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Correcting a Major Error in Assessing Organic Carbon Pollution in Natural Waters

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Short title: Major Error in Assessing Organic Water Pollution

Teaser: A widely used method is found to overestimate organic pollution in natural waters and an alternative method is proposed

46 **Abstract**

47 Microbial degradation of dissolved organic carbon (DOC) in aquatic environments can cause oxygen depletion, water
48 acidification and CO₂ emissions. These problems are caused by labile DOC (LDOC), and not refractory DOC (RDOC)
49 that resists degradation and is thus a carbon sink. For nearly a century, chemical oxygen demand (COD) has been widely
50 used for assessment of organic pollution in aquatic systems. Here we show, through a multi-country survey and
51 experimental studies, that COD is not an appropriate proxy of microbial degradability of organic matter because it
52 oxidizes both LDOC and RDOC, and the latter contributes up to 90% of DOC in high-latitude forested areas. Hence COD
53 measurements do not provide appropriate scientific information on organic pollution in natural waters, and can mislead
54 environmental policies. We propose the replacement of the COD method with an optode-based biological oxygen demand
55 method to accurately and efficiently assess organic pollution in natural aquatic environments.

56 **INTRODUCTION**

57 About one quarter of the net carbon fixation on land enters the dissolved organic carbon (DOC) pool of natural waters (*1-*
58 *3*). The nature and behavior of DOC in aquatic systems determine its fate and environmental effects. DOC is often
59 classified based on how rapidly it turns over in the natural environment (*4*). Labile DOC (LDOC) is rapidly degraded and
60 taken up by microbes, and when high amounts of LDOC are released into the environment, the resulting consumption of
61 oxygen can cause oxygen depletion (*5, 6*), with detrimental effects on aquatic ecosystems. Also, respiration of LDOC to
62 CO₂ can result in water acidification (*6, 7*) and release of excess CO₂ (supersaturation) to the atmosphere where it
63 contributes to the greenhouse effect. In this way, a productive coastal region could become a source rather than a sink of
64 atmospheric CO₂ (*7, 8*). It follows that the microbial degradation of LDOC can lead to a series of environmental problems.
65 In contrast, the refractory components of DOC (RDOC) in the aquatic environment are not readily or rapidly metabolized
66 by microbes and so can be preserved in natural waters where they act as a carbon sink (*4, 9*). While RDOC includes
67 chelating agents (*10*) and therefore may act as an important transport pathway or sink for heavy metals, RDOC is not a
68 pollutant but contributes instead to carbon sequestration. In fact, RDOC accounts for more than 95% of the total DOC in
69 the deep ocean (*4, 11*) (man-made persistent organic pollutants are not discussed in this paper because they represent very
70 small amounts of the DOC, *Supplementary Materials 1.1*). A purely chemical view of organic pollution could identify
71 both LDOC and RDOC as organic pollutants, whereas the ecological view of organic pollution clearly restricts pollutants
72 to LDOC. The negative environmental consequences of the microbial degradation of organic compounds mentioned
73 above (i.e., oxygen depletion, acidification, and release of CO₂ to the atmosphere) depend only on the magnitude of the
74 LDOC fraction.

75 The concern generated by organic pollution led governments to monitor microbial degradability of organic matter
76 in water bodies, which became a fundamental tool in environmental policy and management. The biodegradability of

77 organic matter can be evaluated via its oxygen demand by microorganisms, i.e., the amount of oxygen consumed by
78 bacteria and other microorganisms while they decompose and metabolize the organic matter under aerobic conditions.
79 The oxygen demand of LDOC in aquatic environments is best measured as the biological (or biochemical) oxygen demand
80 (BOD) (12). However, the existing standard BOD method is time consuming as it requires 5-day incubations, and has
81 low reproducibility as it involves initial and final measurements on different subsamples (bottles) of the water samples
82 (12). Consequently, BOD estimates have largely been replaced by measurements of chemical oxygen demand (COD),
83 i.e. the determination of the amount of oxygen consumed by chemical reactions in the solution. In COD, potassium
84 dichromate or potassium permanganate is used to rapidly oxidize the organic matter (and also possibly existing reductive
85 inorganic ions) by chemical reactions, thus shortening the measurement time to only a few hours. Given its convenience,
86 relative simplicity, and repeatability, the COD method has been widely used by agencies and scientists for nearly a century
87 for monitoring and managing waste effluents and natural waters (13) (*Supplementary Materials* 1.2 and 1.3). However,
88 the COD method requires the addition of high amounts of strong chemical oxidants (i.e., potassium dichromate and
89 permanganate), which do not exist in natural waters. Hence the COD method artificially oxidizes both LDOC and much
90 or all of the RDOC, whereas oxygen consumption in natural waters is only caused by LDOC oxidation. Although the use
91 of the COD method is justified when rapid measurements are required, such as in the management of wastewater treatment
92 plants, we question its scientific basis and effectiveness for the assessment of organic pollution in natural water bodies.

93 Here, we hypothesize that the COD method substantially overestimates the DOC that can be degraded by microbes
94 in natural waters, with the consequence that using this method could mislead the assessment of organic pollution in aquatic
95 environments (Fig. 1).

96 To test our hypothesis, we analyzed COD and BOD data from experiments conducted for this study and
97 measurements collated from the literature (see Materials and Methods). These data cover a wide variety of natural aquatic
98 environments ranging from tropical to subarctic zones, farmlands to forest watersheds, high plateaus to coastal waters,
99 and freshwaters to saline lakes and marine waters (Fig. S1 and Table S1). We thus examined how COD and BOD vary
100 across gradients of salinity and DOC, with latitude and between ecosystems.

101 Two methods are currently used to determine COD, based on potassium dichromate (COD_{Cr}) and potassium
102 permanganate oxidation (COD_{Mn}) (14) (see Materials and Methods). Comparison of COD_{Cr} and COD_{Mn} values determined
103 on natural waters of different salinities and DOC concentrations ([DOC]), indicated that COD_{Cr} is not a valid measure of
104 oxidized organic matter because salinity interferes with the determination of [DOC] (salinity effect already reported in
105 previous publications including 14), whereas COD_{Mn} may provide appropriate measurements (Figs. S2 and S3, Tables S2
106 and S3). Hence, we only use COD_{Mn} values in the following analysis. To simplify terminology, we use “COD” instead of
107 “ COD_{Mn} ” hereinafter, and “DOC” instead of total organic carbon (TOC) for the following discussion (*Supplementary*

108 *Materials* 1.4).

109 We also used a water-column macrocosm for a long-term incubation of natural water to better understand the
110 problems involved in the current COD method, and the chemical nature of the organic matter oxidized by this method.
111 We incubated in the Aquatron Tower Tank of Dalhousie University 100 m³ of natural river water rich in humic material
112 in darkness for 510 days (see *Materials and Methods*). The DOC in the incubated water was therefore subjected to
113 microbial degradation for a much longer time than the 5 days required by the BOD method. Operationally speaking, any
114 organic matter remaining after the 510-day incubation would have been refractory. We used, for the first time in the
115 literature, ultra-high resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) to analyze
116 the water samples subjected to different treatments regarding the COD methodology (see *Materials and Methods*). A
117 water sample from 1000-m depth in the South China Sea was used as a reference for natural-seawater RDOC.

118 **RESULTS AND DISCUSSION**

119 **Investigating the COD Problems with Field Data**

120 Data from our samples and the literature (Fig. S1 and Table S1) show that the relationships of COD and BOD with [DOC]
121 vary in different natural environments (Fig. 2). The COD values increase linearly with increasing [DOC] in all the
122 sampled natural environments, indicating that COD oxidizes both LDOC and RDOC, as expected. In contrast, the BOD
123 values are much lower than their COD counterparts, as they reflect only LDOC. The relationships observed between BOD
124 and [DOC] across different environments, and the variation therein can be explained by our current understanding of
125 organic matter cycling as follows:

126 First, we explored latitudinal differences in COD and BOD as a function of [DOC] by grouping the data into high
127 latitudes (subpolar areas), mid latitudes (temperate zone), and low latitudes (subtropical zone) (Fig. 2A-C). While the
128 relationships of COD and BOD with [DOC] are totally decoupled at high latitudes (Fig. 2A), they are better aligned at
129 lower latitudes (Fig. 2B and C). In the subpolar environment, the low BOD values and their independence from [DOC]
130 (low correlation and regression coefficients, i.e. 0.16 and 0.39, respectively) indicate generally low LDOC concentration
131 while the increase of (COD-BOD) with increasing [DOC] indicates accumulation of RDOC with increasing [DOC]. In
132 the temperate zone, the values of COD and BOD both increase with [DOC], and the (COD-BOD) values are generally
133 similar to the BOD values. This indicates similar concentrations of LDOC and RDOC at mid-latitudes. In the subtropical
134 zone, the (COD-BOD) values are lower than BOD, indicating that COD is dominated by LDOC with less RDOC
135 accumulating in the environment than at mid-latitudes (Fig. 2B and C). In terms of the absolute value of COD, the
136 subpolar zone ranks the highest, followed by the temperate and subtropical zones, the latter being the lowest, whereas the
137 BOD values remain at the same general level (Fig. 2). If these COD values were assessed according to conventions used
138 in environmental management, the high COD values at high latitude would be interpreted as highly organic-polluted

139 compared with low latitudes. Instead, the high COD values are due to high concentrations of non-polluting RDOC (see
140 above).

141 Second, we grouped the same samples as in Fig. 2A-C by ecosystems (Fig. 2D-F). This led to the emergence of
142 distinct patterns in LDOC and RDOC that reflect changes in organic matter as it moves through the hydrological cycle
143 towards the sea. In waters of forested regions, BOD is almost independent of [DOC] and (COD-BOD) increased
144 proportionally with [DOC]. The latter is consistent with DOC in forested watersheds consisting mostly of humic-like
145 compounds, which are common components of RDOC (15, 16). In the other freshwater samples (Fig. 2E), the linear
146 relations of (COD-BOD) and BOD with [DOC] were similar, indicating similar fractions of LDOC and RDOC in DOC.
147 In coastal water samples, the values of BOD are higher than those of (COD-BOD), indicating that COD is dominated by
148 LDOC. If the conventional COD standards were applied to the assessment of water quality in these different ecosystems,
149 waters of forested regions would be considered as loaded with organic pollutants. Instead, the high COD values are due
150 to high concentrations of non-polluting humic-like RDOC compounds (see above). This shows again the drawback of
151 relying on COD as an indicator of organic pollution in natural aquatic systems.

152 Taken together, the above field observations are consistent with our hypothesis that COD reflects the oxidation of
153 both LDOC, which can be naturally degraded by microbes, and RDOC, which resists biodegradation. In contrast, BOD
154 reflects the oxidation of LDOC only. Hence, COD is not a valid indicator of the microbial degradability of organic
155 compounds, and thus organic pollution in aquatic environments, whereas BOD provides realistic estimates of
156 biodegradability.

157 **Investigating the COD Problems Experimentally**

158 To further investigate which fractions of naturally occurring organic matter are oxidized by the COD method, samples
159 from the 510-day incubation in the Aquatron Tower Tank were treated with/without the COD method, and FT-ICR MS
160 analyses were used to identify differences between treatments. Results are summarized in Fig. 3, where a water sample
161 from 1000-m depth in the South China Sea provides a reference for natural-seawater RDOC (Fig. 3G) (17). The FT-ICR
162 MS raw peak distributions (m/z 200~600) showed no major changes in components of the samples before and after the
163 510-day incubation (Figs. 3A and 3B, respectively), reflecting the natural richness of the river water in RDOC. In contrast,
164 there was a large change in the FT-ICR MS peak distributions after the COD treatment of both the initial and the 510-day
165 incubated samples (Figs. 3C and 3D). This shows that most DOC molecules in the m/z range of 200-600 persisted during
166 the 510-day incubation (Figs. 3A and B), but were oxidized by the COD treatment of both the initial and incubated water
167 (Figs. 3A vs. 3C, and 3B vs. 3D).

168 The FT-ICR MS analysis provides a proxy for the naturally occurring RDOC, i.e., the polygons in Figs. 3E to 3G
169 delineate carboxyl-rich alicyclic-like (CRAM-like) molecules based on the literature (10, 18). These molecules dominate

170 the DOC of the deep ocean, where they are identified as RDOC (10, 17, 19). Figures 3E and 3F show the molecules that
171 were oxidized by the COD method (i.e., samples in Figs. 3A *minus* 3C, and 3B *minus* 3D, respectively). A large part of
172 the oxidized molecules corresponds to the naturally occurring CRAM-like molecules in the deep seawater (Fig. 3G).
173 These results demonstrate that the COD treatment rapidly oxidizes RDOC molecules that would otherwise persist for
174 long periods as part of the carbon sink in natural waters.

175 **Resolving Paradoxical Results Arising From Monitoring Pollution as COD**

176 In the practical application of COD methods in natural waters, there is often a paradoxical decoupling between COD and
177 BOD, including in situations where environmental protection measures have been carried out for decades. Representative
178 examples are Lake Biwa in Japan (20), the Han River in Korea (21), and Finnish rivers (22) (Fig. 4). Lake Biwa was
179 notorious for its organic pollution in the 1970s, but this pollution was reduced over the past three decades. It might
180 therefore be expected that COD, as an indicator of organic pollution, would have decreased in response to the abatement
181 of organic pollution. However, COD has increased since the 1980s, whereas BOD has decreased (Fig. 4A). This apparent
182 paradox can be explained by a long-term accumulation of RDOC in the lake, which can be oxidized by the COD but not
183 the BOD method. In cases such as Lake Biwa, environmental protection agencies should definitely use BOD instead of
184 COD for assessing water quality. In the Han River (Fig. 4B), the COD values remained fairly constant over 20 years,
185 whereas the BOD values continuously decreased. This means that the relative fraction of RDOC increased, while the
186 LDOC fraction decreased over the past 20 years along with less eutrophication that would remobilize RDOC for
187 decomposition (23). In Finnish rivers (Fig. 4C), COD and BOD both decreased over the past decades, and since BOD
188 decreased faster than COD, the (COD-BOD)/COD ratio increased. This indicates that the relative fraction of RDOC
189 increased and that of LDOC decreased.

190 Again, these long-term observations show that COD measurements on their own do not provide consistent estimates
191 of organic pollution, whereas the BOD values yield such estimates in all circumstances. Furthermore, COD data used
192 alone may fail to detect, or mask, the success of environmental protection countermeasures at curbing organic pollution.

193 **Replacing COD by a Modern BOD Method**

194 The above analyses clearly show that COD is not a valid indicator of the microbial degradability of organic compounds,
195 and thus organic pollution in natural waters. This is because COD reflects the oxygen demand of both LDOC and RDOC,
196 and the latter is not, or at least is very inefficiently, oxidizable by microbes and is thus part of the carbon sink. The fact
197 that COD confounds RDOC with organic pollution implies that it can mislead environmental assessments or the
198 application of environmental policies. However, COD is currently used widely for the monitoring and management of
199 natural waters (13, 24-26). As explained above, the present study has no bearing on the use of COD in wastewater
200 treatment plants, but addresses its use with natural waters. Many governmental and international organizations presently

201 rely on COD data to establish environmental standards and policies (*Supplementary materials* 1.2 and Table S4 and S5).
202 Hence, there is a pressing need to prevent the misinterpretation created by the use of COD, especially considering that
203 the International Organization for Standardization recommended COD as one of the parameters for assessing the quality
204 of natural waters (27). Many countries use COD as the primary standard for water quality control and environmental
205 assessment. For example, in China and Japan, the performance of environmental policies has been assessed based on the
206 reduction of COD (Tables S4 and S5).

207 A substitute for the COD method is therefore required. TOC has been proposed for the monitoring of wastewater
208 treatment and aquatic environments (13, 28). However, TOC measurements include RDOC, which disqualifies it as an
209 appropriate measurement to determine the microbial degradability of organic compounds. Similarly, total oxygen demand
210 (TOD) (29) is not an appropriate alternative to COD as it incorporates the oxidation of RDOC. In contrast, BOD has clear
211 scientific basis, and remains the first choice as an alternative to COD. However, the traditional BOD method has been
212 abandoned in many instances because of its labor-intensive nature, and also the variability introduced by the heterogeneity
213 among the bottles used for oxygen titrations before and after incubation. Here we recommend a modern BOD method
214 that uses oxygen optodes (30, 31) instead of oxygen titration for the measurement of oxygen concentration, where the
215 latter can be conducted in the same incubated bottles before and after incubation (or even continuously). This reduces the
216 number of incubation bottles, reduces procedural errors, and eliminates the use of hazardous chemicals (see Materials and
217 Methods). The optode-based BOD measurements provide repeatable values that are more indicative of water quality than
218 COD (Figs. S4 and S5).

219 **From Field Measurements to Environmental Policy**

220 The above results of our multi-country field survey and experimental studies are consistent with our hypothesis that the
221 COD method substantially overestimates the DOC that can be degraded by microbes in natural waters, showing that the
222 application of the COD method often misleads the assessment of organic pollution in aquatic environments. We
223 recommend the modern optode-based BOD method to replace the COD method for application in natural aquatic
224 environments. Such measurements are required to inform policy makers of the risks of adverse environmental conditions
225 that can be triggered by high concentrations of LDOC, and to design and implement measures to improve water quality.
226 With the increasing need to monitor and manage water quality, it is imperative to refine and improve the scientific
227 measurements on which policy depends.

228

229 **MATERIALS AND METHODS**

230 **Sampling sites and data from the literature.**

231 The field data used in this paper include new measurements made for this study and data collated from the literature. The

232 field measurements were conducted in China (coastal water samples from the Xiamen Bay, Sanya Bay, Bohai Sea and
233 Yellow Sea, and freshwater samples from Fujian, Sichuan and the Tibetan Plateau), Canada (Nova Scotia, New
234 Brunswick, Quebec and British Columbia), and the USA (Florida). The sampling locations are shown in Fig. S1, and
235 detailed information is provided in Table S1. In order to keep the data comparable, we only took from the literature COD
236 values measured using the titration COD_{Mn} method and BOD data using the BOD₅ method (described below) (20-22, 32-
237 35).

238 **Potassium dichromate oxidation (COD_{Cr}) method**

239 There are two methods for COD measurements: one with potassium dichromate as oxidant (COD_{Cr}) and the other with
240 potassium permanganate (COD_{Mn}, which has two variants or protocols described next section). The measurement of
241 COD_{Cr} was based on the International Standard ISO6060 "Determination of Chemical Oxygen Demand in Water"
242 (<https://www.iso.org/standard/12260.html>), which was officially reviewed and confirmed in 2017. Briefly, 10 mL of a
243 water sample was added into a 250 mL conical flask. Five mL K₂Cr₂O₇ solution was added into the water and thoroughly
244 mixed. After connecting the conical flask into a condensing system, 15 mL AgSO₄-H₂SO₄ solution was slowly added into
245 the mixture, which was then heated to boiling point for 2h. After that, about 45 mL of ultra-pure water was added. Cooling
246 to room temperature, one or two drops of ferroin were added into the mixture to serve as a titration indicator, and titration
247 was conducted with (NH₄)₂Fe(SO₄)₂·6H₂O solution and ended after the color of the mixture turned brown. The consumed
248 volume of (NH₄)₂Fe(SO₄)₂·6H₂O solution was recorded as V₁ (mL). As a control, 10 mL ultra-pure water was used for the
249 titration described above, and the consumed volume of the (NH₄)₂Fe(SO₄)₂·6H₂O solution was recorded as V₀ (mL).
250 COD_{Cr} (mg O₂ L⁻¹) was calculated from the following equation: $COD_{Cr} = (c((NH_4)_2Fe(SO_4)_2 \cdot 6H_2O) \times (V_0 - V_1) \times 8000) / 10$.
251 Triplicate water samples were analyzed at each station.

252 **Potassium permanganate oxidation (COD_{Mn}) protocols**

253 There are two COD_{Mn} protocols in the literature: alkaline COD_{Mn} and acidic COD_{Mn} protocols. The alkaline COD_{Mn}
254 protocol is described in the Chinese national standard method of COD for seawater (GB1737.4-2007) and uses KMnO₄
255 as oxidant in alkaline conditions. Briefly, a 100 mL water sample was added into a 250 mL conical flask. One mL NaOH
256 (250 g L⁻¹) and 10 mL KMnO₄ solution (0.01 mol L⁻¹) were added to the water and thoroughly mixed. The mixture was
257 heated to boil for 10 min, after which it was quickly cooled to room temperature. After this, 5 mL H₂SO₄ solution (5 mol
258 L⁻¹) and 0.5 g KI were added to the cooled mixture, which was then placed in the dark for 5 min. With the solution
259 continuously shaken, titration was conducted with Na₂S₂O₃·5H₂O solution ($c \approx 0.01$ mol L⁻¹, calibrated by KIO₃ standard
260 solution) until the color of the mixture turned light yellow. Then, 1 mL of starch solution (5 g L⁻¹) was added to the
261 mixture and the titration was continued until the mixture turned transparent. The consumed volume of the Na₂S₂O₃·5H₂O
262 solution was recorded as V₁ (mL). As a control, 100 mL ultra-pure water was used for the titration described above, and

263 the consumed volume of the $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ solution was recorded as V_0 (mL). Triplicate water samples were analyzed at
264 each station. COD_{Mn} ($\text{mg O}_2 \text{L}^{-1}$) was calculated using the following equation:

$$265 \text{ Alkaline } \text{COD}_{\text{Mn}} = (c(\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}) \times (V_0 - V_1) \times 8000) / 100$$

266 The acidic COD_{Mn} protocol is described in the Chinese national standard method of COD for surface water
267 (GB11892-89) and uses KMnO_4 as oxidant in acidic conditions. Briefly, a 100 mL water sample was added into a 250
268 mL conical flask. Five mL H_2SO_4 solution (5 mol L^{-1}) and 10 mL KMnO_4 solution (0.01 mol L^{-1}) were added to the water
269 and evenly mixed. The mixture was heated for 30 min in a boiling water bath. Ten mL $\text{Na}_2\text{C}_2\text{O}_4$ solution (0.01 mol L^{-1})
270 was then added to the mixture, which turned transparent. With the solution continuously shaken, the titration was
271 conducted with KMnO_4 solution (0.01 mol L^{-1}) until the color of the mixture turned pink, and remained pink for at least
272 30 sec. The consumed volume of the KMnO_4 solution was recorded as V_1 (mL). As a control, 100 mL ultra-pure water
273 was used for the titration described above, 10 mL $\text{Na}_2\text{C}_2\text{O}_4$ solution (0.01 mol L^{-1}) was added to the mixture, KMnO_4
274 solution was used as the titrant, and the consumed volume recorded as V_0 (mL). Triplicate water samples were analyzed
275 at each station. Acidic COD_{Mn} ($\text{mg O}_2 \text{L}^{-1}$) was calculated using the following equation:

$$276 \text{ Acidic } \text{COD}_{\text{Mn}} = ((10 + V_1) \times 10 / (V_0 - 10)) \times c(\text{KMnO}_4) \times 8000 / 100$$

277 The acidic COD_{Mn} protocol is recognized to be applicable for freshwater but not saline water, because of a salinity
278 effect, i.e. an over-estimation due to interference of inorganic ions (36-38). We investigated this by comparing results
279 from the acidic and alkaline protocols for samples with salinities ranging from 0 to 30 (Table S3). The data from the
280 acidic COD_{Mn} protocol were systematically larger than those obtained with the alkaline COD_{Mn} protocol for salinities
281 >0.3 , and the difference increased with salinity (Fig. S3). In fresh waters (salinities ≤ 0.3), some data from the acidic
282 COD_{Mn} protocol were smaller than those from the alkaline COD_{Mn} protocol. Since both methods use excessive amounts
283 of oxidants, they are unlikely to produce underestimated values. Given that the data in this study came from freshwater,
284 estuarine and marine environments, we decided to use only the values obtained with the alkaline COD_{Mn} protocol, in
285 order to avoid overestimation of COD values in estuarine and saline waters.

286 **Comparison of COD_{Cr} and alkaline COD_{Mn} measurements**

287 The COD_{Cr} and alkaline COD_{Mn} measurements of natural water samples with different salinities showed that the COD
288 values from the two methods were not influenced in the same way by the presence of inorganic reductants (Table S2).
289 The values of COD_{Cr} were significantly higher than those of COD_{Mn} in all samples, the former being up to 80 times the
290 latter in saline waters (Fig. S2A). In addition, the coefficients of correlation of COD_{Cr} and COD_{Mn} with salinity ($r = 0.94$,
291 $\text{prob} < 0.001$, and $r = 0.54$, $\text{prob} = 0.075$, respectively) indicate a significant positive relationship between COD_{Cr} and
292 salinity, and no relationship between COD_{Mn} , and salinity. As a consequence, the ratio $\text{COD}_{\text{Cr}}/\text{COD}_{\text{Mn}}$ significantly
293 increased with salinity (Fig. S2B). These results show that salinity had a systematic effect on COD_{Cr} measurements.

294 It follows that the COD_{Cr} does not provide a proper measure of oxidized organic matter especially in saline waters,
295 whereas alkaline COD_{Mn} may provide realistic estimates of oxidized DOC. Hence in order to make all our data
296 comparable, we only used COD_{Mn} measurements, either made for this study or collated from the literature (as listed in
297 Table S1). To simplify terminology, we use “COD” instead of “alkaline COD_{Mn} ” in this paper.

298 **Protocol of Biochemical Oxygen Demand (BOD) by the BOD₅ Winkler method**

299 Five-day BOD (BOD_5) measurement of oxygen consumption by Winkler titration is a standard method by the
300 International Organization for Standardization. Water samples for BOD measurements were incubated in the dark at 20°C
301 for 5 days. The measurement of dissolved oxygen ($[\text{O}_2]$) was based on the ISO 5813:1983 Determination of dissolved
302 oxygen-Iodometric (Winkler) method (<https://www.iso.org/obp/ui/#iso:std:iso:5813:ed-1:v1:en>). Briefly, to determine
303 the initial oxygen concentration, 1 mL of MnCl_2 solution (420 g L^{-1}) and 1 mL of alkaline KI solution (150 g L^{-1}) were
304 sequentially added into triplicate water samples in 140 mL opaque BOD bottles, then mixed thoroughly and the samples
305 allowed to sit in a water bath held at 20°C for at least 4 h. Thereafter, the precipitate was dissolved with, 2 mL of H_2SO_4
306 solution (5 mol L^{-1}). After transferring 100 mL of the solution into a 250 mL conical flask, the titration was conducted as
307 described for the COD_{Mn} method, and the titrated volume of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ solution (c , mol L^{-1}) recorded as V_0 (mL).
308 After the 5-day incubation, triplicate water samples were collected and treated by the same procedure as described above,
309 and the titrated volume of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ solution was recorded as V_5 (mL). BOD_5 ($\text{mg O}_2 \text{ L}^{-1}$) was calculated using the
310 following equation:

$$311 \text{BOD}_5 = c(\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}) \times (V_0 - V_5) \times 1000 \times 8/100$$

312 Calibration for concentration of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ standard solution: 10 mL KIO_3 standard solution ($0.0100 \text{ mol L}^{-1}$)
313 were poured into a 250 mL conical flask, and 0.5 g KI and 1 mL H_2SO_4 solution (5 mol L^{-1}) were sequentially added to
314 the flask, which was then sealed and gently shaken. After keeping the mixture in the dark for 2 min, 50 mL of ultra-pure
315 water were added and gently mixed, in preparation for titration. The titration was conducted with a $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ solution
316 until the color of the mixture turned light yellow, after which 1 mL of starch solution (5 g L^{-1}) was added, and the titration
317 was continued until the mixture became transparent. The consumed volume of the $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ solution was recorded
318 as V (mL). The concentration of the $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ solution (mol L^{-1}) was calculated using the following equation:

$$319 c(\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}) = 10 \times 0.0100 / V$$

320 **Determination of dissolved organic carbon (DOC)**

321 Samples for DOC measurements were filtered through pre-combusted (450°C, 4 h) Whatman GF/F glass fiber filters. All
322 the samples were then acidified to pH=2 with H_3PO_4 and stored at -20°C until analyzed. The carbon content of samples
323 was measured using the high-temperature combustion method with a Shimadzu TOC-LCPH TOC analyzer and ultrapure
324 water for system blank subtraction (39). Reference deep seawater (provided by the Hansell Organic Biogeochemistry

325 Laboratory at the University of Miami, USA) served as an additional control (40). The analytical methodology for DOC
326 was the same for all studies reported in our work.

327 **Aquatron Tower Tank and long-term incubation experiments**

328 Located at Dalhousie University (Halifax, Canada), the Aquatron is the site of the Tower Tank, which is 10.64 m deep
329 and 3.66 m in diameter, with an approximate water volume of 117 m³,
330 (<https://www.dal.ca/faculty/science/biology/research/facilities/aquatron.html>). It is well suited for biogeochemical
331 research requiring depth and stratification. To conduct our long-term incubation experiment, we filled the Tower Tank
332 with about 20 tons of humic-like water from the Ingranport River near Halifax. The incubation was run at room
333 temperature (20°C) in the dark for 510 days. Water samples were taken before and after the incubation, and filtered
334 through Whatman GF/F filters (pre-combusted as above) for solid-phase extraction of dissolved organic matter (see
335 below).

336 **Solid-phase extraction of natural DOM and COD treated DOM, and Fourier Transformation Cyclotron** 337 **Resonance Mass Spectrometry (FT-ICR MS) analysis**

338 DOM was solid-phase extracted following a standard procedure (41). For the initial (DOC concentration = 885.96±6.60
339 μmol C L⁻¹) and long-term incubation (510-day) (DOC concentration = 744.06±6.80 μmol C L⁻¹), DOM was extracted
340 from water samples using 500 mg Bond Elut-PPL cartridges (Agilent) activated with HPLC grade methanol (Merck) and
341 rinsed with acidified Milli-Q water (pH=2). An aliquot of 200 mL water sample was filtered through a pre-combusted
342 (450°C) GF/F glass fiber filter and then passed by gravity through the cartridge, which was subsequently extensively
343 rinsed with acidified Milli-Q water (pH=2) and completely dried before elution with HPLC grade methanol. Each
344 cartridge was eluted with 3 mL HPLC grade methanol, and this DOM extract was adjusted to yield almost the same DOC
345 concentration for each sample before injecting to the FT-ICR MS for analysis.

346 To investigate which fractions of naturally occurring organic matter were oxidized by the COD method, the initial
347 and long-term incubation of river water samples were subjected to COD_{Mn} prior to DOM extraction. Two mL NaOH
348 solution (250 g L⁻¹) and 20 mL KMnO₄ solution (0.01 mol L⁻¹) were added to a 200 mL aliquot of the water sample in a
349 500 mL conical flask. The mixture was then heated to boil for 10 min. After cooling down to room temperature and being
350 neutralized by HCl (HPLC grade) to pH=7, 0.02 g of NaHSO₃ (Sigma-Aldrich) was added to the mixture to reduce the
351 residue KMnO₄. Then DOM was extracted using the standard solid phase extraction procedure described above. As a
352 control, 200 mL Milli-Q water was used for the COD treatment described above, and DOM molecules commonly existing
353 in the control and the COD_{Mn} treated water samples were excluded from further analyses. All the glassware used for COD
354 treatments was acid cleaned and combusted (480°C for 4 h).

355 The DOM extracts were adjusted to yield approximately 25 mM DOC and analyzed using a Bruker Apex Ultra FT-

356 ICR mass spectrometer equipped with a 9.4 T superconducting magnet. Sample solutions were infused via an Apollo II
357 electrospray ion source (ESI) at 180 $\mu\text{L h}^{-1}$ with a syringe pump. Typical operating conditions for negative ESI were as
358 follows: spray shield voltage 3.5 kV, capillary column initial voltage 4 kV, and capillary column end voltage -320 V .
359 The mass range was set to m/z 150–800. The 4M word size was selected for the time domain signal acquisition. A number
360 of 128-time domain signals were co-added to enhance the signal-to-noise ratio and dynamic range. The magnitude
361 threshold for the peak assignment was set to a signal-to-noise ratio of ≥ 4 . The FT-ICR MS was calibrated using a known
362 homologous series of the Suwannee River natural organic matter sample (obtained from the International Humic
363 Substances Society, USA), which contained a relatively high abundance of oxygen-containing compounds. Molecular
364 formulae were assigned with the calibrated mass data using in-house software (40). The elemental compositions were
365 assigned from the m/z peaks using a mass calculator program limited to molecular formulae consisting of $^{12}\text{C}_{0-100}$, $^{13}\text{C}_{0-2}$,
366 $^1\text{H}_{0-200}$, $^{14}\text{N}_{0-5}$, $^{16}\text{O}_{0-35}$, $^{32}\text{S}_{0-2}$ and $^{34}\text{S}_{0-1}$ (40, 42). All assigned formulae had to meet the following basic chemical criteria:
367 (1) the number of H atoms should not exceed $2C + N + 2$; (2) the sum of H and N atoms should be even (the “nitrogen
368 rule”); and (3) the number of N or O atoms should not exceed the number of C atoms (43, 44).

369 **Proposed new technique for BOD determination: The oxygen-optode BOD method**

370 Oxygen optodes are optical sensors that are based on a chemical indicator (dynamic fluorescence quencher) (45). These
371 robust and high-resolution sensors (46, 47) have been used to study a number of oxygen-related processes in freshwater
372 and marine systems (48-52), yielding the same sensitivity as the chemical Winkler method (53, 54). For example, oxygen
373 optodes have already been used in oceanography for measurements of community respiration rates in the mesopelagic
374 and surface waters of the oligotrophic open ocean (48-50). They have also been used for measuring BOD in wastewater
375 (55, 56). Here, we propose a novel, modern BOD method using oxygen optodes instead of the traditional Winkler titration
376 for the measurement of dissolved oxygen concentration $[\text{O}_2]$ in the BOD bottles. Oxygen optodes allow the recording of
377 oxygen consumption in the incubated BOD bottles continuously in a non-invasive and non-destructive manner, so that
378 the initial and final dissolved oxygen determinations can be conducted in the same BOD bottles (Fig. S4). This is a major
379 advantage over the Winkler method, where the initial and final titrations must be done on different bottles. After proper
380 calibration of the optodes (see below), the $[\text{O}_2]$ and thus BOD values meet the quality standard of those obtained with the
381 conventional Winkler titration method.

382 A detailed description of the BOD optode method will be provided in a separate specialized paper. Briefly, the steps are:
383 (1) water sampling and filling of BOD bottles, which are incubated for 5 days; (2) oxygen optode measurements in
384 triplicate incubated BOD bottles, and (3) calculation of BOD_5 (where the index 5 stands for 5 days) from oxygen-optode
385 measurements.

386 Before using the OXSP5 optodes (PyroScience, Germany) for measuring O_2 in samples, we calibrated them with

387 Winkler titrations. We used a Metrohm auto-titrator (888 Titrande with a combined platinum ring electrode) for the
388 Winkler O₂ determinations. The 5-day incubations were conducted at 20 ± 0.1°C. Winkler O₂ was measured at t=0, every
389 second hour until t=8 hours, and every day until day 5 on triplicate bottles during the course of the incubation (total of 30
390 bottles). The optode signal was measured every 10 min in triplicate bottles during the course of the incubation, with one
391 measurement every 3 s during 2.5 min to acquire 50 values at each Winkler sampling point (total of 3 bottles).

392 We tested the validity of the optode BOD method on a variety of natural freshwater and seawater samples. One
393 example was from the DaRen River, Qingdao, China. The results showed good agreement between the optode and
394 Winkler measurements (Fig. S5). The coefficient of variation (CV) of the measurements by the optode method (CV =
395 0.0824; n=145) was an order of magnitude lower than that of the Winkler method (CV =0.4472; n=42), indicating that
396 the novel oxygen-optode approach can improve the reliability of the oxygen measurement in a BOD determination.

397 In summary, the novel oxygen-optode BOD method offers several advantages over the traditional Winkler method.
398 Firstly, it provides a more precise measurement of BOD, i.e., replicates from a given sample measured by the optode
399 method reveal a much smaller standard deviation than the respective Winkler replicates do. Secondly, it eliminates the
400 chemical waste associated with the Winkler method as well as the need to take into the field chemicals that are toxic to
401 aquatic life such as alkaline iodide azide and MnCl₂. Thirdly, it removes operator error associated with labor-intensive
402 titrations.

403

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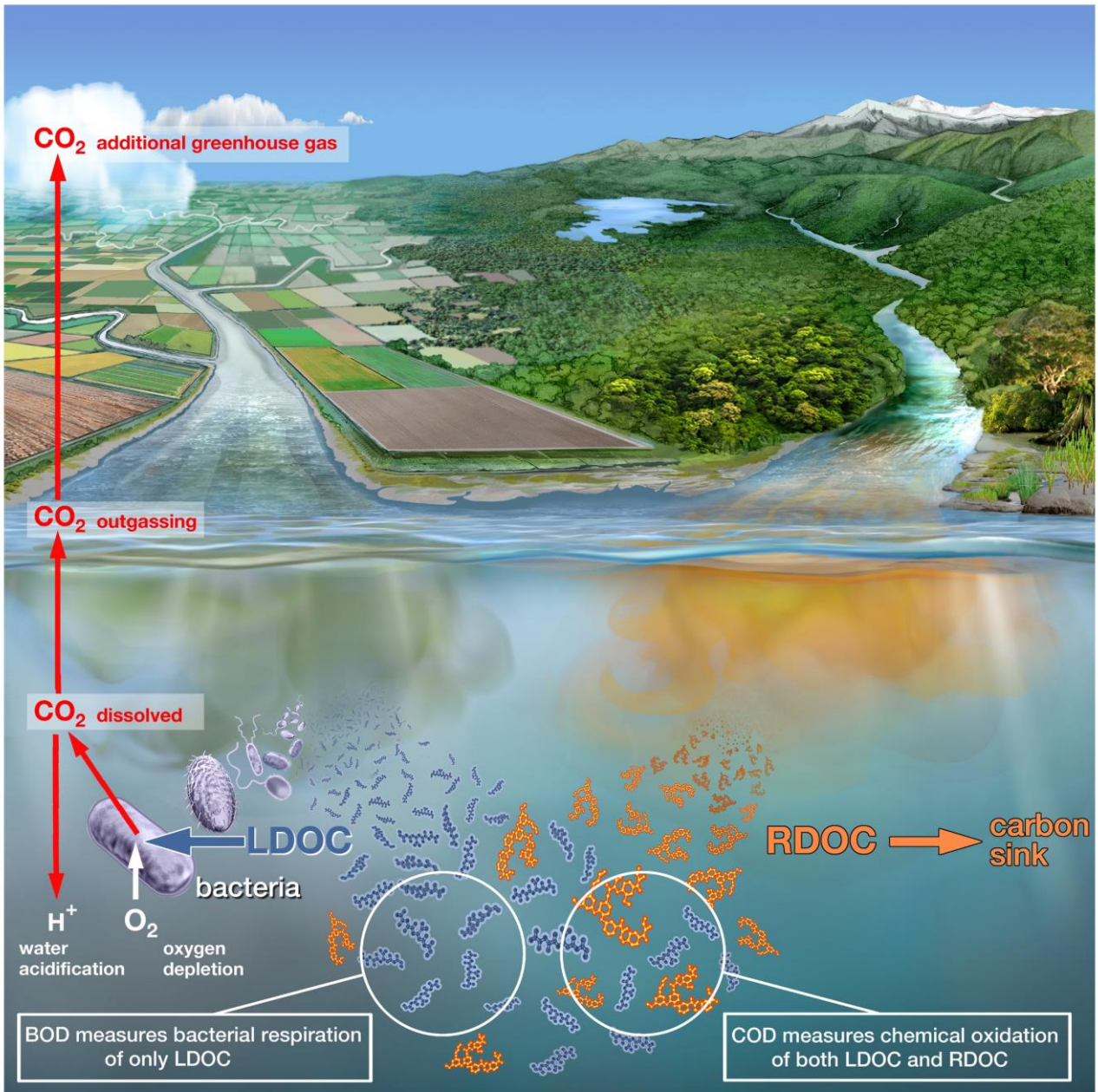
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633 and BOD data. X. X., Z. L., X. H., J. S. and N. J., collected the literature data; N. J., J. L. and B. E. conducted the Optode-
634 based BOD experiments and analysis; R. C., C. H. and Q. S. conducted the FT-ICR MS measurements and data analysis;
635 N. J. and L. L. wrote the paper with contributions from all the coauthors, including R. Z., Y. Z., K. T., Q. Z., F. A., J. B.,
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637 declare no competing interest. **Data and materials availability:** All the COD and BOD data and related information on

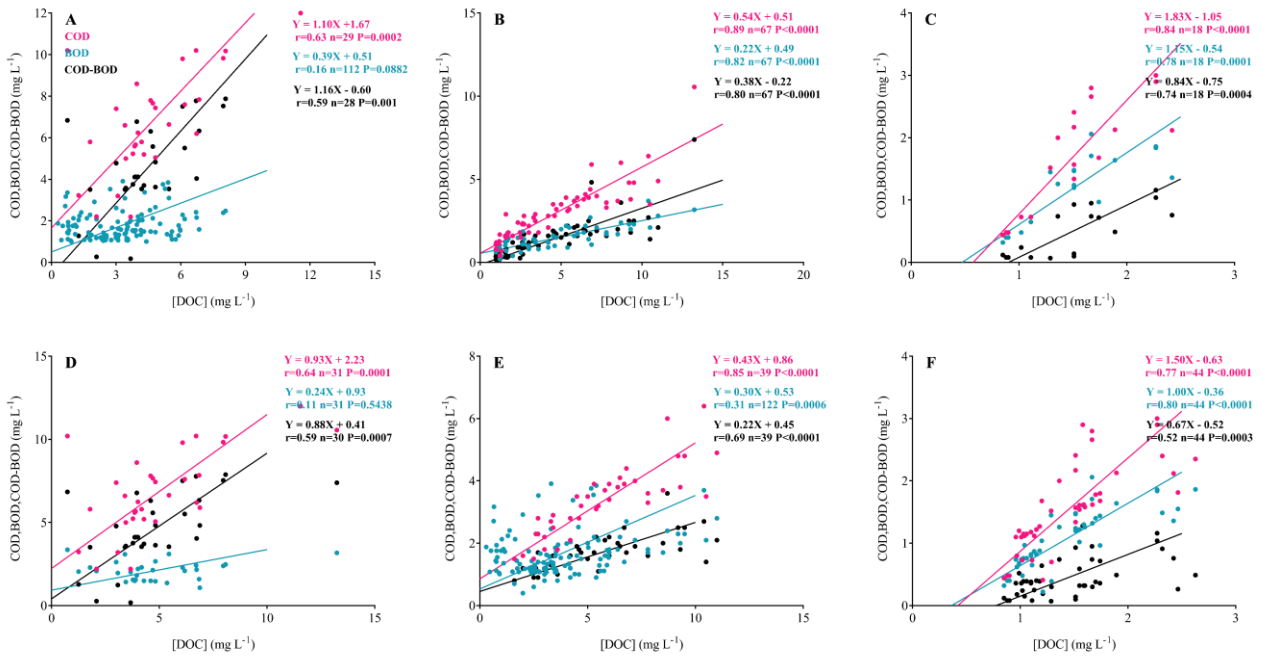
638 sampling and data mining are given in the Materials and Methods, Fig. S1 and Tables S1, S2 and S3. The mass
639 spectrometry data are available on PANGAEA ([doi.pangaea.de/10.1594/PANGAEA.910007](https://doi.org/10.1594/PANGAEA.910007)). We are grateful to the
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643 **Fig. 1. Schematic representation of LDOC and RDOC in the environment, and their determination using the BOD**
 644 **and COD approaches.** Degradation of LDOC can cause oxygen depletion, water acidification and CO_2 emission, and is
 645 best assessed by the BOD method. Only LDOC is readily degradable by microbes in natural waters; RDOC has no adverse
 646 environmental effects and is a carbon sink. The widely used COD method oxidizes both LDOC and RDOC, and so could
 647 result in a major error in the assessment of organic pollution.

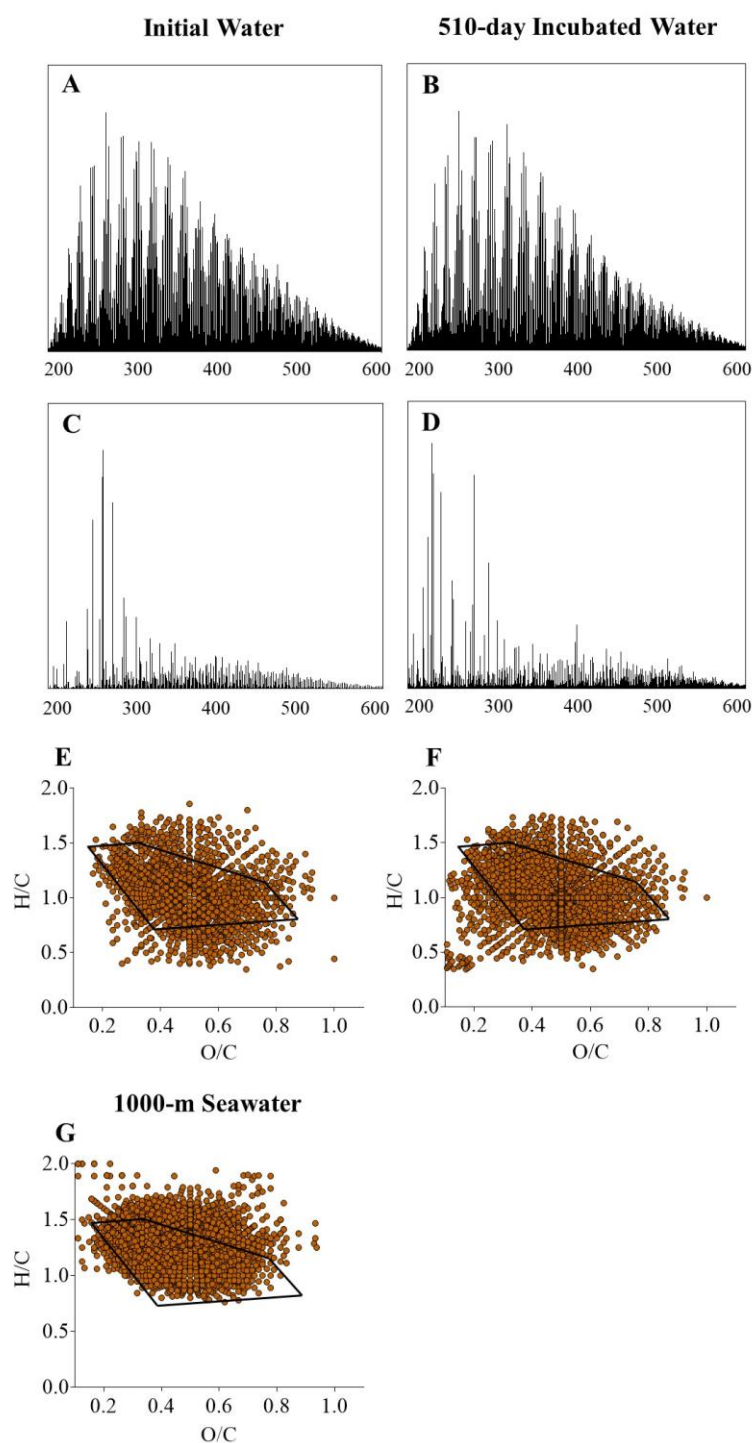
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650 **Fig. 2. COD and BOD as a function of [DOC] in different environments: (A)** high latitudes/subpolar areas, **(B)** mid-
 651 latitudes/temperate zone, **(C)** low latitudes/subtropical zone, **(D)** forested watersheds, **(E)** fresh waters, **(F)** seawater. Note
 652 the different X and Y-axes scales of the different panels. The same samples were grouped by **(A-C)** latitudes and also **(D-**
 653 **F)** ecosystems. Regressions: Model 2 Standard Major Axis. n: number of samples.

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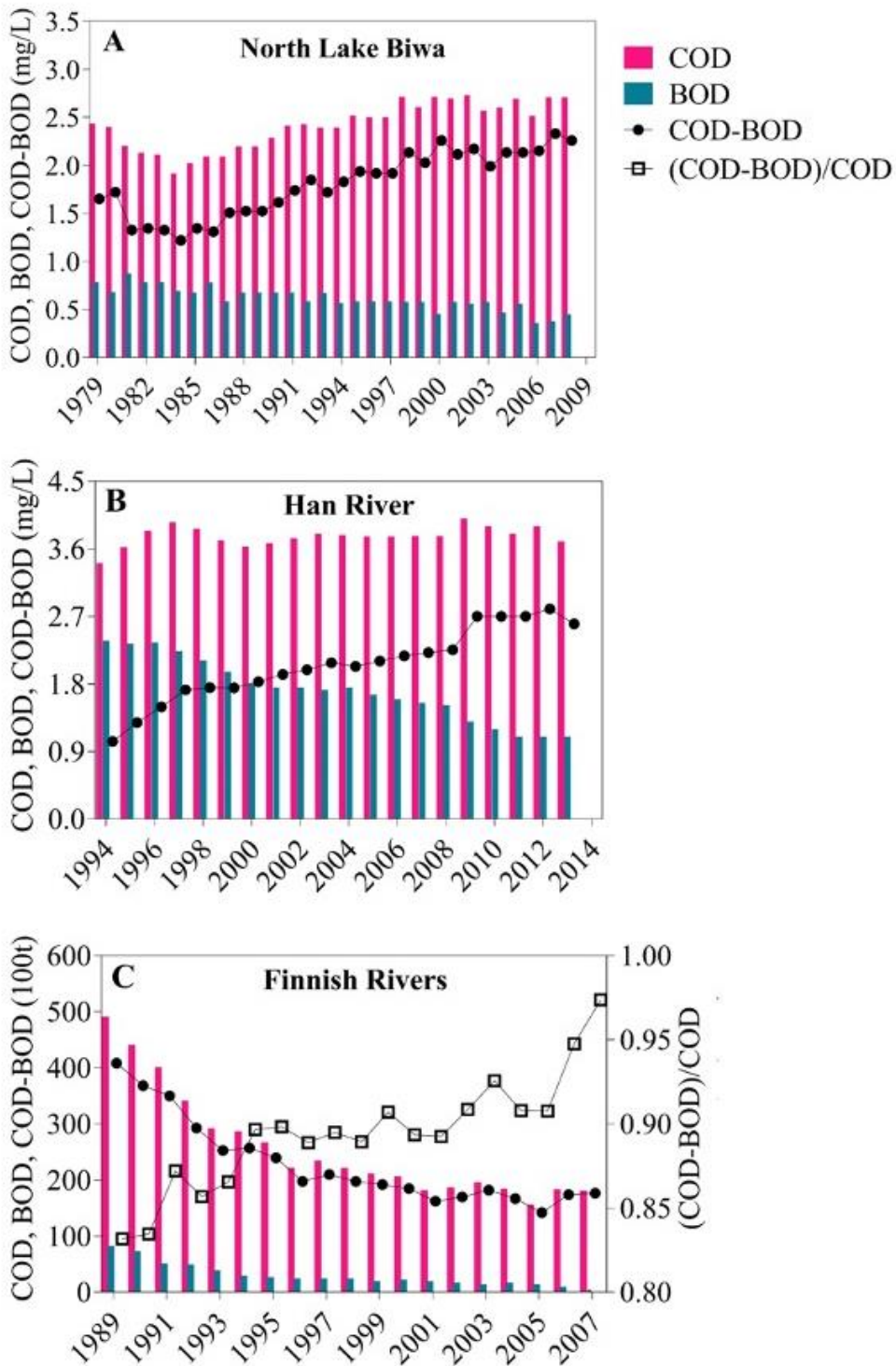
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Fig. 3. Results of FT-ICR MS analyses showing changes in organic matter in the natural and incubated river water samples before and after COD treatment. Panels **A** and **B** are the raw peak distributions (m/z 200~600) of organic matter in the water samples before and after long-term (510 days) incubation, respectively, showing no major differences before and after long-term microbial degradation. Panels **C** and **D** show the raw peak distributions (m/z 200~600) of remaining organic matter after the COD treatment of the same samples as in panels **A** and **B**, respectively. Panels **E** and **F** show the van Krevelen diagrams of the RDOC-like components oxidized by the COD treatment, i.e., samples in panels **A** minus **C**, and **B** minus **D**, respectively. Panel **G** is a deep-water (1000-m) sample from the South China Sea, used as a RDOC reference. The black polygons in panels **E** to **G** delineate the CRAM-like molecules (RDOC proxy), based on the literature.



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Fig. 4. Three representative field cases of long-term trends in COD and BOD changes: (A) increase in COD and decrease in BOD, and thus accumulation of RDOC (as indicated by [COD-BOD]) in Lake Biwa, Japan; (B) sharp decrease in BOD and relatively stable COD, and thus accumulation of RDOC in the Han River, Korea; and (C) decrease in both BOD and COD, but increase in the fraction of RDOC in Finnish rivers

Supplementary Materials for

Correcting a Major Error in Assessing Organic Carbon Pollution in Natural Waters

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This file includes:

1. Supplementary statements
2. Supplementary Figs. S1 to S5
3. Supplementary Tables S1 to S5

1. Supplementary statements

1.1. Persistent organic pollutants (POPs)

Persistent organic pollutants (POPs) are organic compounds that persist in the environment for a long time, migrating in the air, water and soil and accumulating in sediments and food webs (57, 58). The POPs are mainly man-made chemicals that can be divided into intentionally produced compounds (including industrial chemicals and organochlorine pesticides) and unintentional substances resulting from the combustion of organic compounds. The total concentration of recognized POPs in natural waters is usually very low, but can be high in some polluted areas, ranging from a few to thousands of nanograms per liter in natural waters (59, 60). Although the COD method can oxidize many POPs (61, 62), the total amount of carbon in POPs is trivial compared to natural DOC concentrations (63, 64).

1.2. Applications of COD to water quality assessment, and related standards and policy

The COD methods have been used for nearly a century around the world for water quality assessment (13). The International Organization for Standardization recommends COD as one of the parameters for assessing the quality of natural waters (27). In many countries, such as China and Japan, reduction of COD in aquatic environments is used as a measure of environmental policy performance in the evaluation of governmental accomplishments (Table S4). Scientists from different countries also use COD as an indicator to monitor natural waters (examples are shown in the references of (28, 36, 65-70). In addition, various countries (for example Japan, China, and Malaysia) categorize natural waters based on their COD values (Table S5).

1.3. Chemical oxygen demand, and dissolved organic carbon: A Google Scholar search

In a Google Scholar search conducted on January 26, 2020, there were 2,020,000 returns for "chemical oxygen demand" and 210,000 for a combination of "chemical oxygen demand" and "dissolved organic carbon". This shows the great interest of the community for the chemical oxygen demand, and the close connection of this topic with dissolved organic carbon.

1.4. Terminology of organic carbon

Total organic carbon (TOC) includes particulate organic carbon (POC) and dissolved organic carbon (DOC), the latter two being operationally differentiated based on filtration of water samples. Although the proportion of POC and DOC in a given water sample varies with the pore size of the filters used by the investigators, the term DOC is generally found in the scientific literature. Given the fact that DOC accounts for the majority of the TOC and is even equivalent to TOC in many waters, we only use DOC for the discussion in this study (71, 72).

2. Supplementary figures

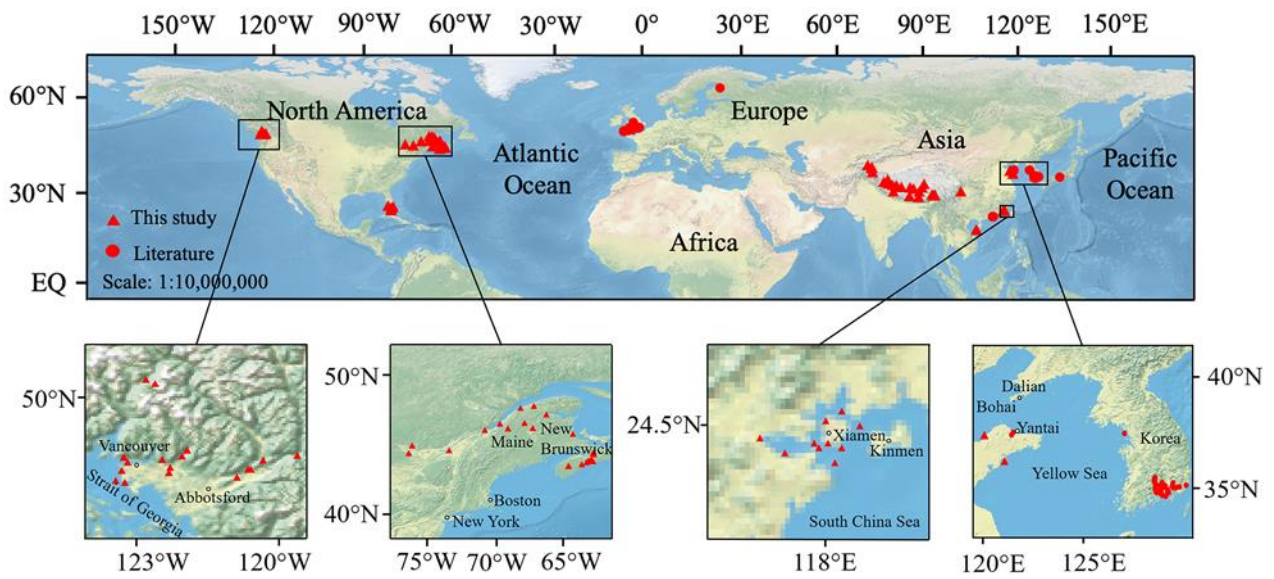


Fig. S1. Locations of the sampling sites (triangles) and data from the literature (circles).

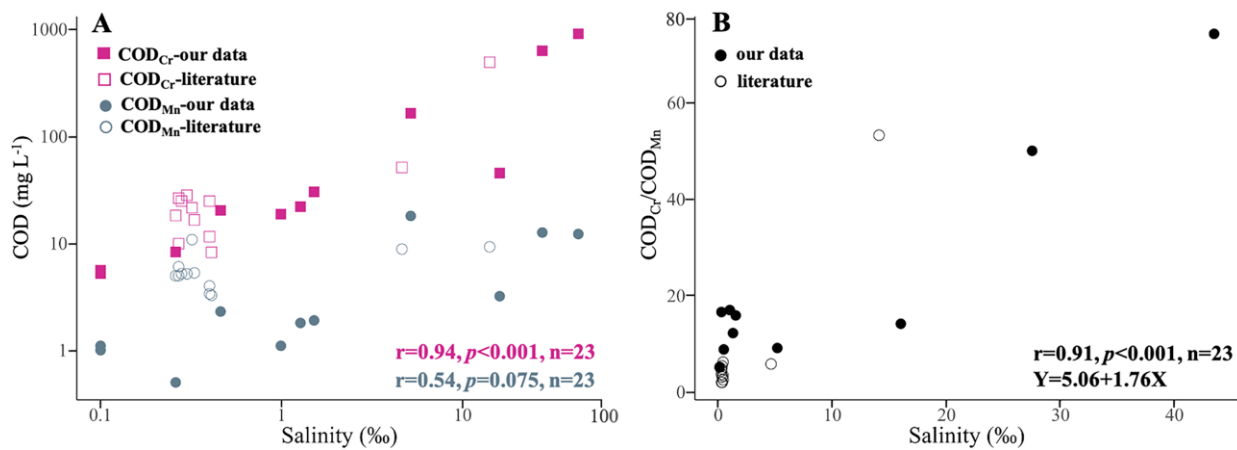


Fig. S2. (A) COD_{Cr} and alkaline COD_{Mn} as a function of salinity, and coefficients of linear correlations, and (B) ratio COD_{Cr}/COD_{Mn} as a function of salinity, coefficient of linear correlation and equation of Model 2 Standard Major Axis regression. n: number of samples.

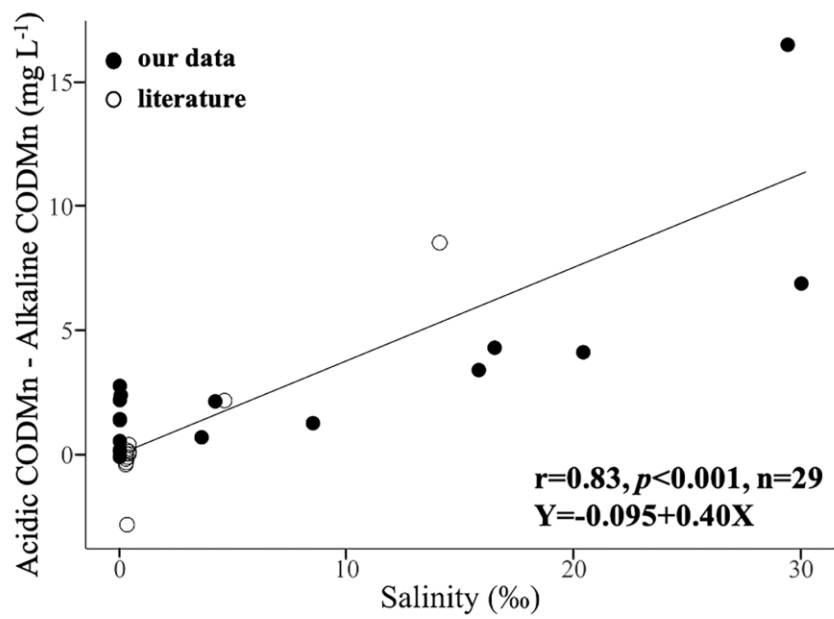


Fig. S3. Acidic minus alkaline CODMn as a function of salinity. Coefficient of linear correlation and equation of Model 2 Standard Major Axis regression. n: number of samples.

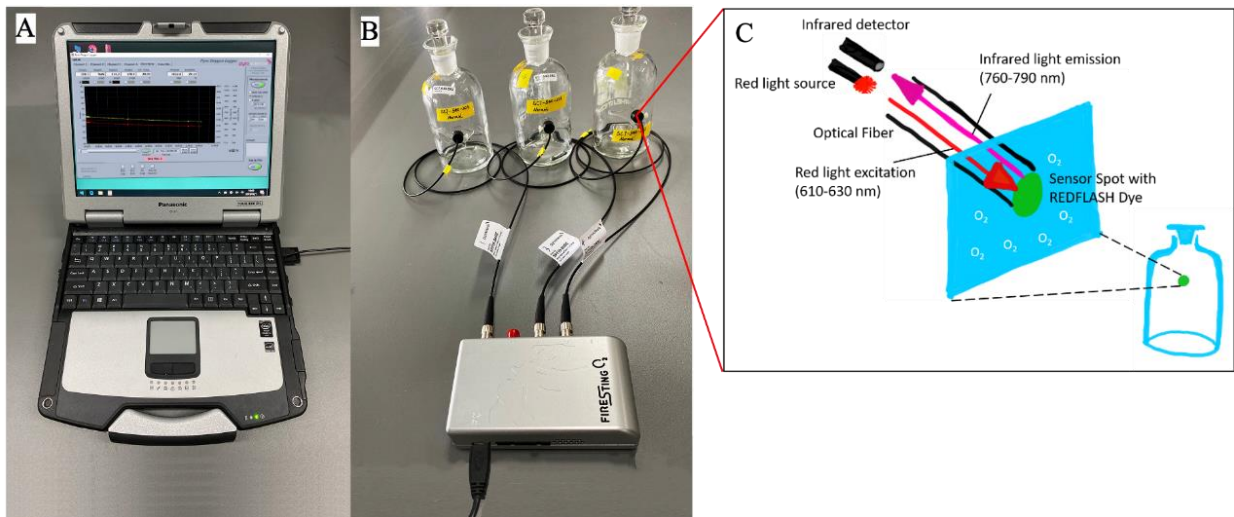


Fig. S4. System to measure dissolved oxygen concentrations with oxygen optodes in triplicate. (A) Computer with the data logging software (Pyro Oxygen logger) used for O₂ measurements. (B) Optical fiber sensors attached to the outside of BOD bottles with Pyroscience optodes installed internally, and connected to an optical oxygen meter (FireStingO₂) through which the signals are transmitted to the computer. (C) Diagram depicting how O₂ measurements are made using red light to excite the REDFLASH dye within the optode/sensor spot in contact with the water sample inside the BOD bottles. The dye emits infrared light that is channeled by the optical fiber into the optical oxygen meter, where it is converted into O₂ concentration (Modified from diagrams on the Pyroscience website: www.pyroscience.com). Photo Credit: Jihua Liu, Institute of Marine Science and Technology, Shandong University, Qingdao, China.

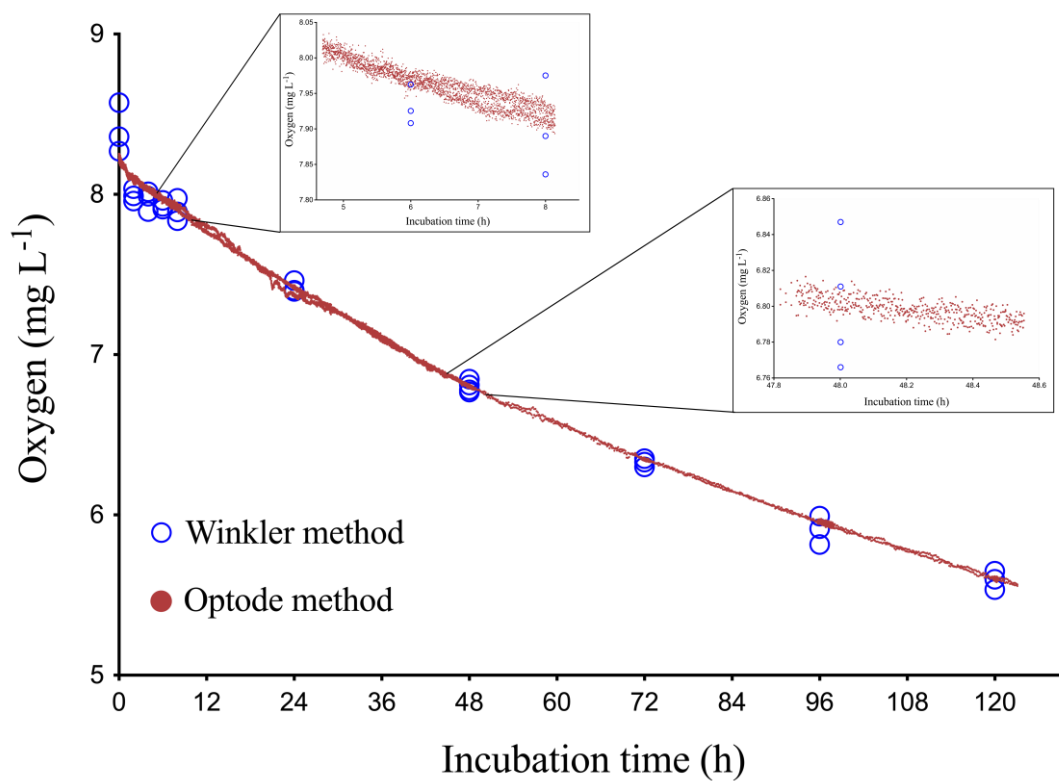


Fig. S5. Comparison of the new optode-based and usual Winkler BOD methods. Oxygen concentrations measured with the two methods during the course of the 5-day incubation. The incubated water was from the DaRen River, Qingdao, China. The two inset figures provide details of measurements with the two methods from 4.7 to 8.1 h, and 47.8 to 48.6 h.

3. Supplementary tables

Table S1. Sampling locations and data sources.

Locality	Latitude (°N)	Longitude (°E)	DOC (mg/L)	COD (mg/L)	BOD (mg/L)	COD-BOD (mg/L)	Source
Text Fig. 2							
(A) High latitudes / Subpolar region							
Richibucto River, Canada	46.65	-64.85	3.00	7.40	2.62	4.78	This study
Miramichi Bay, Canada	47.08	-65.21	3.41	6.60	3.09	3.51	This study
Chaleurs Bay, Canada	47.99	-66.74	3.08	3.20	1.96	1.24	This study
			3.78	5.23	1.55	3.76	This study
Lac Matapedia, Canada	48.54	-67.56	3.86	5.60	1.49	4.11	This study
			3.90	5.67	1.55	4.12	This study
Saint Lawrence River, Canada	48.45	-68.52	3.45	5.00	1.42	3.58	This study
			4.01	6.24	2.21	4.12	This study
Montmorency River, Canada	46.89	-71.15	1.79	5.80	2.29	3.51	This study
			4.18	5.80	2.30	3.54	This study
Grand Falls Dam, Canada	45.28	-67.48	4.60	7.80	1.49	6.31	This study
			4.70	7.66	2.13	5.58	This study
Saint John River, Canada	47.06	-67.78	3.67	2.20	2.02	0.18	This study
			4.82	7.44	2.66	4.83	This study
Bay of Fundy, Canada	45.81	-64.57	0.74	10.20	3.36	6.84	This study
			4.82	5.05	1.46	3.63	This study
Stewiacke River, Canada	45.14	-63.35	5.36		1.36		This study

Locality	Latitude (°N)	Longitude (°E)	DOC (mg/L)	COD (mg/L)	BOD (mg/L)	COD-BOD (mg/L)	Source
			5.45	6.64	3.10	3.54	This study
Shubenacadie River, Canada	44.93	-63.54	6.18	7.60	2.09	5.51	This study
			6.85	7.84	1.59	6.33	This study
Ingramport River, Canada	44.67	-63.97	11.56	12.00			This study
			7.97	9.83	2.39	7.53	This study
Mersey River, Canada	44.43	-65.21	6.71	10.20	2.42	7.78	This study
			8.08	10.18	2.48	7.88	This study
Kejimkujik Lake, Canada	44.38	-65.21	6.08	9.80	2.29	7.51	This study
Shubenacadie Grand Lake, Canada	44.89	-63.6	4.29	5.20	1.49	3.71	This study
Lake Major, Canada	44.72	-63.48	3.96	8.60	1.82	6.78	This study
Pockwock Lake, Canada	44.78	-63.84	6.73	6.20	2.16	4.04	This study
Yealm River D/S Yealmpton Stw, UK	50.38	-3.97	2.55		1.30		(32)
Yealm At Yealm Bridge, UK	50.31	-4.07	2.51		1.08		(32)
Yealm At Puslinch Bridge, UK	50.34	-4.01	2.77		1.08		(32)
Tort. Bk. Falfield, UK	51.64	-2.45	4.21		2.04		(32)
Tn Bwtr C N Newton, UK	50.31	-3.35	4.57		2.52		(32)
T R Avill Timberscom, UK	51.17	-3.5	3.55		1.07		(32)
T River Avill Timberscom, UK	NA	NA	5.90		1.30		(32)
Sydling Water, Downstream Shearplace, UK	50.22	-5.39	2.55		1.21		(32)
Sydling D/S Huish Fm, UK	51.18	-2.27	3.08		1.19		(32)

Locality	Latitude (°N)	Longitude (°E)	DOC (mg/L)	COD (mg/L)	BOD (mg/L)	COD-BOD (mg/L)	Source
St. Austell River Downstream Of, UK	50.33	-4.79	3.09		1.63		(32)
St Austell At Pentewan Bridge, UK	50.33	-4.79	2.35		1.11		(32)
Rodden D/S Langton Herring Stw, UK	50.64	-2.55	1.16		1.73		(32)
River Wey At Radipole, UK	50.61	-2.46	2.40		1.23		(32)
River Wey At Nottingham, UK	50.61	-2.46	2.28		1.20		(32)
River Mole D/S South Molton Stw, UK	51.24	-0.31	1.80		1.08		(32)
River Cober D/S Helston Stw, UK	50.09	-5.28	2.99		1.19		(32)
River Char At Whitchurch Canonicorum, UK	50.75	-2.86	3.49		1.17		(32)
Ramsgate (Reen) Roseworthy, UK	50.20	-1.25	3.54		1.72		(32)
River Yeo (Lapford)-Bow Bridge, UK	50.86	-3.81	5.54		1.29		(32)
River Wey At Radipole, UK	50.63	-2.47	1.64		2.13		(32)
River Teign-Preston, UK	50.62	-3.64	3.30		2.46		(32)
River Teign-Chudleigh Bridge, UK	50.62	-3.64	3.50		1.59		(32)
River Teign D/S Heathfield Tip, UK	50.62	-3.64	3.50		1.85		(32)
River Char U/S Whitchurch Can., UK	50.75	-2.86	3.76		1.53		(32)
River Yeo Yeovil Bridge, UK	50.94	-2.61	2.44		1.10		(32)
River Yeo Yeovil Bridge, UK	50.94	-2.61	2.44		1.10		(32)
River Yeo Over Compton, UK	50.93	-2.60	3.31		3.91		(32)
River Yeo Goldings Lane, UK	51.00	-2.65	0.52		1.76		(32)
River Yeo Goathill, UK	50.95	-2.47	3.63		1.95		(32)

Locality	Latitude (°N)	Longitude (°E)	DOC (mg/L)	COD (mg/L)	BOD (mg/L)	COD-BOD (mg/L)	Source
R Wey At Nottingham, UK	50.64	-2.48	4.32		3.38		(32)
River Wey At Broadwey, UK	51.15	-0.80	3.13		1.33		(32)
River Wey At Broadwey, UK	NA	NA	0.30		1.88		(32)
River Tone Coalharbor Br, UK	NA	NA	5.27		3.55		(32)
River Tone Clatworthy, UK	51.02	-3.14	1.72		1.44		(32)
River Tone Bishops Hull, UK	51.02	-3.14	2.41		1.43		(32)
River Tone Bathpool, UK	51.04	-3.05	4.15		1.56		(32)
River Brue Cow Bridge, UK	51.13	-2.71	1.10		1.81		(32)
River Banwell At M5 M'way, UK	51.36	-2.90	0.77		1.94		(32)
River Banwell @ M5 M'way, UK	51.36	-2.90	2.96		1.38		(32)
River Banwell @ Ebdon Br, UK	51.38	-2.92	5.04		1.86		(32)
River Axe Loxton, UK	51.29	-2.90	5.90		1.78		(32)
River Axe Henley Hill, UK	53.50	-1.40	3.49		1.07		(32)
River Axe Clewer, UK	51.26	-2.80	4.17		1.56		(32)
River Axe, UK	51.27	-2.83	2.40		1.05		(32)
River Avill Frackford Br, UK	51.16	-3.51	1.74		1.19		(32)
Point Above South Crofty R, UK	50.22	-5.28	3.54		1.13		(32)
Pill R Blue Anchor, UK	51.18	-3.39	0.74		1.44		(32)
Pill R Bilbrook Ford, UK	51.15	-3.40	0.64		2.71		(32)
Penponds Roseworthy Stream, UK	50.21	-5.32	3.22		1.58		(32)
Ozle. Bk Low. Barnes, UK	51.28	-0.13	3.95		1.28		(32)

Locality	Latitude (°N)	Longitude (°E)	DOC (mg/L)	COD (mg/L)	BOD (mg/L)	COD-BOD (mg/L)	Source
North Brook At Northbrook Park, UK	51.20	-0.85	1.52		1.09		(32)
Misc Lower Frome, UK	51.23	-2.32	5.98		1.54		(32)
Mill Stream D/S Horsepool, UK	51.16	-2.73	5.59		1.49		(32)
Medlyn Stream At Chy Bridge, UK	NA	NA	3.55		1.07		(32)
Lt. Dart R., D/S Chawleigh Stw, UK	50.91	-3.83	5.59		1.11		(32)
Lt. Dart R., D/S Chawleigh Stw, UK	NA	NA	3.09		1.07		(32)
Huish Trout Farm Easthill Inlet, UK	50.79	-2.52	1.10		1.36		(32)
Hancocks U/S St Ivel, UK	50.12	-5.29	5.17		3.76		(32)
Halse Water Tyler Br, UK	51.05	-3.25	0.99		1.76		(32)
Halse W Norton Br, UK	52.87	-2.19	1.38		2.41		(32)
Halse W Halse G Stn, UK	51.25	-3.13	0.78		1.76		(32)
Halse W Asylum Br, UK	51.25	-3.13	1.02		2.13		(32)
Gwithian Towans Red River, UK	50.22	-5.39	2.72		3.53		(32)
Frome U/S Louds Mill, UK	50.71	-2.41	5.76		1.11		(32)
Exeter Canal At A38 Bridge Countess, UK	50.69	-3.49	1.85		1.33		(32)
Ebble U/S Chalkvalley Inlet Rside, UK	51.04	-1.87	0.46		1.08		(32)
Ebble D/S Chalkevalley, UK	51.02	-1.99	4.14		1.34		(32)
Dawlish Water At Dawlish, UK	50.60	-3.51	4.14		1.34		(32)
Congresbury Yeo A370, UK	51.37	-2.81	0.77		1.41		(32)
Congresby Yeo Beam B, UK	NA	NA	2.08		1.18		(32)

Locality	Latitude (°N)	Longitude (°E)	DOC (mg/L)	COD (mg/L)	BOD (mg/L)	COD-BOD (mg/L)	Source
Congres Yeo Tutshill, UK	51.40	-2.40	3.40		1.37		(32)
Congres Yeo Iwood, UK	51.36	-2.79	5.96		1.59		(32)
Carminowe Creek Inflow To Loe Pool, UK	50.07	-5.28	5.41		3.85		(32)
By Brook Middlehill, UK	51.42	-2.27	0.89		1.05		(32)
By Brook Fosse, UK	51.50	-2.24	4.40		1.01		(32)
By Bk Long Dean Mill, UK	51.48	-2.22	0.92		1.01		(32)
Back Stream Fitzroy, UK	51.04	-3.15	0.66		3.17		(32)
Avon Scotland Road, UK	NA	NA	1.30		2.24		(32)
Avon Melksham Bypass, UK	51.37	-2.14	1.99		2.92		(32)
Avon Malford Church, UK	51.50	-2.06	0.81		1.55		(32)
Avon Lacock, UK	51.42	-2.12	2.27		1.74		(32)
At Austell At Moliney G Stat, UK	50.20	-4.48	2.81		1.67		(32)
Alphin Brook At Countess Wear Bridge, UK	50.70	-3.50	0.76		1.12		(32)
(B) Mid-latitudes/Temperate zone							
Edward B. Knight Pier, USA	24.55	-81.78	2.32	2.40	1.49	0.91	This study
South Pointe Pier, USA	25.76	-80.13	2.46	1.81	1.55	0.26	This study
Naples Pier, USA	26.13	-81.81	6.88	5.89	1.07	4.82	This study
Pine Glades Lake, USA	25.43	-80.72	13.24	10.56	3.17	7.39	This study
Nine Mine Pond, USA	25.25	-80.80	2.63	2.35	1.86	0.49	This study
Jiulong River, China	24.36	118.13	1.29	0.70	0.39	0.30	This study

Locality	Latitude (°N)	Longitude (°E)	DOC (mg/L)	COD (mg/L)	BOD (mg/L)	COD-BOD (mg/L)	Source
Jiulong River, China	24.42	118.06	1.21	0.41	0.22	0.19	This study
Jiulong River, China	24.4	117.91	1.55	1.61	1.02	0.59	This study
Jiulong River, China	24.46	117.8	1.58	2.90	1.61	1.28	This study
Xiamen Bay, China	24.44	118.04	0.99	1.20	0.68	0.52	This study
Xiamen Bay, China	24.42	118.16	0.97	0.80	0.62	0.18	This study
Xiamen Bay, China	24.51	118.24	1.04	1.12	0.97	0.15	This study
Xiamen Bay, China	24.57	118.16	1.13	1.12	0.87	0.25	This study
Xiamen Bay, China	24.53	118.09	1.20	1.68	1.04	0.64	This study
Bohai Sea, China	37.39	119.95	1.67	1.62	1.32	0.30	This study
Bohai Sea, China	37.39	119.95	1.59	1.62	1.30	0.32	This study
Bohai Sea, China	37.39	119.94	1.70	1.78	1.40	0.38	This study
Bohai Sea, China	37.39	119.93	1.60	1.58	1.26	0.32	This study
Bohai Sea, China	37.39	119.93	1.55	1.54	1.22	0.32	This study
Bohai Sea, China	37.39	119.94	1.74	1.80	1.44	0.36	This study
Yellow Sea, China	36.37	120.88	1.10	1.18	0.80	0.38	This study
Yellow Sea, China	36.37	120.88	1.15	1.22	0.82	0.40	This study
Yellow Sea, China	36.37	120.88	1.01	1.10	0.74	0.36	This study
Yellow Sea, China	36.37	120.88	1.18	1.27	0.88	0.39	This study
Yellow Sea, China	36.37	120.88	0.96	1.10	0.74	0.36	This study
Yellow Sea, China	36.37	120.88	1.03	1.15	0.76	0.39	This study
Yellow Sea, China	36.37	120.88	1.10	1.18	0.82	0.36	This study

Locality	Latitude (°N)	Longitude (°E)	DOC (mg/L)	COD (mg/L)	BOD (mg/L)	COD-BOD (mg/L)	Source
Yellow Sea, China	36.37	120.88	1.06	1.15	0.76	0.39	This study
Gilgok, South Korea	35.4	129.29	7.20	4.00	2.10	1.90	(33)
Shincheon, South Korea	35.36	128.64	6.40	3.80	1.80	2.00	(33)
Deokgok, South Korea	35.11	128.48	5.80	3.70	1.60	2.10	(33)
Imgok, South Korea	35.11	128.46	6.80	4.40	2.70	1.70	(33)
Jungchon, South Korea	35.13	128.43	3.00	1.80	0.80	1.00	(33)
Mari, South Korea	35.7	127.86	4.70	3.20	1.50	1.70	(33)
Anha, South Korea	35.31	128.83	9.20	4.80	2.30	2.50	(33)
Juwhang, South Korea	35.29	128.71	6.00	3.40	1.80	1.60	(33)
Wolpyeong, South Korea	34.95	128.35	2.70	2.80	1.10	1.70	(33)
Sangdong, South Korea	35	128.2	2.70	2.30	1.40	0.90	(33)
Deokam, South Korea	35.51	128.18	10.50	3.50	2.10	1.40	(33)
Uicho, South Korea	35.42	128.14	6.70	3.90	1.40	2.50	(33)
Daehyun, South Korea	35.45	128.16	7.80	3.30	1.70	1.60	(33)
Jikjun, South Korea	35.12	127.9	2.60	2.30	1.10	1.20	(33)
Hogye, South Korea	35.2	127.88	2.00	1.60	0.40	1.20	(33)
Sachon, South Korea	35.32	128.32	4.20	2.10	0.90	1.20	(33)
Ssanggye, South Korea	35.22	128.44	3.60	1.80	0.80	1.00	(33)
Gwigok, South Korea	35.64	127.84	5.30	3.90	2.20	1.70	(33)
Anui, South Korea	35.64	127.81	6.50	4.10	2.20	1.90	(33)
Jiwoo, South Korea	35.66	127.81	1.60	1.50	0.70	0.80	(33)

Locality	Latitude (°N)	Longitude (°E)	DOC (mg/L)	COD (mg/L)	BOD (mg/L)	COD-BOD (mg/L)	Source
Juksan, South Korea	35.52	127.81	6.00	3.90	1.70	2.20	(33)
Hachon, South Korea	35.23	128.12	10.40	6.40	3.70	2.70	(33)
Whagye, South Korea	35.11	128.1	11.00	4.90	2.80	2.10	(33)
Jinae, South Korea	35.23	128.14	8.70	6.00	2.40	3.60	(33)
Unjung, South Korea	35.49	128.68	4.20	2.80	1.20	1.60	(33)
Whansa, South Korea	35.14	127.99	5.00	3.50	2.00	1.50	(33)
Seongbang, South Korea	35.12	127.96	5.50	3.20	2.10	1.10	(33)
Daegok, South Korea	35.06	128.13	4.50	3.50	1.60	1.90	(33)
Gamgok, South Korea	35.05	128.15	3.40	2.50	1.20	1.30	(33)
Gobong, South Korea	35.04	128.17	3.30	2.70	1.40	1.30	(33)
Jeonggok, South Korea	35.41	127.91	3.00	2.20	1.00	1.20	(33)
Banggok, South Korea	35.36	127.87	9.30	3.80	2.00	1.80	(33)
Migok, South Korea	35.36	128.08	7.80	3.60	1.80	1.80	(33)
Wolgok, South Korea	35.49	127.86	9.50	4.80	2.30	2.50	(33)
Massang, South Korea	35.37	128.11	8.50	3.70	1.70	2.00	(33)
Garye, South Korea	35.33	127.86	3.40	2.90	1.30	1.60	(33)
Unam, South Korea	35.34	128.23	4.60	2.80	1.00	1.80	(33)
Jukjeon, South Korea	35.37	128.32	5.40	3.10	0.90	2.20	(33)
Whajung, South Korea	35.34	128.98	2.50	1.50	0.60	0.90	(33)
(C) Low latitudes/Tropical zone							
Sanya Bay, China	18.19	109.08	0.88	0.48	0.40	0.08	This study

Locality	Latitude (°N)	Longitude (°E)	DOC (mg/L)	COD (mg/L)	BOD (mg/L)	COD-BOD (mg/L)	Source
Sanya Bay, China	18.20	109.08	1.11	0.73	0.65	0.08	This study
Sanya Bay, China	18.19	109.07	1.02	0.73	0.48	0.24	This study
Sanya Bay, China	18.17	109.06	0.85	0.44	0.32	0.12	This study
Sanya Bay, China	18.15	109.18	0.90	0.48	0.40	0.08	This study
Mirs Bay, China	22.53	114.48	1.89	2.13	1.64	0.49	(34)
Mirs Bay, China	22.53	114.46	1.29	1.52	1.45	0.07	(34)
Mirs Bay, China	22.50	114.48	1.51	1.34	1.20	0.14	(34)
Mirs Bay, China	22.53	114.48	1.74	1.68	0.97	0.72	(34)
Mirs Bay, China	22.53	114.47	1.67	2.80	2.06	0.74	(34)
Mirs Bay, China	22.53	114.46	1.51	1.57	1.47	0.10	(34)
Mirs Bay, China	22.50	114.48	1.67	2.66	1.71	0.95	(34)
Mirs Bay, China	22.50	114.48	1.51	2.41	1.48	0.93	(34)
Mirs Bay, China	22.53	114.48	2.42	2.12	1.36	0.76	(34)
Mirs Bay, China	22.53	114.47	2.27	2.90	1.86	1.04	(34)
Mirs Bay, China	22.53	114.46	1.36	2.00	1.26	0.74	(34)
Mirs Bay, China	22.50	114.47	2.27	3.00	1.84	1.16	(34)
Mirs Bay, China	22.50	114.48	1.51	2.17	1.24	0.93	(34)
(D) Forest watershed							
Pine Glades Lake, USA	25.43	-80.72	6.88	5.89	1.07	4.82	This study
Nine Mine Pond, USA	25.25	-80.796	13.24	10.56	3.17	7.39	This study
Richibucto River, Canada	46.65	-64.85	3.00	7.40	2.62	4.78	This study

Locality	Latitude (°N)	Longitude (°E)	DOC (mg/L)	COD (mg/L)	BOD (mg/L)	COD-BOD (mg/L)	Source
			1.26	3.23	2.04	1.28	This study
Miramichi Bay, Canada	47.08	-65.21	3.41	6.60	3.09	3.51	This study
			2.09	2.21	2.08	0.27	This study
Chaleurs Bay, Canada	47.99	-66.74	3.08	3.20	1.96	1.24	This study
			3.78	5.23	1.55	3.76	This study
Lac Matapedia, Canada	48.54	-67.56	3.86	5.60	1.49	4.11	This study
			3.90	5.67	1.55	4.12	This study
Saint Lawrence River, Canada	48.45	-68.52	3.45	5.00	1.42	3.58	This study
			4.01	6.24	2.21	4.12	This study
Montmorency River, Canada	46.89	-71.15	1.79	5.80	2.29	3.51	This study
			4.18	5.80	2.30	3.54	This study
Grand Falls Dam, Canada	45.28	-67.48	4.60	7.80	1.49	6.31	This study
			4.70	7.66	2.13	5.58	This study
Saint John River, Canada	47.06	-67.78	3.67	2.20	2.02	0.18	This study
			4.82	7.44	2.66	4.83	This study
Bay of Fundy, Canada	45.81	-64.57	0.74	10.20	3.36	6.84	This study
			4.82	5.05	1.46	3.63	This study
Stewiacke River, Canada	45.14	-63.35	5.36		1.36		This study
			5.45	6.64	3.10	3.54	This study
Shubenacadie River, Canada	44.93	-63.54	6.18	7.60	2.09	5.51	This study
			6.85	7.84	1.59	6.33	This study

Locality	Latitude (°N)	Longitude (°E)	DOC (mg/L)	COD (mg/L)	BOD (mg/L)	COD-BOD (mg/L)	Source
Ingramport River, Canada	44.67	-63.97	11.56	12.00			This study
			7.97	9.83	2.39	7.53	This study
Mersey River, Canada	44.43	-65.21	6.71	10.20	2.42	7.78	This study
			8.08	10.18	2.48	7.88	
Kejimikujik Lake, Canada	44.38	-65.21	6.08	9.80	2.29	7.51	This study
Shubenacadie Grand Lake, Canada	44.89	-63.6	4.29	5.20	1.49	3.71	This study
Lake Major, Canada	44.72	-63.48	3.96	8.60	1.82	6.78	This study
Pockwock Lake, Canada	44.78	-63.84	6.73	6.20	2.16	4.04	This study
(E) Fresh waters							
Gilgok, South Korea	35.4	129.29	7.20	4.00	2.10	1.90	(33)
Shincheon, South Korea	35.36	128.64	6.40	3.80	1.80	2.00	(33)
Deokgok, South Korea	35.11	128.48	5.80	3.70	1.60	2.10	(33)
Imgok, South Korea	35.11	128.46	6.80	4.40	2.70	1.70	(33)
Jungchon, South Korea	35.13	128.43	3.00	1.80	0.80	1.00	(33)
Mari, South Korea	35.7	127.86	4.70	3.20	1.50	1.70	(33)
Anha, South Korea	35.31	128.83	9.20	4.80	2.30	2.50	(33)
Juwhang, South Korea	35.29	128.71	6.00	3.40	1.80	1.60	(33)
Wolpyeong, South Korea	34.95	128.35	2.70	2.80	1.10	1.70	(33)
Sangdong, South Korea	35.00	128.20	2.70	2.30	1.40	0.90	(33)
Deokam, South Korea	35.51	128.18	10.50	3.50	2.10	1.40	(33)
Uicho, South Korea	35.42	128.14	6.70	3.90	1.40	2.50	(33)

Locality	Latitude (°N)	Longitude (°E)	DOC (mg/L)	COD (mg/L)	BOD (mg/L)	COD-BOD (mg/L)	Source
Daehyun, South Korea	35.45	128.16	7.80	3.30	1.70	1.60	(33)
Jikjun, South Korea	35.12	127.9	2.60	2.30	1.10	1.20	(33)
Hogye, South Korea	35.20	127.88	2.00	1.60	0.40	1.20	(33)
Sachon, South Korea	35.32	128.32	4.20	2.10	0.90	1.20	(33)
Ssanggye, South Korea	35.22	128.44	3.60	1.80	0.80	1.00	(33)
Gwigok, South Korea	35.64	127.84	5.30	3.90	2.20	1.70	(33)
Anui, South Korea	35.64	127.81	6.50	4.10	2.20	1.90	(33)
Jiwoo, South Korea	35.66	127.81	1.60	1.50	0.70	0.80	(33)
Juksan, South Korea	35.52	127.81	6.00	3.90	1.70	2.20	(33)
Hachon, South Korea	35.23	128.12	10.40	6.40	3.70	2.70	(33)
Whagye, South Korea	35.11	128.1	11.00	4.90	2.80	2.10	(33)
Jinae, South Korea	35.23	128.14	8.70	6.00	2.40	3.60	(33)
Unjung, South Korea	35.49	128.68	4.20	2.80	1.20	1.60	(33)
Whansa, South Korea	35.14	127.99	5.00	3.50	2.00	1.50	(33)
Seongbang, South Korea	35.12	127.96	5.50	3.20	2.10	1.10	(33)
Daegok, South Korea	35.06	128.13	4.50	3.50	1.60	1.90	(33)
Gamgok, South Korea	35.05	128.15	3.40	2.50	1.20	1.30	(33)
Gobong, South Korea	35.04	128.17	3.30	2.70	1.40	1.30	(33)
Jeonggok, South Korea	35.41	127.91	3.00	2.20	1.00	1.20	(33)
Banggok, South Korea	35.36	127.87	9.30	3.80	2.00	1.80	(33)
Migok, South Korea	35.36	128.08	7.80	3.60	1.80	1.80	(33)

Locality	Latitude (°N)	Longitude (°E)	DOC (mg/L)	COD (mg/L)	BOD (mg/L)	COD-BOD (mg/L)	Source
Wolgok, South Korea	35.49	127.86	9.50	4.80	2.30	2.50	(33)
Massang, South Korea	35.37	128.11	8.50	3.70	1.70	2.00	(33)
Garye, South Korea	35.33	127.86	3.40	2.90	1.30	1.60	(33)
Unam, South Korea	35.34	128.23	4.60	2.80	1.00	1.80	(33)
Jukjeon, South Korea	35.37	128.32	5.40	3.10	0.90	2.20	(33)
Whajung, South Korea	35.34	128.98	2.50	1.50	0.60	0.90	(33)
Yealm River D/S Yealmpton Stw, UK	50.38	-3.97	2.55		1.30		(32)
Yealm At Yealm Bridge, UK	50.31	-4.07	2.51		1.08		(32)
Yealm At Puslinch Bridge, UK	50.34	-4.01	2.77		1.08		(32)
Tort. Bk. Falfield, UK	51.64	-2.45	4.21		2.04		(32)
Tn Bwtr C N Newton, UK	50.31	-3.35	4.57		2.52		(32)
T R Avill Timberscom, UK	51.17	-3.50	3.55		1.07		(32)
T River Avill Timberscom, UK	NA	NA	5.90		1.30		(32)
Sydling Water, UK Downstream Shearplace, UK	50.22	-5.39	2.55		1.21		(32)
Sydling D/S Huish Fm, UK	51.18	-2.27	3.08		1.19		(32)
St. Austell River Downstream Of, UK	50.33	-4.79	3.09		1.63		(32)
St Austell At Pentewan Bridge, UK	50.33	-4.79	2.35		1.11		(32)
Rodden D/S Langton Herring Stw, UK	50.64	-2.55	1.16		1.73		(32)
River Wey At Radipole, UK	50.61	-2.46	2.40		1.23		(32)
River Wey At Nottingham, UK	50.61	-2.46	2.28		1.20		(32)

Locality	Latitude (°N)	Longitude (°E)	DOC (mg/L)	COD (mg/L)	BOD (mg/L)	COD-BOD (mg/L)	Source
River Mole D/S South Molton Stw, UK	51.24	-0.31	1.80		1.08		(32)
River Cober D/S Helston Stw, UK	50.09	-5.28	2.99		1.19		(32)
River Char At Whitchurch Canonicorum, UK	50.75	-2.86	3.49		1.17		(32)
Ramsgate (Reen) Roseworthy, UK	50.20	-1.25	3.54		1.72		(32)
River Yeo (Lapford)-Bow Bridge, UK	50.86	-3.81	5.54		1.29		(32)
River Wey At Radipole, UK	50.63	-2.47	1.64		2.13		(32)
River Teign-Preston, UK	50.62	-3.64	3.30		2.46		(32)
River Teign-Chudleigh Bridge, UK	50.62	-3.64	3.50		1.59		(32)
River Teign D/S Heathfield Tip, UK	50.62	-3.64	3.50		1.85		(32)
River Char U/S Whitchurch Can., UK	50.75	-2.86	3.76		1.53		(32)
River Yeo Yeovil Bridge, UK	50.94	-2.61	2.44		1.10		(32)
River Yeo Yeovil Bridge, UK	50.94	-2.61	2.44		1.10		(32)
River Yeo Over Compton, UK	50.93	-2.60	3.31		3.91		(32)
River Yeo Goldings Lane, UK	51.00	-2.65	0.52		1.76		(32)
River Yeo Goathill, UK	50.95	-2.47	3.63		1.95		(32)
R Wey At Nottingham, UK	50.64	-2.48	4.32		3.38		(32)
River Wey At Broadwey, UK	51.15	-0.80	3.13		1.33		(32)
River Wey At Broadwey, UK	NA	NA	0.30		1.88		(32)
River Tone Coalharbor Br, UK	NA	NA	5.27		3.55		(32)
River Tone Clatworthy, UK	51.02	-3.14	1.72		1.44		(32)

Locality	Latitude (°N)	Longitude (°E)	DOC (mg/L)	COD (mg/L)	BOD (mg/L)	COD-BOD (mg/L)	Source
River Tone Bishops Hull, UK	51.02	-3.14	2.41		1.43		(32)
River Tone Bathpool, UK	51.04	-3.05	4.15		1.56		(32)
River Brue Cow Bridge, UK	51.13	-2.71	1.10		1.81		(32)
River Banwell At M5 M'way, UK	51.36	-2.90	0.77		1.94		(32)
River Banwell @ M5 M'way, UK	51.36	-2.90	2.96		1.38		(32)
River Banwell @ Ebdon Br, UK	51.38	-2.92	5.04		1.86		(32)
River Axe Loxton, UK	51.29	-2.90	5.90		1.78		(32)
River Axe Henley Hill, UK	53.50	-1.40	3.49		1.07		(32)
River Axe Clewer, UK	51.26	-2.80	4.17		1.56		(32)
River Axe, UK	51.27	-2.83	2.40		1.05		(32)
River Avill Frackford Br, UK	51.16	-3.51	1.74		1.19		(32)
Point Above South Crofty R, UK	50.22	-5.28	3.54		1.13		(32)
Pill R Blue Anchor, UK	51.18	-3.39	0.74		1.44		(32)
Pill R Bilbrook Ford, UK	51.15	-3.40	0.64		2.71		(32)
Penponds Roseworthy Stream, UK	50.21	-5.32	3.22		1.58		(32)
Ozle. Bk Low. Barnes, UK	51.28	-0.13	3.95		1.28		(32)
North Brook At Northbrook Park, UK	51.20	-0.85	1.52		1.09		(32)
Misc Lower Frome, UK	51.23	-2.32	5.98		1.54		(32)
Mill Stream D/S Horsepool, UK	51.16	-2.73	5.59		1.49		(32)
Medlyn Stream At Chy Bridge, UK	NA	NA	3.55		1.07		(32)
Lt. Dart R.,D/S Chawleigh Stw, UK	50.91	-3.83	5.59		1.11		(32)

Locality	Latitude (°N)	Longitude (°E)	DOC (mg/L)	COD (mg/L)	BOD (mg/L)	COD-BOD (mg/L)	Source
Lt. Dart R., D/S Chawleigh Stw, UK	NA	NA	3.09		1.07		(32)
Huish Trout Farm Easthill Inlet, UK	50.79	-2.52	1.10		1.36		(32)
Hancocks U/S St Ivel, UK	50.12	-5.29	5.17		3.76		(32)
Halse Water Tyler Br, UK	51.05	-3.25	0.99		1.76		(32)
Halse W Norton Br, UK	52.87	-2.19	1.38		2.41		(32)
Halse W Halse G Stn, UK	51.25	-3.13	0.78		1.76		(32)
Halse W Asylum Br, UK	51.25	-3.13	1.02		2.13		(32)
Gwithian Towans Red River, UK	50.22	-5.39	2.72		3.53		(32)
Frome U/S Louds Mill, UK	50.71	-2.41	5.76		1.11		(32)
Exeter Canal At A38 Bridge Countess, UK	50.69	-3.49	1.85		1.33		(32)
Ebble U/S Chalkvalley Inlet Rside, UK	51.04	-1.87	0.46		1.08		(32)
Ebble D/S Chalkevalley, UK	51.02	-1.99	4.14		1.34		(32)
Dawlish Water At Dawlish, UK	50.60	-3.51	4.14		1.34		(32)
Congresbury Yeo A370, UK	51.37	-2.81	0.77		1.41		(32)
Congresby Yeo Beam B, UK	NA	NA	2.08		1.18		(32)
Congres Yeo Tutshill, UK	51.40	-2.40	3.40		1.37		(32)
Congres Yeo Iwood, UK	51.36	-2.79	5.96		1.59		(32)
Carminowe Creek Inflow To Loe Pool, UK	50.07	-5.28	5.41		3.85		(32)
By Brook Middlehill, UK	51.42	-2.27	0.89		1.05		(32)
By Brook Fosse, UK	51.50	-2.24	4.40		1.01		(32)

Locality	Latitude (°N)	Longitude (°E)	DOC (mg/L)	COD (mg/L)	BOD (mg/L)	COD-BOD (mg/L)	Source
By Bk Long Dean Mill, UK	51.48	-2.22	0.92		1.01		(32)
Back Stream Fitzroy, UK	51.04	-3.15	0.66		3.17		(32)
Avon Scotland Road, UK	NA	NA	1.30		2.24		(32)
Avon Melksham Bypass, UK	51.37	-2.14	1.99		2.92		(32)
Avon Malford Church, UK	51.50	-2.06	0.81		1.55		(32)
Avon Lacock, UK	51.42	-2.12	2.27		1.74		(32)
At Austell At Moliney G Stat, UK	50.20	-4.48	2.81		1.67		(32)
Alphin Brook At Countess Wear Bridge, UK	50.70	-3.50	0.76		1.12		(32)

(F) Seawater

Edward B. Knight Pier, USA	24.55	-81.78	2.32	2.40	1.49	0.91	This study
South Pointe Pier, USA	25.76	-80.130	2.46	1.81	1.55	0.26	This study
Naples Pier, USA	26.13	-81.807	2.63	2.35	1.86	0.49	This study
Sanya Bay, China	18.19	109.08	0.88	0.48	0.40	0.08	This study
Sanya Bay, China	18.20	109.08	1.11	0.73	0.65	0.08	This study
Sanya Bay, China	18.19	109.07	1.02	0.73	0.48	0.24	This study
Sanya Bay, China	18.17	109.06	0.85	0.44	0.32	0.12	This study
Sanya Bay, China	18.15	109.18	0.90	0.48	0.40	0.08	This study
Jiulong River, China	24.36	118.13	1.29	0.70	0.39	0.30	This study
Jiulong River, China	24.42	118.06	1.21	0.41	0.22	0.19	This study
Jiulong River, China	24.40	117.91	1.55	1.61	1.02	0.59	This study

Locality	Latitude (°N)	Longitude (°E)	DOC (mg/L)	COD (mg/L)	BOD (mg/L)	COD-BOD (mg/L)	Source
Jiulong River, China	24.46	117.80	1.58	2.90	1.61	1.28	This study
Xiamen Bay, China	24.44	118.04	0.99	1.20	0.68	0.52	This study
Xiamen Bay, China	24.42	118.16	0.97	0.80	0.62	0.18	This study
Xiamen Bay, China	24.51	118.24	1.04	1.12	0.97	0.15	This study
Xiamen Bay, China	24.57	118.16	1.13	1.12	0.87	0.25	This study
Xiamen Bay, China	24.53	118.09	1.20	1.68	1.04	0.64	This study
Bohai Sea, China	37.39	119.95	1.67	1.62	1.32	0.30	This study
Bohai Sea, China	37.39	119.95	1.59	1.62	1.30	0.32	This study
Bohai Sea, China	37.39	119.94	1.70	1.78	1.40	0.38	This study
Bohai Sea, China	37.39	119.93	1.60	1.58	1.26	0.32	This study
Bohai Sea, China	37.39	119.93	1.55	1.54	1.22	0.32	This study
Bohai Sea, China	37.39	119.94	1.74	1.80	1.44	0.36	This study
Yellow Sea, China	36.37	120.88	1.10	1.18	0.80	0.38	This study
Yellow Sea, China	36.37	120.88	1.15	1.22	0.82	0.40	This study
Yellow Sea, China	36.37	120.88	1.01	1.10	0.74	0.36	This study
Yellow Sea, China	36.37	120.88	1.18	1.27	0.88	0.39	This study
Yellow Sea, China	36.37	120.88	0.96	1.10	0.74	0.36	This study
Yellow Sea, China	36.37	120.88	1.03	1.15	0.76	0.39	This study
Yellow Sea, China	36.37	120.88	1.10	1.18	0.82	0.36	This study
Yellow Sea, China	36.37	120.88	1.06	1.15	0.76	0.39	This study
Mirs Bay, China	22.53	114.48	1.89	2.13	1.64	0.49	(34)

Locality	Latitude (°N)	Longitude (°E)	DOC (mg/L)	COD (mg/L)	BOD (mg/L)	COD-BOD (mg/L)	Source
Mirs Bay, China	22.53	114.46	1.29	1.52	1.45	0.07	(34)
Mirs Bay, China	22.50	114.48	1.51	1.34	1.20	0.14	(34)
Mirs Bay, China	22.53	114.48	1.74	1.68	0.97	0.72	(34)
Mirs Bay, China	22.53	114.47	1.67	2.80	2.06	0.74	(34)
Mirs Bay, China	22.53	114.46	1.51	1.57	1.47	0.10	(34)
Mirs Bay, China	22.50	114.48	1.67	2.66	1.71	0.95	(34)
Mirs Bay, China	22.50	114.48	1.51	2.41	1.48	0.93	(34)
Mirs Bay, China	22.53	114.48	2.42	2.12	1.36	0.76	(34)
Mirs Bay, China	22.53	114.47	2.27	2.90	1.86	1.04	(34)
Mirs Bay, China	22.53	114.46	1.36	2.00	1.26	0.74	(34)
Mirs Bay, China	22.50	114.47	2.27	3.00	1.84	1.16	(34)
Mirs Bay, China	22.50	114.48	1.51	2.17	1.24	0.93	(34)
Text Fig. 3							
Ingramport River, Canada	44.67	-63.97					This study
Text Fig. 4							
Biwa Lake, Japan	35.33	136.17					(20)
Han River, South Korea	37.48	126.43					(21, 73)
Finnish rivers, Finland (1989)	64.00	26.00					(22)

Table S2. Sampling information and data corresponding to Fig. S2. The samples were from various lakes on the Qinghai Tibet Plateau, China (this study), and the Jiahe River valley (35, Table 2). The data cover a range of salinities from near zero to 43.

Locality	Salinity	COD _{Cr} (mg L ⁻¹)	COD _{Mn} (mg L ⁻¹)	COD _{Cr} /COD _{Mn}	Data source
Kala Kuli Lake, China	0.10	5.60	1.10	5.09	This study
Qiangyong Lake, China	0.10	5.20	1.00	5.20	This study
Songmuxi Co, China	0.26	8.30	0.50	16.60	This study
Bangong Co, China	0.46	20.30	2.30	8.83	This study
Namu Co, China	0.99	18.70	1.10	17.00	This study
Darebu Co, China	1.27	22.00	1.80	12.22	This study
Lang Co, China	1.51	30.20	1.90	15.89	This study
Gongzhu Co, China	5.16	164.10	18.00	9.12	This study
Daze Co, China	15.99	45.30	3.20	14.16	This study
Bieruoze Co, China	27.50	630.50	12.60	50.04	This study
Dong Co, China	43.46	906.70	12.20	74.32	This study
Jiahe River valley, China	0.40	24.74	4.00	6.19	(35)
Jiahe River valley, China	0.41	8.25	3.26	2.53	(35)
Jiahe River valley, China	0.40	11.55	3.37	3.43	(35)
Jiahe River valley, China	0.30	28.04	5.18	5.41	(35)
Jiahe River valley, China	0.26	18.15	4.97	3.65	(35)
Jiahe River valley, China	0.28	24.74	5.20	4.76	(35)
Jiahe River valley, China	0.27	9.90	4.97	1.99	(35)
Jiahe River valley, China	0.33	16.50	5.29	3.12	(35)
Jiahe River valley, China	0.27	26.39	6.04	4.37	(35)
Jiahe River valley, China	0.32	21.44	10.82	1.98	(35)
Jiahe River valley, China	4.61	51.14	8.82	5.80	(35)
Jiahe River valley, China	14.08	493.23	9.26	53.26	(35)

Table S3. Comparison of measurements with the alkaline COD_{Mn} and acidic COD_{Mn} protocols along a salinity gradient.

Sample Source	Salinity	Alkaline COD _{Mn} (mg L ⁻¹)	Acidic COD _{Mn} (mg L ⁻¹)	Acid. COD _{Mn} – Alk. COD _{Mn} (mg L ⁻¹)	Data source
Xiamen U. Reservoir, China	0	2.73	2.64	-0.09	This study
Furong Lake, China	0	10.19	11.62	1.43	This study
Xiang'an Mountain Lake, China	0	2.62	4.01	1.39	This study
Xiang'an Artificial Lake, China	0	6.08	6.26	0.18	This study
Wenqing Lake, China	0	3.78	6.55	2.77	This study
Xiamen botanical Garden Lake, China	0	2.88	5.08	2.20	This study
Tibet Xironggou, China	0	1.61	1.74	0.13	This study
Tibet Lulang, China	0	11.15	11.70	0.55	This study
Jiulong R. Estuary, China	4.20	2.19	4.34	2.15	This study
Xiamen Bay, China	16.50	1.55	5.86	4.31	This study
Xiamen Bay, China	29.40	0.76	17.28	16.52	This study
Sackville River, Canada	0.04	4.82	7.22	2.40	This study
Sackville Estuary, Canada	3.60	4.82	5.52	0.70	This study
Sackville Estuary, Canada	8.50	5.08	6.35	1.27	This study
Sackville Estuary, Canada	15.80	2.78	6.19	3.41	This study
Sackville Estuary, Canada	20.40	2.15	6.28	4.13	This study
Northwest Arm, Canada	30.00	0.52	7.42	6.90	This study
Jiahe River valley, China	0.40	4.00	4.40	0.40	(35)
Jiahe River valley, China	0.41	3.26	3.38	0.12	(35)
Jiahe River valley, China	0.40	3.37	3.40	0.03	(35)
Jiahe River valley, China	0.30	5.18	5.36	0.18	(35)
Jiahe River valley, China	0.26	4.97	4.57	-0.40	(35)
Jiahe River valley, China	0.28	5.20	4.88	-0.32	(35)
Jiahe River valley, China	0.27	4.97	4.80	-0.17	(35)
Jiahe River valley, China	0.33	5.29	5.19	-0.10	(35)
Jiahe River valley, China	0.27	6.04	6.08	0.04	(35)
Jiahe River valley, China	0.32	10.82	8.00	-2.82	(35)
Jiahe River valley, China	4.61	8.82	11.00	2.18	(35)
Jiahe River valley, China	14.08	9.26	17.80	8.54	(35)

Table S4. Examples of the use of the COD index to natural water quality assessment by governmental organizations.

Country or organization	Application	Reference
United Nations Environment Program	Before Aquifer	(74)
USA	River	(75)
USA	Natural Water	(76)
USA-Geological Survey	Stream	(77)
USA-Geological Survey	Lake and River	(78)
USA-Geological Survey	Before Aquifer	(79)
USA	Natural Water	(80)
Europe Union	Lake and River	(81)
UK	Natural Water and Waste Water	(82)
UK	River and Running Surface Water	(83)
Netherlands	River	(84)
Romania	River and Drinking Water	(85)
Ireland	Surface Water	(86)
Sweden	Laker	(87)
South Africa	All water	(88)
China	Lake and River	(89)
China	Ocean	(90)
China	Reservoir	(91)
China	Natural Water	(92)
China	Drinking Water	(93)
Korea	River	(73)
India	Surface Water	(94)
Japan	River, Lake and Ocean	(95)
Tunisia	All Water	(96)
Uruguay	Estuary	(97)
Peru	All Water	(98)

Table S5. Classification of natural waters by COD standards and practical applications.

Nation	Document	Class	COD Standards	Applications	Practical Examples (reference)
Japan	Environmental Quality Standards for lakes	AA	0~1 mg/L	Drinkable after simple treatment	(99, 100)
		A	1~3 mg/L	Drinkable after normal treatment	
		B	3~5 mg/L	For industry after normal treatment	
		C	5~8 mg/L	For industry after specific treatment	
China	Environmental Quality Standard for Surface Water, GB 3838-2002	I	0~15 mg/L	Standard of headwaters	(89)
		II	0~15 mg/L	Standard of source of running water (first class), habitats of rare aquatic species	
		III	15~20 mg/L	Standard of source of running water (second class), aquaculture and swimming	
		IV	20~30 mg/L	Standard of industrial water	
		V	30~40 mg/L	For agricultural utilizations	
Malaysia	National Water Quality Standards of Malaysia	I	0~10 mg/L	Water Supply I – Practically no treatment necessary; fishery I – Very sensitive aquatic species	(101)
		II	10~25 mg/L	Water Supply II – Conventional treatment required; fishery II – Sensitive aquatic species; recreational use with body contact	
		III	25~50 mg/L	Water Supply III – Extensive treatment required; fishery III – Common, of economic value and tolerant species; livestock drinking water	
		IV	50~100 mg/L	Irrigation	

Nation	Document	Class	COD Standards	Applications	Practical Examples (reference)
		V	more than100 mg/L	None of the above	