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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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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[1], 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_2. 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)[2].

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 (λ nm) to [DOC], and with units of l g^{-1} cm^{-1}. Thacker
81   et al.[3] 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 [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 [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 [DOC]. If
88   the monotonic relationship of Figure 1 applies generally, optical absorbance values at two
89   wavelengths offer a means to estimate [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

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

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.[3] 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 $(E_{\lambda,obs}-E_{\lambda,calc})/E_{\lambda,obs}$. 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 l g^{-1} cm^{-1} (equivalent
104   to 6.0 l mg^{-1} m^{-1} in commonly used SUVA units). This can be justified from the SUVA
105   values of isolated DOM[2] and from the results of streamwater surveys at a variety of
106   locations[3-8]. In none of these reports is a SUVA value exceeding 6.0 l mg^{-1} m^{-1}
107   reported, although values exceeding 5.0 l mg^{-1} m^{-1} are not uncommon[3,4,7,8]. Therefore
108   we can make the reasonable approximation that an E_{254} value of 60 l g^{-1} 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 l g^{-1} 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^{-1} cm^{-1}, since the other model parameters could change to compensate

116   (Table 1). Outside this range of $E_{254,B}$ however, the fits were always worse. Although

117   fixing $E_{254,A}$ 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_A in a new water sample from the following equation,

122   obtained by combining the versions of equation (1) for each wavelength;

123            $f_A = (E_{\lambda 1,B} - R\,E_{\lambda 2,B}) / (R\,E_{\lambda 2,A} - R\,E_{\lambda 2,B} - E_{\lambda 1,A} + E_{\lambda 1,B})$ (2)

124   where R is the ratio of optical absorbance values ($A_{\lambda 1}/A_{\lambda 2}$) for the sample in question.

125   The value of f_A can be substituted into equation (1) to obtain $E_{\lambda 1}$ and $E_{\lambda 2}$ for the sample,

126   which can then be divided into either $A_{\lambda 1}$ or $A_{\lambda 2}$ respectively to obtain [DOC].

127   We used $E_{254,A}$, $E_{254,B}$ $E_{340,A}$ and $E_{340,B}$ 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_λ 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 mg l^{-1}. The slope of 0.98 and intercept of -0.3 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 l g^{-1} 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 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 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 mg l^{-1}, with a 5/95 percentile range of 0.2/3.3 mg l^{-1}. Note that interference by
187   nitrate, the most common non-DOM chromophoric compound in surface waters[9], is
188   unlikely to be serious in these samples, since the highest nitrate concentration in these

189 waters is c. 7 mg l^{-1}, which would add less than 0.5 mg l^{-1} 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.[10] used
193 absorbance at 546 nm to correct values at 254 nm for turbidity. Simonsson et al.[11]
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.[12] 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^{-1}) and again the range of DOM quality would have been limited.
200 The book edited by Thomas & Burgess[9] devotes a chapter to the UV-visible
201 spectroscopy of natural waters[13] 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^{-1} 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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237 **References**

238 [1]   Monteith, D.T., Stoddard, J.L., Evans, C.D., de Wit, H.A., Forsius, M., Høgåsen,
239   Wilander, A., Skjelkvåle, Jeffries, D.S., Vuorenmaa, J., Keller, B., Kopácek and
240   Vesely, J. (2007)   Dissolved organic carbon trends resulting from changes in
241   atmospheric deposition chemistry. Nature, 450, 537-541.

242 [2]   Weishaar JL, Aiken GR, Bergamaschi BA, Fram MS, Fujii R, Mopper K. (2003)
243   Evaluation of specific ultraviolet absorbance as an indicator of the chemical
244   composition and reactivity of dissolved organic carbon. Environ. Sci. Technol. 37:
245   4702-4708.

246 [3]   Thacker, S.A., Tipping, E., Gondar, D., Baker, A. (2008) Functional properties of
247   DOM in a stream draining blanket peat. Sci. Tot. Environ., 407, 566-573.

248 [4]   Hood, E., Williams, M.W., McKnight, D.M. (2005) Sources of dissolved organic
249   matter (DOM) in a Rocky Mountain stream using chemical fractionation and stable
250   isotopes. Biogeochem. 74, 231-255.

251 [5]   Striegl, R.G., Dornblaser, M.M., Aiken, G.R., Wickland, K.P., Raymond, P.A.
252   (2007) Carbon export and cycling by the Yukon, Tanana, and Porcupine rivers,
253   Alaska,   2001-2005.   Water   Resour.   Res.   43,   W02411,
254   doi:10.1029/2006WR005201.

255 [6]   Moore, T.R., Calrkson, B.R. (2007) Dissolved organic carbon in New Zealand
256   peatlands. N.Z. J. Mar. Freshwat. Res., 41, 137-141.

257 [7]   Balcarczyk, K., Jones, K.J., Jaffé, R., Maie, N. (2009) Stream dissolved organic
258   matter bioavailability and composition in watersheds underlain with discontinuous
259   permafrost. Biogeochem., 94, 255-270.

260 [8]   Temnerud, J., Düker, A, Karlsson, S, Allard, B., Köhler, S., Bishop, K. (2009)
261   Landscape scale patterns in the character of natural organic matter in a Swedish
262   boreal stream network. Hydrol. Earth Syst. Sci., 13, 1567–1582.
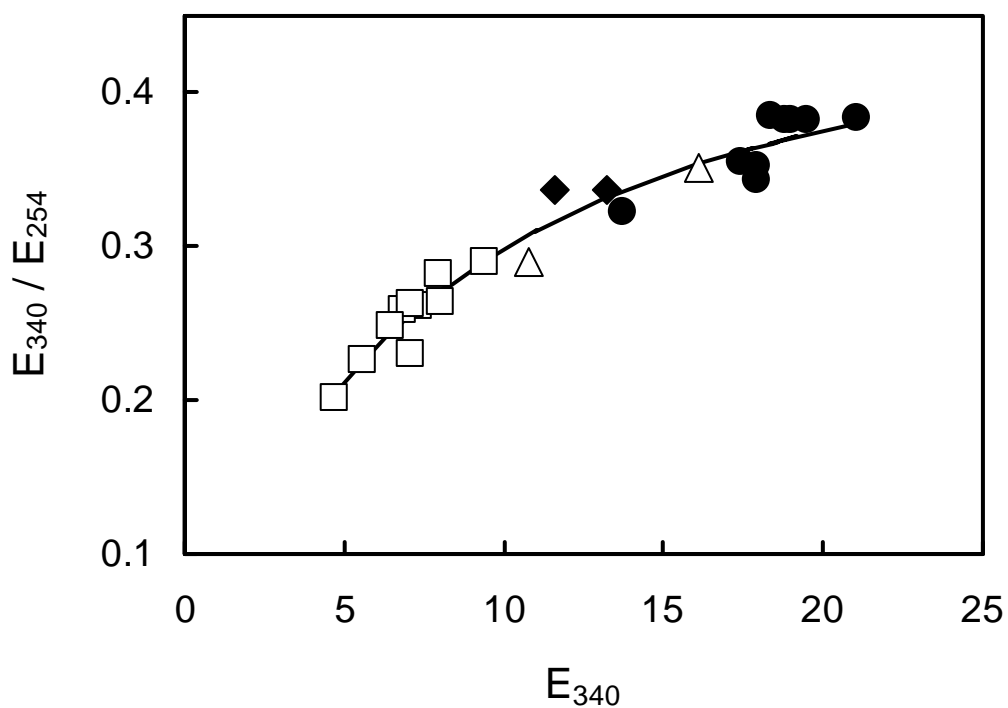
263   [9]   Thomas O, Burgess C 2007; UV-Visible Spectrophotometry of Water and
264   Wastewater, Elsevier.
265   [10]   Mattson, J.S., Smith, C.A., Jones, T.T., Gerchakov, S.M. (1974) Continuous
266   monitoring of dissolved organic matter by UV-visible photometry. Limnol.
267   Oceanogr. 19, 530-535.
268   [11]   Simonsson, M., Kaiser, K., Danielsson, R., Andreux, F., Ranger, J. (2005)
269   Estimating nitrate, dissolved organic carbon and DOC fractions in forest floor
270   leachates using ultraviolet absorbance spectra and multivariate analysis.
271   Geoderma 124, 157-168.
272   [12]   Downing, B.D., Boss, E., Bergamaschi, B.A., Fleck, J.A., Lionberger, M.A., Ganju,
273   N.K., Schoellhamer, D.H., Fujii, R. (2009) Quantifying fluxes and characterizing
274   compositional changes of dissolved organic matter in aquatic systems in situ using
275   combined acoustic and optical measurements. Limnol. Oceanogr. Methods, 7,
276   119-131.
277   [13]   Pouet MF, Theraulaz F, Mesnage V, Thomas O 2007 Natural water, in Thomas O,
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.

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Parameters				Calculations			Observations		
$E_{254,A}$	**60**	**60**	**60**						
$E_{280,A}$	*49*	*49*	*49*						
$E_{340,A}$	*23*	*23*	*23*						
$E_{254,B}$	**14**	**18**	**22**						
$E_{280,B}$	*8*	*11*	*15*						
$E_{340,B}$	*0*	*2*	*4*						
	f_A	f_A	f_A	E_{254}	E_{280}	E_{340}	E_{254}	E_{280}	E_{340}
	0.19	*0.12*	*0.02*	22.9	15.8	4.7	23.3	15.4	4.7
	0.24	*0.16*	*0.07*	24.8	17.5	5.6	24.8	17.7	5.6
	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
	0.31	*0.24*	*0.16*	28.1	20.5	7.3	28.0	20.5	7.3
	0.33	*0.26*	*0.19*	29.1	21.4	7.8	28.3	21.2	8.0
	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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Figure 1. Relationship between the ratio of extinction coefficients at 340 and 254 nm and the extinction coefficient at 340 nm for 23 samples of DOM from four differing waters collected at different times.   Key to symbols: squares, eutrophic lake; triangles and diamonds, two streams draining mineral soils; circles, peatland stream. The line is calculated from the model output shown in Table 1.

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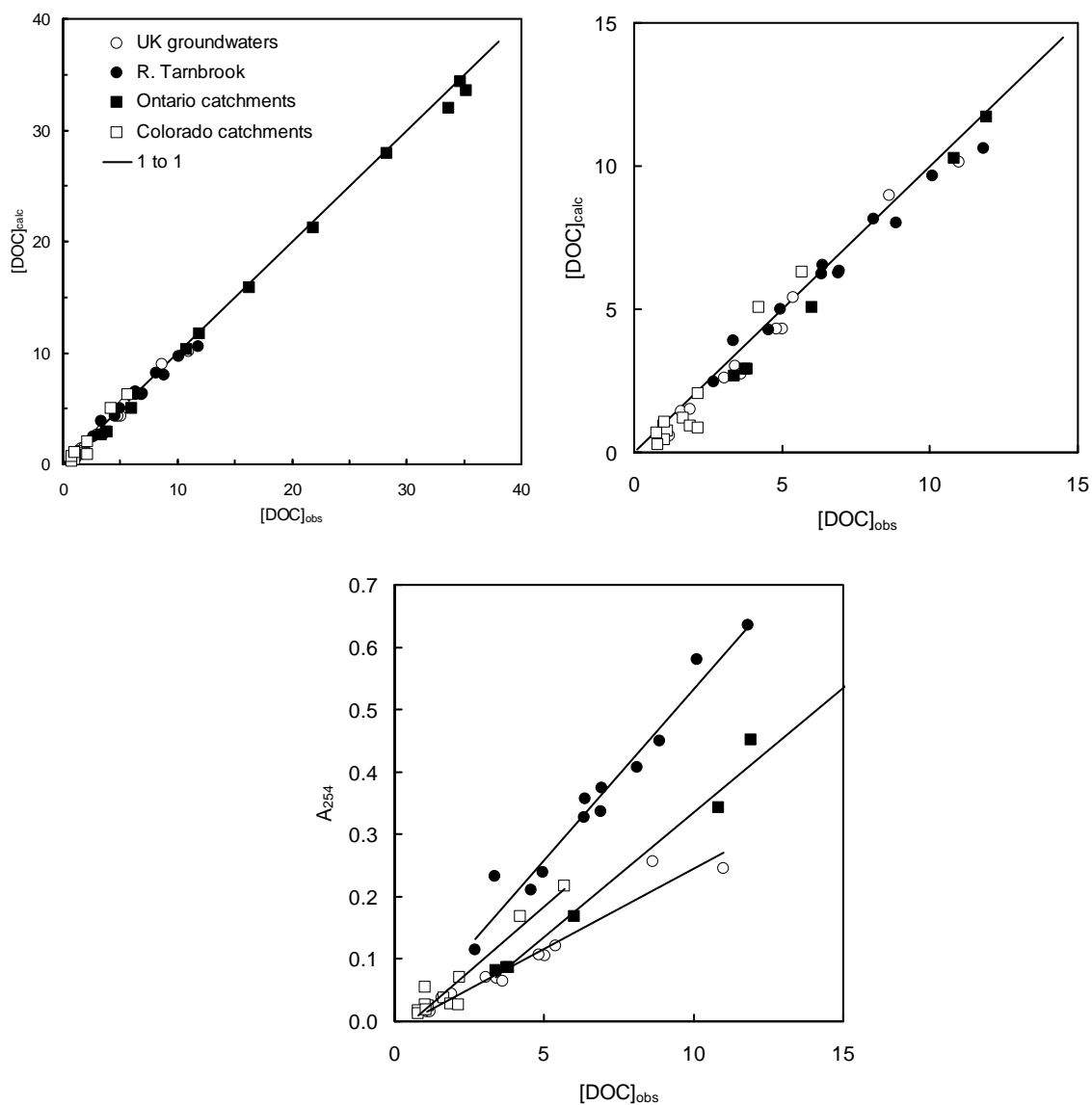325
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335 Figure 2. Predicted vs observed [DOC] in mg l^{-1} for samples of UK groundwaters
336 (open circles), River Tarnbrook (closed circles), Ontario sites (closed squares) and
337 Colorado sites (open squares). Panels (a) and (b) show the same data on different
338 scales. Panel (c) shows the contrasting relationships between A$_{254}$ and [DOC] for the
339 different sub-sets of samples, in the low concentration range.

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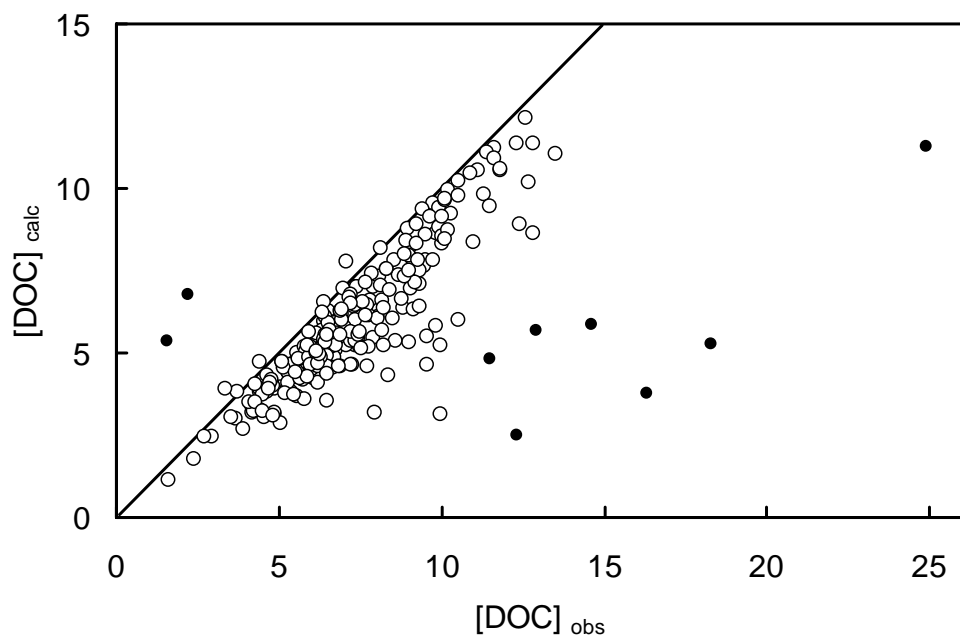
Figure 3.   Observed and calculated [DOC] for 26 river sites in the Ribble-Wyre catchment, 9 or 10 points for each.   The 9 filled circles are judged to be outliers, by comparison with other data for the sites in question.   The 1:1 line is shown.

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