

## Article (refereed)

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## 6 **Quantification of natural DOM from UV Absorption at Two**

## 7 **Wavelengths**

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34 **Environmental Context.** Dissolved organic matter (DOM) is part of the global carbon  
35 cycle, ecologically and geochemically active, and costly to remove in water treatment.  
36 Spectroscopic monitoring at a single wavelength provides some indication of DOM  
37 concentration, but variations in optical properties mean that accurate determinations  
38 currently rely on slow and costly laboratory methods. We show that for water samples  
39 containing non-anthropogenic DOM, ultraviolet absorbance at two wavelengths can  
40 quantify DOM rapidly, cheaply and accurately, and also indicate its quality.

41 **Abstract.** A two-component model permitted the precise simulation of ultraviolet  
42 absorption by 23 contrasting surface-water DOM samples. Although a unique set of  
43 model parameters could not be established, the results could still be used to predict  
44 [DOC] in water samples simply from absorbance values at two wavelengths (we used  
45 254 and 340 nm). The parameterised model was used to predict [DOC] for a separate  
46 dataset obtained by combining results for 12 samples each from a UK river draining  
47 upland pasture, UK groundwaters from a range of formations, stream and lake waters  
48 from a forested region of Ontario, and high-altitude alpine and subalpine streams from  
49 Colorado. A close correlation ( $R^2 = 0.997$ ) was obtained, with only slight  
50 underestimation of the true [DOC]. Precise prediction of [DOC] from absorbance data at  
51 a single wavelength was not possible, because of differences in DOM extinction  
52 coefficients among the samples. When the model was applied to samples collected from  
53 river locations in a heterogeneous UK catchment with areas of industry and high human  
54 population, [DOC] was underestimated in many cases, which may indicate the presence  
55 of non-absorbing pollutant DOM.

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57 *Keywords.* dissolved organic carbon - dissolved organic matter – two-component model  
58 – UV spectra

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60 Dissolved organic matter (DOM) is a ubiquitous collection of components in surface, soil  
61 and ground waters, comprising the partial decomposition products of living material,  
62 chiefly plants and algae, but also derived from agricultural, industrial and domestic  
63 human activities. Differences in source material and rates of decomposition, and physical  
64 fractionation processes, generate substantial heterogeneity in DOM concentrations and  
65 properties. DOM participates in many ecological and geochemical reactions, and is costly  
66 to remove from water intended for domestic and industrial supply. Interest in the  
67 formation and transport of DOM has intensified because of widespread increases in DOC  
68 concentrations and fluxes seen over recent years<sup>[1]</sup>, with possible links to changes in the  
69 terrestrial carbon cycle. Routine methods for the accurate determination of DOM in  
70 different samples are based on the measurement of DOC, usually after conversion to  
71 CO<sub>2</sub>. This requires the return of samples to the laboratory, and is both time-consuming  
72 and fairly expensive. Optical absorbance at a single wavelength in the UV-visible range  
73 usually correlates strongly with [DOC], and is therefore often used to monitor natural  
74 DOM. However, differences in DOM properties among waters, and temporally within a  
75 given water, mean that this can only be an approximate method. Indeed, variation in  
76 the ratio of absorbance to [DOC] is widely used to characterise the quality of DOM,  
77 notably through the specific UV absorbance at 254 nm (SUVA)<sup>[2]</sup>.

78 The measure of optical properties used here is the extinction coefficient ( $E$ ; also referred  
 79 to as specific absorbance and specific absorptivity) obtained as the ratio of optical  
 80 absorbance at a given wavelength ( $\lambda$  nm) to  $[\text{DOC}]$ , and with units of  $\text{l g}^{-1} \text{cm}^{-1}$ . Thacker  
 81 et al.<sup>[3]</sup> determined the extinction coefficients of 23 concentrated samples of DOM from a  
 82 variety of surface waters in northern England. They demonstrated a monotonic increase  
 83 of the  $E_{340}/E_{254}$  ratio with  $E_{340}$  (Figure 1), which suggests that  $[\text{DOC}]$  can be deduced  
 84 from absorbance data alone, by the following argument. For a given water sample, the  
 85  $E_{340}/E_{254}$  ratio is exactly the same as the ratio of optical absorbances  $A_{340}/A_{254}$  since both  
 86 measurements refer to the same  $[\text{DOC}]$ . Therefore the  $A_{340}/A_{254}$  ratio of the sample  
 87 corresponds to a single value of  $E_{340}$ , which can be divided into  $A_{340}$  to obtain  $[\text{DOC}]$ . If  
 88 the monotonic relationship of Figure 1 applies generally, optical absorbance values at two  
 89 wavelengths offer a means to estimate  $[\text{DOC}]$  accurately, despite variations in sample  
 90 extinction coefficients at the individual wavelengths.

91 In fact, the relationship in Figure 1 is expected for a two-component system. The  
 92 extinction coefficient at any wavelength is given by

$$93 \quad E_{\lambda} = f_A E_{\lambda,A} + f_B E_{\lambda,B} = f_A E_{\lambda,A} + (1 - f_A) E_{\lambda,B} \quad (1)$$

94 where  $f_A$  and  $f_B$  are the fractions of components A and B ( $f_A + f_B = 1$ ). For the 23  
 95 samples studied by Thacker et al.<sup>[3]</sup> there are 46 versions of this equation if two  
 96 wavelengths are considered, and 23 values of  $f_A$ . We treated the  $f_A$  values and the four  
 97 extinction coefficients as adjustable parameters, and used Microsoft Excel Solver to  
 98 optimise them by minimizing the sum of the squares of  $(E_{\lambda,\text{obs}} - E_{\lambda,\text{calc}})/E_{\lambda,\text{obs}}$ . Excellent fits  
 99 could be obtained, with average differences between observed and calculated values <  
 100 2%, thereby supporting the two-component hypothesis. However, the model is  
 101 overparameterised and so a unique parameter set cannot be obtained from this relatively  
 102 small data set.

103 We constrained the model by specifying the value of  $E_{254,A}$  to be  $60 \text{ l g}^{-1} \text{cm}^{-1}$  (equivalent  
 104 to  $6.0 \text{ l mg}^{-1} \text{m}^{-1}$  in commonly used SUVA units). This can be justified from the SUVA  
 105 values of isolated DOM<sup>[2]</sup> and from the results of streamwater surveys at a variety of  
 106 locations<sup>[3-8]</sup>. In none of these reports is a SUVA value exceeding  $6.0 \text{ l mg}^{-1} \text{m}^{-1}$   
 107 reported, although values exceeding  $5.0 \text{ l mg}^{-1} \text{m}^{-1}$  are not uncommon<sup>[3,4,7,8]</sup>. Therefore  
 108 we can make the reasonable approximation that an  $E_{254}$  value of  $60 \text{ l g}^{-1} \text{cm}^{-1}$  represents  
 109 an end-member, i.e. the sample in question is entirely component A. Refitting the model  
 110 with  $E_{254,A}$  set to  $60 \text{ l g}^{-1} \text{cm}^{-1}$ , and using data for three wavelengths (254, 280, 340 nm)  
 111 to increase the ratio of observations to parameters, reduced the range of parameter sets  
 112 that fitted the model. Consistent values of  $E_{254,A}$ ,  $E_{280,A}$  and  $E_{340,A}$  were now obtained, but  
 113 ranges of values of  $E_{254,B}$ ,  $E_{280,B}$  and  $E_{340,B}$ , combined with different sets of  $f_A$  values, gave  
 114 equally good fits. The same goodness-of-fit was obtained for any value of  $E_{254,B}$  in the

115 range 14 to 22 l g<sup>-1</sup> cm<sup>-1</sup>, since the other model parameters could change to compensate  
 116 (Table 1). Outside this range of E<sub>254,B</sub> however, the fits were always worse. Although  
 117 fixing E<sub>254,A</sub> reduces the parameter ranges that can fit the data, the prediction of [DOC],  
 118 (see below), is not affected. However, constraining the parameters to physically realistic  
 119 values may lead to useful correlations with other DOM physico-chemical properties.

120 Any of the sets of extinction coefficients shown in Table 1, or indeed any intermediate  
 121 set, can be used to compute f<sub>A</sub> in a new water sample from the following equation,  
 122 obtained by combining the versions of equation (1) for each wavelength;

$$123 \quad f_A = (E_{\lambda_1,B} - R E_{\lambda_2,B}) / (R E_{\lambda_2,A} - R E_{\lambda_2,B} - E_{\lambda_1,A} + E_{\lambda_1,B}) \quad (2)$$

124 where R is the ratio of optical absorbance values (A<sub>λ1</sub>/A<sub>λ2</sub>) for the sample in question.  
 125 The value of f<sub>A</sub> can be substituted into equation (1) to obtain E<sub>λ1</sub> and E<sub>λ2</sub> for the sample,  
 126 which can then be divided into either A<sub>λ1</sub> or A<sub>λ2</sub> respectively to obtain [DOC].

127 We used E<sub>254,A</sub>, E<sub>254,B</sub>, E<sub>340,A</sub> and E<sub>340,B</sub> to predict [DOC] for a set of 48 data assembled  
 128 from the results of monitoring by four separate research organisations. The field  
 129 locations were judged to be free of local anthropogenic influences, and none of the  
 130 samples was noticeably turbid. Samples from the River Tarnbrook were collected by the  
 131 Centre for Ecology and Hydrology as part of a river monitoring programme on the Ribble-  
 132 Wyre catchment of north-west England (see below). The river drains an area of upland  
 133 pasture with low human population. The water samples were passed through Whatman  
 134 GF/F glass-fibre filters (0.7 μm nominal size cut-off), concentrations of DOC were  
 135 determined by a combustion method using a Shimadzu TOC-VCPH instrument, and  
 136 absorption spectra were measured with an Agilent 8453 diode array instrument. The  
 137 British Geological Survey collected groundwater samples from piezometers or where they  
 138 emerged as springs from formations in the UK. Samples for DOC and absorbance  
 139 analysis were filtered using silver filters (0.45 μm Millipore™) and analysed using a  
 140 Thermalox™ C analyser after acidification and sparging (DOC) and a Varian™  
 141 spectrophotometer (optical absorbance). Trent University collected stream and lake  
 142 samples from a forested region of the Precambrian Shield in Ontario; the data used here  
 143 refer to November 2007. Samples were filtered with Millipore™ 0.45 μm membrane  
 144 filters, and analysed for DOC (Shimadzu TOC-VPH) and optical absorbance (Cary 59  
 145 UV/Vis spectrophotometer). Colorado samples were collected from alpine and subalpine  
 146 stream sites in the Green Lakes Valley and adjacent Como Creek watershed. The Green  
 147 Lakes Valley is part of the Niwot Ridge Long Term Ecological Research (NWTLTER) site  
 148 and is not influenced by direct human impacts. Samples were filtered with Whatman GF/F  
 149 glass-fibre filters (0.7 μm nominal pore size), DOC was measured by high temperature  
 150 catalytic oxidation with a Shimadzu 5050A TOC analyzer, and absorption spectra were  
 151 measured on an Agilent 8453 UV-visible spectroscopy system. Twelve data points were

152 used for each sub-set, this being the total available for the River Tarnbrook; values from  
153 the other sub-sets were chosen at random.

154 Values of  $A_{254}$  and  $A_{340}$  for each sample were used to calculate  $f_A$  from equation (2) using  
155 calibrated extinction coefficients, then the overall sample extinction coefficients  $E_\lambda$  were  
156 calculated with equation (1), and [DOC] obtained from the ratio  $A_{254}/E_{254}$ .  
157 Indistinguishable results were obtained whichever of the three parameter sets of Table 1  
158 was used. The model predicted [DOC] well (Figure 2), with  $R^2=0.997$  and a root-mean-  
159 squared-deviation (RMSD) of  $0.7 \text{ mg l}^{-1}$ . The slope of 0.98 and intercept of  $-0.3 \text{ mg l}^{-1}$   
160 (significant at  $p<0.01$ ) result in slight underestimation of [DOC] on average, and a  
161 proportionately greater error at low [DOC]. The calculated values of  $f_A$  differed among  
162 the sub-sets; with  $E_{254,B}$  set to  $18 \text{ l g}^{-1} \text{ cm}^{-1}$ , the averages were 0.86 for the River  
163 Tarnbrook, 0.18 for the groundwaters, 0.42 for the Ontario samples, and 0.46 for the  
164 Colorado samples. Of course the absolute  $f_A$  values depend upon the choice of  $E_{254,B}$ , but  
165 their relative order is always the same.

166 An important feature of the data sub-sets is that they differ appreciably in their  
167 extinction coefficients at a single wavelength. For each sub-set there is quite a strong  
168 correlation of  $A_{254}$  with [DOC] (Figure 2), but the slopes and intercepts differ noticeably;  
169 the results are still more divergent at 340 nm. Use of the  $A_{254}$  regression for the full data  
170 set ( $R^2=0.955$ ) to predict [DOC] produces an RMSD of  $1.86 \text{ mg l}^{-1}$ , more than twice the  
171 value from the two-component model.

172 A study by CEH and Lancaster University of the catchments of the Rivers Ribble and  
173 Wyre has involved fortnightly sampling of 26 representative river sites (including the  
174 River Tarnbrook site of Figure 2) in north-west England. The total catchment area of  
175  $1920 \text{ km}^2$  has a wide range of agricultural land-uses, including pasture, arable and  
176 upland moorlands. There are also several intensely urban locations in the main towns of  
177 Accrington, Blackburn and Burnley, as well as considerable current industrial activity and  
178 the legacy of past heavy industry. We analysed 251 samples collected over the period  
179 October 2008 to February 2009, using the methods described above for the River  
180 Tarnbrook. As shown by Figure 3, the model underestimates [DOC] in many cases, but  
181 there are only two significant overestimates, and even these are probably outliers. The  
182 fact that the cloud of data points has a well-defined upper edge that corresponds to the  
183 1:1 line suggests that the model provides good estimates of "natural" [DOC] but,  
184 inevitably, fails to predict concentrations of non-absorbing DOM produced by human  
185 activities. From the results, excluding likely outliers, the average non-absorbing [DOC] is  
186  $1.3 \text{ mg l}^{-1}$ , with a 5/95 percentile range of  $0.2/3.3 \text{ mg l}^{-1}$ . Note that interference by  
187 nitrate, the most common non-DOM chromophoric compound in surface waters<sup>[9]</sup>, is  
188 unlikely to be serious in these samples, since the highest nitrate concentration in these

189 waters is c. 7 mg l<sup>-1</sup>, which would add less than 0.5 mg l<sup>-1</sup> to [DOC] estimated  
190 spectroscopically. The three parameter sets of Table 1 gave nearly identical results.

191 The spectral analysis described here is a simple idea that has apparently not been  
192 proposed before, although there are some relevant reports. Mattson et al.<sup>[10]</sup> used  
193 absorbance at 546 nm to correct values at 254 nm for turbidity. Simonsson et al.<sup>[11]</sup>  
194 performed Principal Components Analysis on absorbance data in the range 210-300 nm  
195 to estimate [DOC] and [nitrate] in different forest floor leachates, but the samples did  
196 not vary greatly in DOM quality and so a generally-applicable model was not derived.  
197 Downing et al.<sup>[12]</sup> used absorbance data only in the visible range (412-715 nm) to derive  
198 a statistical model for samples from a tidal wetland, but this covered only a small range  
199 of [DOC] (2.4 – 4.0 mg l<sup>-1</sup>) and again the range of DOM quality would have been limited.  
200 The book edited by Thomas & Burgess<sup>[9]</sup> devotes a chapter to the UV-visible  
201 spectroscopy of natural waters<sup>[13]</sup> which considers “humic like substances” (equivalent to  
202 the DOM that we are interested in) and recognises variations in their UV-visible spectra,  
203 but does not discuss their absolute quantification from multi-wavelength data. Therefore  
204 we believe that ours is a novel approach.

205 Our method is a significant improvement over single-wavelength monitoring, since it can  
206 provide accurate estimates of [DOC] for samples with differing DOM quality, at least in  
207 natural waters not highly impacted by anthropogenic activities. The non-zero intercept  
208 when [DOC] predictions are regressed against conventionally-measured values (Figure 2)  
209 leads to reduced accuracy for samples with low [DOC], which tend to be dominated by  
210 DOM with weak light absorption, but for [DOC] > c. 2 mg l<sup>-1</sup> spectroscopic data alone can  
211 be used to determine both concentration and quality rapidly and cheaply. The true  
212 detection limit of the dual-wavelength method remains to be established, in part because  
213 of inevitable uncertainty in conventionally-determined [DOC]. These findings could  
214 significantly widen the scope of DOM research in both the laboratory and the field,  
215 including the possibility of continuous monitoring *in situ*, if turbidity influences could be  
216 taken into account. For polluted waters, the model does not provide good estimates of  
217 total [DOC] but may prove useful in distinguishing natural and pollutant DOM. The  
218 method should be tested on a wider range of DOM and water types, and there is clearly a  
219 need to improve the parameterisation, to define component B in particular; as noted  
220 above, this might lead to useful correlations with DOM physico-chemical properties. We  
221 also need to understand why a simple two-component model appears to account so well  
222 for the complex mixture of compounds that constitute natural DOM.

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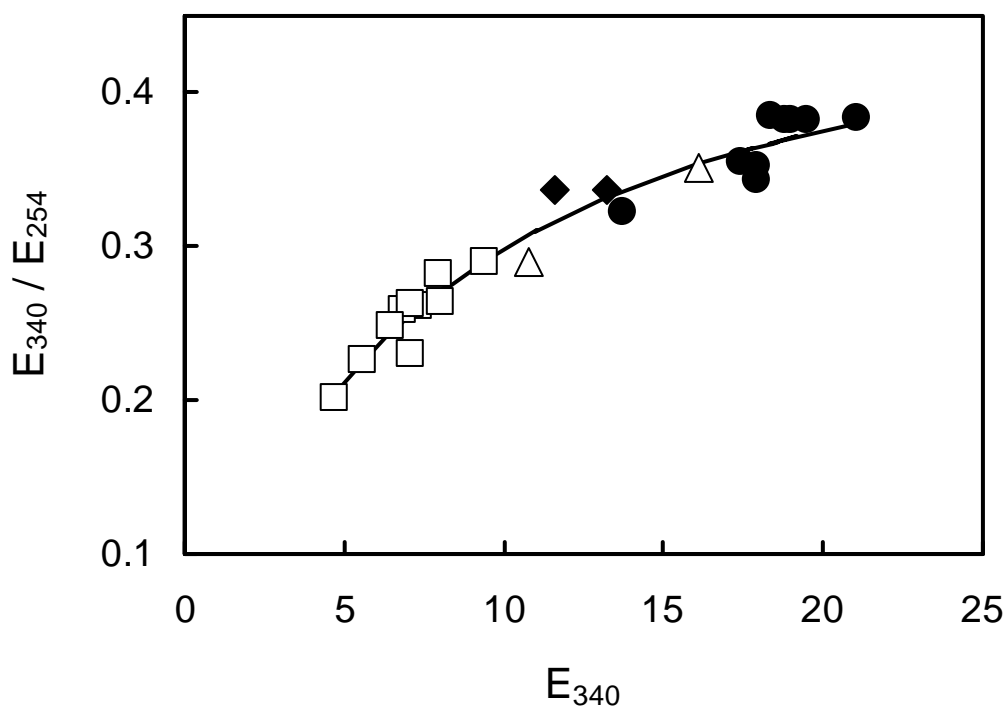
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278 Burgess C 2007; UV-Visible Spectrophotometry of Water and Wastewater,  
279 Elsevier.

280 Table 1 Fitting results for the two-component model. Parameter values in **bold** were  
 281 fixed, those in *italics* are fitted. Within the precision shown, exactly the same  
 282 calculated values were obtained with each of the three parameter sets.

283  
 284

Parameters				Calculations			Observations					
	<b>60</b>	<b>60</b>	<b>60</b>	<i>f<sub>A</sub></i>	<i>f<sub>A</sub></i>	<i>f<sub>A</sub></i>	E <sub>254</sub>	E <sub>280</sub>	E <sub>340</sub>	E <sub>254</sub>	E <sub>280</sub>	E <sub>340</sub>
E <sub>254,A</sub>	<b>60</b>	<b>60</b>	<b>60</b>	0.19	0.12	0.02	22.9	15.8	4.7	23.3	15.4	4.7
E <sub>280,A</sub>	<i>49</i>	<i>49</i>	<i>49</i>	0.24	0.16	0.07	24.8	17.5	5.6	24.8	17.7	5.6
E <sub>340,A</sub>	<i>23</i>	<i>23</i>	<i>23</i>	0.27	0.20	0.12	26.4	19.0	6.4	26.0	19.1	6.5
				0.28	0.21	0.13	27.0	19.5	6.7	26.2	19.4	6.8
				0.29	0.23	0.14	27.5	19.9	7.0	26.9	19.9	7.1
E <sub>254,B</sub>	<b>14</b>	<b>18</b>	<b>22</b>	0.31	0.24	0.16	28.1	20.5	7.3	28.0	20.5	7.3
E <sub>280,B</sub>	<i>8</i>	<i>11</i>	<i>15</i>	0.33	0.26	0.19	29.1	21.4	7.8	28.3	21.2	8.0
E <sub>340,B</sub>	<i>0</i>	<i>2</i>	<i>4</i>	0.35	0.29	0.21	30.0	22.2	8.2	30.5	22.7	8.1
				0.32	0.25	0.17	28.5	20.9	7.5	30.6	22.2	7.1
				0.40	0.34	0.27	32.4	24.3	9.4	32.5	24.4	9.4
				0.47	0.42	0.36	35.5	27.2	11.0	34.5	26.2	11.6
				0.47	0.42	0.35	35.4	27.1	11.0	37.1	27.0	10.8
				0.55	0.51	0.46	39.5	30.7	13.0	39.2	30.4	13.2
				0.60	0.56	0.51	41.5	32.5	14.0	42.5	32.9	13.7
				0.68	0.65	0.62	45.5	36.1	16.1	45.8	35.8	16.1
				0.76	0.74	0.71	48.9	39.2	17.8	47.7	38.8	18.4
				0.75	0.73	0.70	48.5	38.9	17.6	49.0	39.1	17.4
				0.79	0.77	0.74	50.1	40.3	18.4	49.2	40.0	18.8
				0.79	0.78	0.75	50.6	40.7	18.6	49.7	40.4	19.0
				0.78	0.76	0.74	49.9	40.1	18.3	50.7	40.8	17.9
				0.82	0.80	0.78	51.6	41.6	19.2	50.9	41.4	19.5
				0.79	0.77	0.75	50.4	40.6	18.6	52.2	41.4	17.9
				0.90	0.89	0.87	55.2	44.8	21.0	55.0	44.9	21.1

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289 Figure 1. Relationship between the ratio of extinction coefficients at 340 and 254 nm  
290 and the extinction coefficient at 340 nm for 23 samples of DOM from four differing  
291 waters collected at different times. Key to symbols: squares, eutrophic lake;  
292 triangles and diamonds, two streams draining mineral soils; circles, peatland stream.  
293 The line is calculated from the model output shown in Table 1.

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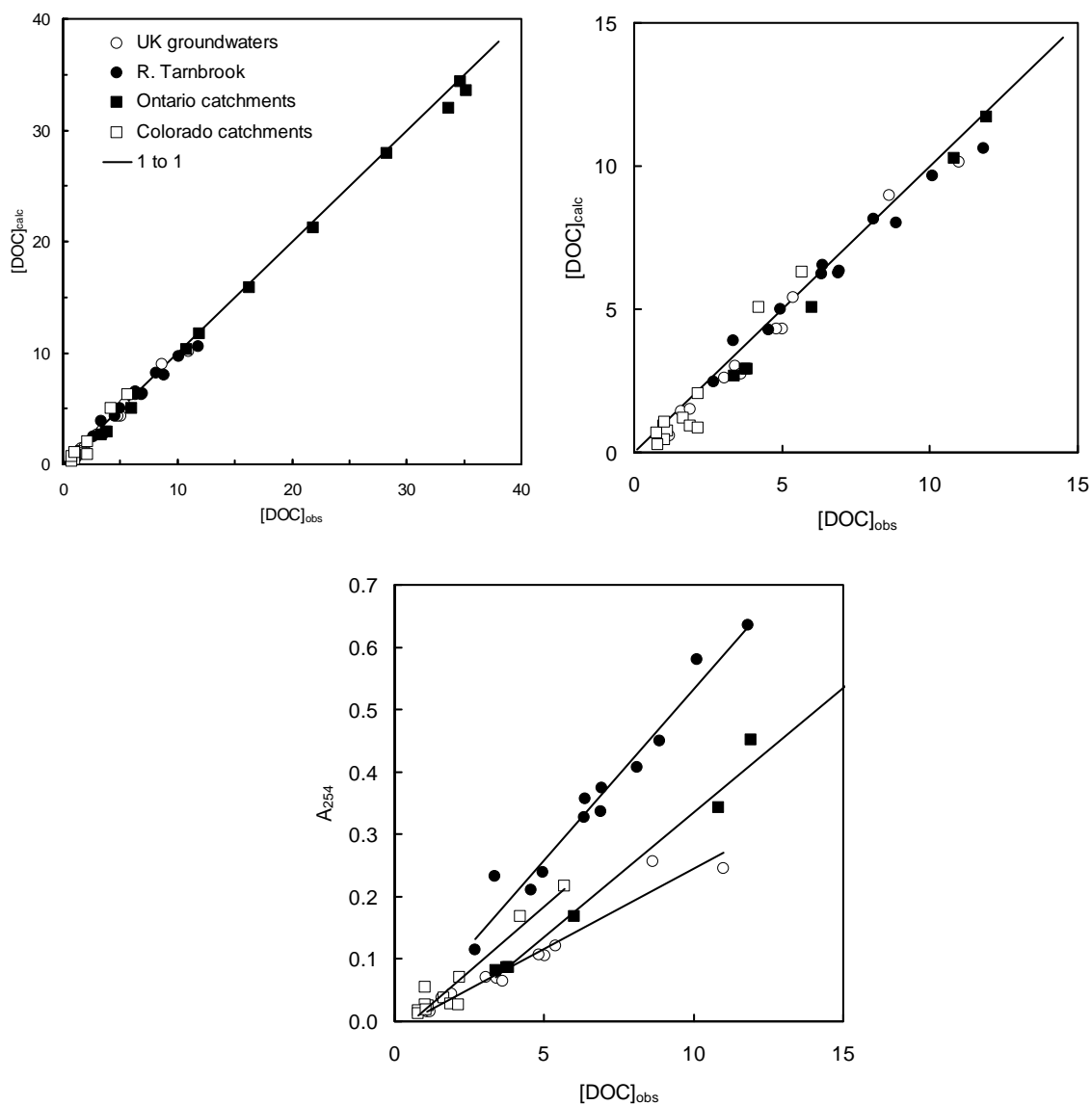
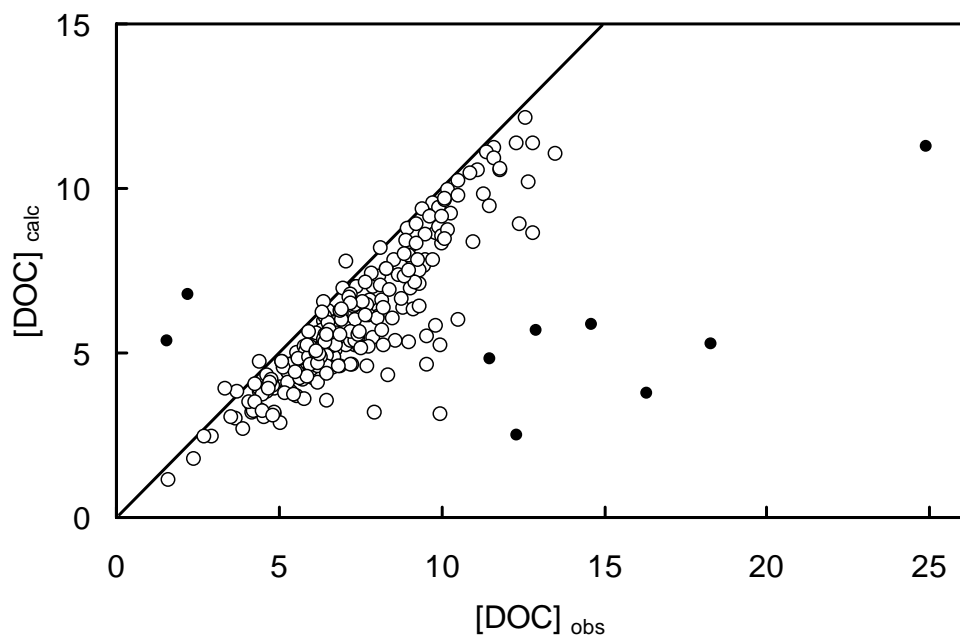


Figure 2. Predicted vs observed [DOC] in mg l<sup>-1</sup> for samples of UK groundwaters (open circles), River Tarnbrook (closed circles), Ontario sites (closed squares) and Colorado sites (open squares). Panels (a) and (b) show the same data on different scales. Panel (c) shows the contrasting relationships between A<sub>254</sub> and [DOC] for the different sub-sets of samples, in the low concentration range.

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Figure 3. Observed and calculated [DOC] for 26 river sites in the Ribble-Wyre catchment, 9 or 10 points for each. The 9 filled circles are judged to be outliers, by comparison with other data for the sites in question. The 1:1 line is shown.