography
HTC:	high temperature combustion
IR:	infrared
LOWESS:	locally weighted scatterplot smooth
LR:	lineal regression

MK:	Mann-Kendall test
OC:	organic carbon
POC:	particulate organic carbon
POM:	particulate organic matter
SMK:	seasonal Mann-Kendall test
TOC:	total organic carbon
TON:	total organic nitrogen
UV:	ultraviolet
WCO:	wet carbon oxidation

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Randerson, J.T.; Chapin, III F.S.; Harden, J.W.; Neff, J.C.; Harmon, M.E. Net ecosystem production: A comprehensive measure of net carbon accumulation by ecosystems. *Ecol. Appl.* **2002**, *12*, 937–947.
2. Battin, T.J.; Luyssaert, S.; Kaplan, L.A.; Aufdenkampe, A.K.; Richter, A.; Tranvik, L.J. The boundless carbon cycle. *Nat. Geosci.* **2009**, *2*, 598–600.
3. Sobek, S.; Tranvik, L.J.; Prairie, Y.T.; Kortelainen, P.; Cole, J.J. Patterns and regulation of dissolved organic carbon: An analysis of 7,500 widely distributed lakes. *Limnol. Oceanogr.* **2007**, *52*, 1208–1219.
4. Porcal, P.; Koprivnjak, J.-F.; Molot, L.A.; Dillon, P.J. Humic substances—part 7: The biogeochemistry of dissolved organic carbon and its interactions with climate change. *Environ. Sci. Pollut. Res.* **2009**, *16*, 714–726.
5. Weyhenmeyer, G.A.; Karlsson, J. Nonlinear response of dissolved organic carbon concentrations in boreal lakes to increasing temperatures. *Limnol. Oceanogr.* **2009**, *54*, 2513–2519.
6. Sucker, C.; Krause, K. Increasing dissolved organic carbon concentrations in freshwaters: what is the actual driver? *iForest* **2010**, *3*, 106–108.
7. Greenberg, S.A. How citation distortions create unfounded authority: analysis of a citation network. *Br. Med. J.* **2009**, *339*, doi: 10.1136/bmj.b2680.
8. Monteith, D.T.; Stoddard, J.L.; Evans, C.D.; de Wit, H.A.; Forsius, M.; Høgåsen, T.; Wilander, A.; Skjelkvåle, B.L.; Jeffries, D.S.; Vuorenmaa, J.; *et al*. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature* **2007**, *450*, 537–541.
9. Skjelkvåle, B.L. *The 15-Year Report: Assessment and Monitoring of Surface Waters in Europe and North America; Acidification and Recovery, Dynamic Modeling and Heavy Metals*; ICP Waters Report 73/2003; Norwegian Institute for Water Research: Oslo, Norway, 2003.
10. Stoddard, J.L.; Kahl, J.S.; Deviney, F.A.; DeWalle, D.R.; Driscoll, C.T.; Herlihy, A.T.; Kellogg, J.H.; Murdoch, P.S.; Webb, J.R.; Webster, K.E. *Response of Surface Water Chemistry to the Clean Air Act Amendments of 1990*; Environmental Protection Agency, Office of Research and Development: Washington, DC, USA, 2003.

11. Gruau, G.; Birgand, F.; Jarde, E.; Novince, E. Pollution des Captages d'Eau Brute de Bretagne par les Matières Organiques. Rapport de Synthèse Tableau de Bord de la Pollution Causes Possibles Recommandations, 2004. Available online: http://www.observatoire-eau-bretagne.fr/Media/Documentation/Bibliographies/Pollution-des-captages-d-eau-brute-de-Bretagne-par-les-matieres-organiques-Rapport-de-synthese.-Tableau-de-bord-de-la-pollution.-Causes-possibles.-Recommandations (accessed on 24 March 2014).
12. Monchy, A.; Gruau, G. Pollution des Captages Superficiels d'Eau Brute des Pays de Loire par les Matières Organiques. Variabilité Spatiale Tendances Evolutives Causes Possibles et Recommandations. Comparaison avec le Cas de la Bretagne, 2010. Available online: http://hal-insu.archives-ouvertes.fr/docs/00/57/81/09/PDF/PL02451.pdf (accessed on 23 March 2014).
13. Zobrist, J.; Sigg, L.; Schoenenberger, U. NADUD—Thematische Auswertung der Messresultate 1974 bis 1998; Schriftenreihe der EAWAG No. 18; Eidgenössische Anstalt für Wasserversorgung, Abwasserreinigung und Gewässerschutz (EAWAG): Dübendorf, Switzerland, 2004; Available online: http://library.eawag-empa.ch/schriftenreihe/schriftenreihe_18.pdf (accessed on 9 May 2014).
14. Freeman, C.; Evans, C.D.; Monteith, D.T. Export of organic carbon from peat soils. *Nature* **2001**, *412*, 785.
15. Evans, C.D.; Chapman, P.J.; Clark, J.M.; Monteith, D.T.; Cresser, M.S. Alternative explanations for rising dissolved organic carbon export from organic soils. *Glob. Chang. Biol.* **2006**, *12*, 2044–2053.
16. Evans, C.D.; Monteith, D.T.; Cooper, D.M. Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. *Environ. Pollut.* **2005**, *137*, 55–71.
17. Eikebrokk, B.; Vogt, R.D.; Liltved, H. NOM increase in Northern European source waters: Discussion of possible causes and impacts on coagulation/contact filtration processes. *Water Sci. Technol. Water Supply* **2004**, *4*, 47–54.
18. Skjelkvåle, B.L.; Stoddard, J.L.; Jeffries, D.S.; Tørseth, K.; Høgåsen, T.; Bowman, J.; Mannio, J.; Monteith, D.T.; Mosello, R.; Rogora, M.; *et al*. Regional scale evidence for improvements in surface water chemistry 1990–2001. *Environ. Pollut.* **2005**, *137*, 165–176.
19. Tranvik, L.J.; Downing, J.A.; Cotner, J.B.; Loiselle, S.A.; Striegl, R.G.; Ballatore, T.J.; Dillon, P.; Finlay, K.; Fortino, K.; Knoll, L.B.; *et al*. Lakes and reservoirs as regulators of carbon cycling and climate. *Limnol. Oceanogr.* **2009**, *54*, 2298–2314.
20. Amann, T.; Weiss, A.; Hartmann, J. Carbon dynamics in the freshwater part of the Elbe estuary, Germany: Implications of improving water quality. *Estuar. Coast. Shelf Sci.* **2012**, *107*, 112–121.
21. Couture, S.; Houle, D.; Gagnon, C. Increases of dissolved organic carbon in temperate and boreal lakes in Quebec, Canada. *Environ. Sci. Pollut. Res.* **2012**, *19*, 361–371.
22. Halliday, S.J.; Wade, A.J.; Skeffington, R.A.; Neal, C.; Reynolds, B.; Rowland, P.; Neal, M.; Norris, D. An analysis of long-term trends, seasonality and short-term dynamics in water quality data from Plynlimon, Wales. *Sci. Total Environ.* **2012**, *434*, 186–200.
23. Neal, C.; Robson, A.J.; Neal, M.; Reynolds, B. Dissolved organic carbon for upland acidic and acid sensitive catchments in mid-Wales. *J. Hydrol.* **2005**, *304*, 203–220.

24. Kerr, J.G.; Eimers, M.C. Decreasing soil water Ca^{2+} reduces DOC adsorption in mineral soils: Implications for long-term DOC trends in an upland forested catchment in southern Ontario, Canada. *Sci. Total Environ.* **2012**, *427–428*, 298–307.
25. Eimers, M.C.; Dillon, P.J.; Schiff, S.L. Sulphate flux from an upland forested catchment in south-central Ontario. *Water Air Soil Pollut.* **2004**, *152*, 3–21.
26. Pärn, J.; Mander, Ü. Increased organic carbon concentrations in Estonian rivers in the period 1992–2007 as affected by deepening droughts. *Biogeochemistry* **2012**, *108*, 351–358.
27. Clair, T.A.; Dennis, I.F.; Vet, R. Water chemistry and dissolved organic carbon trends in lakes from Canada's Atlantic Provinces: no recovery from acidification measured after 25 years of lake monitoring. *Can. J. Fish. Aquat. Sci.* **2011**, *68*, 663–674.
28. Bertoni, R.; Callieri, C.; Corno, G.; Rasconi, S.; Caravati, E.; Contesini, M. Long-term trends of epilimnetic and hypolimnetic bacteria and organic carbon in a deep holo-oligomictic lake. *Hydrobiologia* **2010**, *644*, 279–287.
29. Clutterbuck, B.; Yallop, A.R. Land management as a factor controlling dissolved organic carbon release from upland peat soils 2: Changes in DOC productivity over four decades. *Sci. Total Environ.* **2010**, *408*, 6179–6191.
30. Worrall, F.; Burt, T.; Adamson, J. Can climate change explain increases in DOC flux from upland peat catchments? *Sci. Total Environ.* **2004**, *326*, 95–112.
31. Worrall, F.; Burt, T.P.; Adamson, J. Long-term changes in hydrological pathways in an upland peat catchment–recovery from severe drought? *J. Hydrol.* **2006**, *321*, 5–20.
32. Navrátil, T.; Norton, S.A.; Fernandez, I.J.; Nelson, S.J. Twenty-year inter-annual trends and seasonal variations in precipitation and stream water chemistry at the Bear Brook Watershed in Maine, USA. *Environ. Monit. Assess.* **2010**, *171*, 23–45.
33. van Kleef, H.H.; Brouwer, E.; Leuven, R.S.E.W.; van Dam, H.; de Vries-Brock, A.; van der Velde, G.; Esselink, H. Effects of reduced nitrogen and sulphur deposition on the water chemistry of moorland pools. *Environ. Pollut.* **2010**, *158*, 2679–2685.
34. Zhang, J.; Hudson, J.; Neal, R.; Sereda, J.; Clair, T.; Turner, M.; Jeffries, D.; Dillon, P.; Molot, L.; Somers, K.; *et al*. Long-term patterns of dissolved organic carbon in lakes across eastern Canada: Evidence of a pronounced climate effect. *Limnol. Oceanogr.* **2010**, *55*, 30–42.
35. Hudson, J.J.; Dillon, P.J.; Somers, K.M. Long-term patterns in dissolved organic carbon in boreal lakes: the role of incident radiation, precipitation, air temperature, southern oscillation and acid deposition. *Hydrol. Earth Syst. Sci.* **2003**, *7*, 390–398.
36. Hruška, J.; Krám, P.; McDowell, W.H.; Oulehle, F. Increased dissolved organic carbon (DOC) in central European streams is driven by reductions in ionic strength rather than climate change or decreasing acidity. *Environ. Sci. Technol.* **2009**, *43*, 4320–4326.
37. Oulehle, F.; Hruška, J. Rising trends of dissolved organic matter in drinking-water reservoirs as a result of recovery from acidification in the Ore Mts., Czech Republic. *Environ. Pollut.* **2009**, *157*, 3433–3439.
38. Sarkkola, S.; Koivusalo, H.; Laurén, A.; Kortelainen, P.; Mattsson, T.; Palviainen, M.; Piirainen, S.; Starr, M.; Finér, L. Trends in hydrometeorological conditions and stream water organic carbon in boreal forested catchments. *Sci. Total Environ.* **2009**, *408*, 92–101.

39. Clair, T.A.; Dennis, I.F.; Vet, R.; Laudon, H. Long-term trends in catchment organic carbon and nitrogen exports from three acidified catchments in Nova Scotia, Canada. *Biogeochemistry* **2008**, *87*, 83–97.
40. Dawson, J.J.C.; Malcolm, I.A.; Middlemas, S.J.; Tetzlaff, D.; Soulsby, C. Is the composition of dissolved organic carbon changing in upland acidic streams? *Environ. Sci. Technol.* **2009**, *43*, 7748–7753.
41. Tetzlaff, D.; Malcolm, I.A.; Soulsby, C. Influence of forestry, environmental change and climatic variability on the hydrology, hydrochemistry and residence times of upland catchments. *J. Hydrol.* **2007**, *346*, 93–111.
42. McCartney, A.G.; Harriman, R.; Watt, A.W.; Moore, D.W.; Taylor, E.M.; Collen, P.; Keay, E.J. Long-term trends in pH, aluminium and dissolved organic carbon in Scottish fresh waters; implications for brown trout (*Salmo trutta*) survival. *Sci. Total Environ.* **2003**, *310*, 133–141.
43. Eimers, M.C.; Buttle, J.; Watmough, S.A. Influence of seasonal changes in runoff and extreme events on dissolved organic carbon trends in wetland- and upland-draining systems. *Can. J. Fish. Aquat. Sci.* **2008**, *65*, 796–808.
44. Eimers, M.C.; Watmough, S.A.; Buttle, J.M. Long-term trends in dissolved organic carbon concentration: a cautionary note. *Biogeochemistry* **2008**, *87*, 71–81.
45. Eimers, M.C.; Watmough, S.A.; Buttle, J.M.; Dillon, P.J. Examination of the potential relationship between droughts, sulphate and dissolved organic carbon at a wetland-draining stream. *Glob. Chang. Biol.* **2008**, *14*, 938–948.
46. Erlandsson, M.; Buffam, I.; Fölster, J.; Laudon, H.; Temnerud, J.; Weyhenmeyer, G.A.; Bishop, K. Thirty-five years of synchrony in the organic matter concentrations of Swedish rivers explained by variation in flow and sulphate. *Glob. Chang. Biol.* **2008**, *14*, 1191–1198.
47. Futter, M.N.; Starr, M.; Forsius, M.; Holmberg, M. Modelling the effects of climate on long-term patterns of dissolved organic carbon concentrations in the surface waters of a boreal catchment. *Hydrol. Earth Syst. Sci.* **2008**, *12*, 437–447.
48. Vuorenmaa, J.; Forsius, M.; Mannio, J. Increasing trends of total organic carbon concentrations in small forest lakes in Finland from 1987 to 2003. *Sci. Total Environ.* **2006**, *365*, 47–65.
49. Keller, W.; Paterson, A.M.; Somers, K.M.; Dillon, P.J.; Heneberry, J.; Ford, A. Relationships between dissolved organic carbon concentrations, weather, and acidification in small Boreal Shield lakes. *Can. J. Fish. Aquat. Sci.* **2008**, *65*, 786–795.
50. Lepistö, A.; Kortelainen, P.; Mattsson, T. Increased organic C and N leaching in a northern boreal river basin in Finland. *Glob. Biogeochem. Cycles* **2008**, *22*, GB3029.
51. Monteith, D.T.; Evans, C.D. United Kingdom Acid Waters Monitoring Network 10 Year Report. Analysis and Interpretation of Results, April 1988—March 1998. London, 2000. Available online: http://awmn.defra.gov.uk/resources/interpreports/10yearInterpRpt.pdf (accessed on 23 March 2014).
52. De Wit, H.A.; Mulder, J.; Hindar, A.; Hole, L. Long-term increase in dissolved organic carbon in streamwaters in Norway is response to reduced acid deposition. *Environ. Sci. Technol.* **2007**, *41*, 7706–7713.
53. Worrall, F.; Burt, T.P. Trends in DOC concentration in Great Britain. *J. Hydrol.* **2007**, *346*, 81–92.

54. Worrall, F.; Harriman, R.; Evans, C.D.; Watts, C.D.; Adamson, J.; Neal, C.; Tipping, E.; Burt, T.; Grieve, I.; Monteith, D.; *et al*. Trends in dissolved organic carbon in UK rivers and lakes. *Biogeochemistry* **2004**, *70*, 369–402.
55. Burns, D.A.; McHale, M.R.; Driscoll, C.T.; Roy, K.M. Response of surface water chemistry to reduced levels of acid precipitation: comparison of trends in two regions of New York, USA. *Hydrol. Process.* **2006**, *20*, 1611–1627.
56. Dillon, P.J.; Molot, L.A. Long-term trends in catchment export and lake retention of dissolved organic carbon, dissolved organic nitrogen, total iron, and total phosphorous: The Dorset, Ontario, study, 1978–1998. *J. Geophys. Res.* **2005**, *110*, G01002.
57. Findlay, S.E.G. Increased carbon transport in the Hudson River: Unexpected consequence of nitrogen deposition? *Front. Ecol. Environ.* **2005**, *3*, 133–137.
58. Arvola, L.; Räike, A.; Kortelainen, P.; Järvinen, M. The effect of climate and landuse on TOC concentrations and loads in Finnish rivers. *Boreal Environ. Res.* **2004**, *9*, 381–387.
59. Hongve, D.; Riise, G.; Kristiansen, J.F. Increased colour and organic acid concentrations in Norwegian forest lakes and drinking water—a result of increased precipitation? *Aquat. Sci.* **2004**, *66*, 231–238.
60. Worrall, F.; Burt, T.P. Time series analysis of long-term river dissolved organic carbon records. *Hydrol. Process.* **2004**, *18*, 893–911.
61. Worrall, F.; Burt, T.; Shedden, R. Long term records of riverine dissolved organic matter. *Biogeochemistry* **2003**, *64*, 165–178.
62. Driscoll, C.T.; Driscoll, K.M.; Roy, K.M.; Mitchell, M.J. Chemical response of lakes in the Adirondack region of New York to declines in acidic deposition. *Environ. Sci. Technol.* **2003**, *37*, 2036–2042.
63. Driscoll, C.T.; Van Dreason, R. Seasonal and long-term temporal patterns in the chemistry of Adirondack Lakes. *Water Air Soil Pollut.* **1993**, *67*, 319–344.
64. Forsius, M.; Vuorenmaa, J.; Mannio, J.; Syri, S. Recovery from acidification of Finnish lakes: regional patterns and relations to emission reduction policy. *Sci. Total Environ.* **2003**, *310*, 121–132.
65. Hejzlar, J.; Dubrovský, M.; Buchtele, J.; Růžička, M. The apparent and potential effects of climate change on the inferred concentration of dissolved organic matter in a temperate stream (the Malše River, South Bohemia). *Sci. Total Environ.* **2003**, *310*, 143–152.
66. Jeffries, D.S.; Clair, T.A.; Couture, S.; Dillon, P.J.; Dupont, J.; Keller, W.; McNicol, D.K.; Turner, M.A.; Vet, R.; Weeber, R. Assessing the recovery of lakes in southeastern Canada from the effects of acidic deposition. *Ambio* **2003**, *32*, 176–182.
67. Keller, W.; Heneberry, J.H.; Dixit, S.S. Decreased acid deposition and the chemical recovery of Killarney, Ontario, lakes. *Ambio* **2003**, *32*, 183–189.
68. Gunn, J.N.; Snucins, E.; Yan, N.D.; Arts, M.T. Use of water clarity to monitor the effects of climate change and other stressors on oligotrophic lakes. *Environ. Monit. Assess.* **2001**, *67*, 69–88.
69. Harriman, R.; Watt, A.W.; Christie, A.E.G.; Collen, P.; Moore, D.W.; McCartney, A.G.; Taylor, E.M.; Watson, J. Interpretation of trends in acidic deposition and surface water chemistry in Scotland during the past three decades. *Hydrol. Earth Syst. Sci.* **2001**, *5*, 407–420.
70. Skjelkvåle, B.L.; Stoddard, J.; Andersen, T. Trends in surface water acidification in Europe and North America (1989–1998). *Water Air Soil Pollut.* **2001**, *130*, 787–792.

71. Skjelkvåle, B.L.; Mannio, J.; Wilander, A.; Andersen, T. Recovery from acidification of lakes in Finland, Norway and Sweden 1990–1999. *Hydrol. Earth Syst. Sci.* **2001**, *5*, 327–333.
72. Apsite, E.; Klavins, M. Assessment of the changes of COD and color in rivers of Latvia during the last twenty years. *Environ. Int.* **1998**, *24*, 637–643.
73. Mallory, M.L.; McNicol, D.K.; Cluis, D.A.; Laberge, C. Chemical trends and status of small lakes near Sudbury, Ontario, 1983–1995: evidence of continued chemical recovery. *Can. J. Fish. Aquat. Sci.* **1998**, *55*, 63–75.
74. Bouchard, A. Recent lake acidification and recovery trends in Southern Quebec, Canada. *Water Air Soil Pollut.* **1997**, *94*, 225–245.
75. Schindler, D.W.; Curtis, P.J.; Bayley, S.E.; Parker, B.R.; Beaty, K.G.; Stainton, M.P. Climate-induced changes in the dissolved organic carbon budgets of boreal lakes. *Biogeochemistry* **1997**, *36*, 9–28.
76. Forsberg, C. Will an increased greenhouse impact in Fennoscandia give rise to more humic and coloured lakes? *Hydrobiologia* **1992**, 229, 51–58.
77. Andersson, T.; Nilsson, Å.; Jansson, M. Coloured substances in Swedish lakes and rivers—Temporal variation and regulating factors. *Lect. Notes Earth Sci.* **1991**, *33*, 243–253.
78. Forsberg, C.; Petersen, R.C. A darkening of Swedish lakes due to increased humus inputs during the last 15 years. *Verh. Int. Ver. Limnol.* **1990**, *24*, 289–292.
79. Naden, P.S.; McDonald, A.T. Statistical modelling of water colour in the Uplands: The Upper Nidd catchment 1979–1987. *Environ. Pollut.* **1989**, *60*, 141–163.
80. Watts, C.D.; Naden, P.S.; Machell, J.; Banks, J. Long term variation in water colour from Yorkshire catchments. *Sci. Total Environ.* **2001**, *278*, 57–72.
81. Yallop, A.R.; Clutterbuck, B. Land management as a factor controlling dissolved organic carbon release from upland peat soils 1: Spatial variation in DOC productivity. *Sci. Total Environ.* **2009**, *407*, 3803–3813.
82. Köhler, S.; Hruška, J.; Bishop, K. Influence of organic acid site density on pH modeling of Swedish lakes. *Can. J. Fish Aquat. Sci.* **1999**, *56*, 1461–1470.
83. Koprivnjak, J.-F.; Blanchette, J.G.; Bourbonniere, R.A.; Clair, T.A.; Heyes, A.; Lum, K.R.; McCrea, R.; Moore, T.R. The underestimation of concentrations of dissolved organic carbon in freshwaters. *Water Res.* **1995**, *29*, 91–94.
84. Ivarsson, H.; Jansson, M. Regional variation of dissolved organic-matter in running waters in central northern Sweden. *Hydrobiologia* **1994**, *286*, 37–51.
85. Gadmar, T.C.; Vogt, R.D.; Osterhus, B. The merits of the high temperature combustion method for determining the amount of natural organic carbon in surface freshwater samples. *Int. J. Environ. Anal. Chem.* **2002**, *82*, 451–461.
86. Mattsson, T.; Kortelainen, P.; Räike, A. Export of DOM from boreal catchments: impacts of land use cover and climate. *Biogeochemistry* **2005**, *76*, 373–394.
87. Kortelainen, P. Content of total organic-carbon in Finnish lakes and its relationship to catchment characteristics. *Can. J. Fish. Aquat. Sci.* **1993**, *50*, 1477–1483.
88. Dawson, J.J.C.; Soulsby, C.; Tetzlaff, D.; Hrachowitz, M.; Dunn, S.M.; Malcolm, I.A. Influence of hydrology and seasonality on DOC exports from three contrasting upland catchments. *Biogeochemistry* **2008**, *90*, 93–113.

89. Futter, M.N.; de Wit, H.A. Testing seasonal and long-term controls of streamwater DOC using empirical and process-based models. *Sci. Total Environ.* **2008**, *407*, 698–707.
90. Jonsson, A.; Meili, M.; Bergström, A.-K.; Jansson, M. Whole-lake mineralization of allochthonous organic carbon in a large humic lake (Örträsket, N. Sweden). *Limnol. Oceanogr.* **2001**, *46*, 1691–700.
91. Algesten, G.; Sobek, S.; Bergström, A.-K.; Ågren, A.; Tranvik, L.J.; Jansson, M. Role of lakes for organic carbon cycling in the boreal zone. *Glob. Chang. Biol.* **2004**, *10*, 141–147.
92. Sharp, J.H. Analytical methods for total DOM pools. In *Biogeochemistry of Marine Dissolved Organic Matter*; Hansell, D.A., Carlson, C.A., Eds. Academic Press: San Diego, CA, USA, 2002; pp. 35–58.
93. Suzuki, Y. On the measurement of DOC and DON in seawater. *Mar. Chem.* **1993**, *42*, 287–288.
94. Dafner, E.V.; Wangersky, P.J. A brief overview of modern directions in marine DOC studies. Part I.—Methodological aspects. *J. Environ. Monit.* **2002**, *4*, 48–54.
95. Ogawa, H.; Tanoue, E. Dissolved organic matter in oceanic waters. *J. Oceanogr.* **2003**, *59*, 129–147.
96. Benner, R.; Hedges, J.I. A test of the accuracy of freshwater DOC measurements by high-temperature catalytic oxidation and UV-promoted persulfate oxidation. *Mar. Chem.* **1993**, *41*, 161–165.
97. Kaplan, L.A. Comparison of high-temperature and persulfate oxidation methods. *Limnol. Oceanogr.* **1992**, *37*, 1119–1125.
98. Wangersky, P.J. Dissolved organic carbon methods: A critical review. *Mar. Chem.* **1993**, *41*, 61–74.
99. Buffle, J. Complexation Reactions in Aquatic Systems. An Analytical Approach. Ellis Horwood: Chichester, UK, 1988.
100. Filella, M. Freshwaters: Which NOM matters? *Environ. Chem. Lett.* **2009**, *7*, 21–35.
101. SanClements, M.D.; Oelsner, G.P.; McKnight, D.M.; Stoddard, J.L.; Nelson, S.J. New insights into the source of decadal increases of dissolved organic matter in acid-sensitive lakes of the Northeastern United States. *Environ. Sci. Technol.* **2012**, *46*, 3212−3219.
102. Shiller, A.M.; Boyle, E.A. Variability of dissolved trace metals in the Mississippi River. *Geochim. Cosmochim. Acta* **1987**, *51*, 3273–3277.
103. Windom, H.L.; Byrd, J.T.; Smith, R.G.; Huan, F. Inadequacy of NASQAN data for assessing metal trends in the Nation's rivers. *Environ. Sci. Technol.* **1991**, *25*, 1137–1142.
104. Taylor, H.E.; Shiller, A.M. Mississippi River methods comparison study: Implications for water quality monitoring of dissolved trace elements. *Environ. Sci. Technol.* **1995**, *29*, 1313–1317.
105. Stevenson, K.; Alessa, L.; Altaweel, M.; Kliskey, A.D.; Krieger, K.E. Minding our methods: How choice of time series, reference dates, and statistical approach can influence the representation of temperature change. *Environ. Sci. Technol.* **2012**, *46*, 7435−7441.
106. Hirsch, R.M.; Slack, J.R.; Smith, R.A. Techniques of trend analysis for monthly water quality analysis. *Water Resour. Res.* **1982**, *18*, 107–121.
107. Mann, H.B. Non-parametric test against trend. *Econometrica* **1945**, *13*, 245–249.
108. Kendall, M.G. *Rank Correlation Methods*, 4th ed.; Charles Griffin: London, UK, 1975.
109. Theil, H. A rank-invariant method of linear and polynomial regression analysis. *Adv. Stud. Theor. Appl. Econom*. **1992**, *23*, 345–381.

110. Sen, P.K. Estimates of the regression coefficient based on Kendall's tau. *J. Am. Stat. Assoc.* **1968**, *63*, 1379–1389.
111. Hirsch, R.M.; Slack, J.R. A nonparametric trend test for seasonal data with serial dependence. *Water Resour. Res.* **1984**, *20*, 727–732.
112. Peixoto, J.P.; Oort, A.H. Interannual and interdecadal variability in the climate system. In *Physics of Climate*; American Institute of Physics: New York, NY, USA, 1992; Chapter 16, pp. 412–449.