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5                   **Dissolved organic carbon in soil solutions:  
                          a comparison of collection methods**

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**ABSTRACT**

35 A field study was undertaken to compare the DOC concentrations in soil  
solutions obtained with three different sampling methods over a range of soil types.  
The sampling devices were a tension-free collector, a tension Prenart collector and a  
tension Rhizon collector. Samples were collected fortnightly for a year at seven sites  
in northern England, each collection being replicated three times. The soil solution  
DOC ranged from 1.3 gm<sup>-3</sup> in an acid ranker to 34.7 gm<sup>-3</sup> in a peat. The DOC  
40 concentrations obtained with the three methods were reasonably well correlated ( $r^2$  of  
0.6 to 0.8) but with an indication of bias, as the best fit line differed from the 1:1 line.  
The tension-free collector gave generally higher DOC concentrations except at very  
low concentrations (in the acid ranker soil). The DOC concentrations measured with  
the tension-free collectors were significantly ( $p < 0.05$ ) higher those obtained with  
45 Prenart and Rhizon collectors at four and six sites, out of seven, respectively.  
Subsequent laboratory tests on tension-free collected samples showed no DOC loss on  
filtration through 0.1 and 0.22- $\mu$ m membranes, whereas a significant loss of DOC  
occurred when tension-free collected samples were subsequently passed through  
Prenart and Rhizon collectors, indicating a probable sampling artefact with the tension  
50 devices. The difficulties of acquiring representative soil solution samples are  
discussed, together with the advantages and disadvantages of tension and tension-free  
methods.

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## INTRODUCTION

The soil solution can be defined as the aqueous liquid phase of the soil and its solutes (Tiensing *et al* 2001). The extraction and analysis of soil water is often used  
70 to determine a range of factors within the soil. Monitoring soil solution is an integrative step towards advancing our knowledge and understanding of soil systems. The methods commonly used to obtain soil solution are based on the principles of pressure, vacuum, displacement and centrifugation (Tiensing *et al.* 2001). The extraction of soil solution by displacement, centrifugation and the installation of  
75 lysimeters (with and without tension applied) are described by Hendershot and Courchesne (1991). The sampling devices are variously referred to as samplers, lysimeters and collectors. Each of the different sampling methods available has advantages and disadvantages with regard to possible contamination, efficiency in different soil types, cost, adsorptive losses of solutes and ease of use (Reynolds *et al*  
80 2004). Successful water sampling devices should collect sufficient amounts of soil water for the purposes of the study, with minimal change to chemical and biological properties of the water (Krejzl *et al* 1994).

Previous comparisons of the sampling methods have shown diverse and sometimes conflicting results for inorganic constituents. Reynolds *et al.* (2004)  
85 compared tension and zero-tension lysimeters in peat, and found broad similarities between the solute concentrations measured by the two collector types. In contrast Haines *et al* (1982) found that zero-tension collectors gave significantly lower  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cl}^-$  concentrations at the litter-soil interface, compared to tension devices, whereas at 30cm depth zero-tension collectors gave significantly higher  
90 concentrations of  $\text{NH}_4^+$   $\text{K}^+$   $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and significantly less silica than tension devices. Hendershot and Courchesne (1991) found no consistent differences when comparing tension and tension-free collectors, except for significantly lower  $\text{NO}_3^-$  concentrations with the tension-free devices.

Conflicting results have also been reported for collectors of the same type,  
95 especially with tension collectors constructed from different materials. Some materials have been found to dissolve slowly or alter the soil solution, by either adsorption of compounds or the release of substances from the cup material (Andersen *et al* 2002). Hansen and Harris (1975) used ceramic cups to collect soil

solutions and found that nitrate and phosphate concentrations were not consistent,  
100 displaying substantial bias and variability due to leaching, diffusion, sorption and  
screening by the ceramic cup walls. Conversely, Levin and Jackson (1977) reported  
consistent Ca, Mg and PO<sub>4</sub>-P concentrations sampled by ceramic cups, although they  
did speculate about a possible partial uptake of NO<sub>3</sub><sup>-</sup>. Polysulfone Rhizon collectors  
may retain colloidal iron as the fibres have relative low molecular-weight rejection  
105 level (Reynolds *et al* 2004).

Similar variability appears to occur in the concentrations of dissolved organic  
carbon (DOC) obtained using the various soil-solution collectors, although far fewer  
field based comparisons have been undertaken. DOC is a product of organic matter  
decomposition in soils and is operationally defined as the organic carbon passing  
110 through a filter of 0.45µm pore size. It consists of a wide range of molecules, ranging  
from simple acids and sugars to complex humic substances with large molecular  
weights (Moore 1998). Understanding the dynamics of DOC in terrestrial  
environments is important as it is involved in many biogeochemical processes. In a  
previous field based comparison, Reynolds *et al* (2005) found a twofold difference in  
115 the DOC concentrations between a zero-tension device (23.3 g m<sup>-3</sup> DOC) and a  
tension PTFE collector (45 g m<sup>-3</sup> DOC). On reviewing the literature, Neff and Asner  
(2001) concluded that different sampling procedures may yield different DOC  
concentrations in soil solutions.

Thus there is considerable uncertainty concerning the effectiveness and  
120 reliability of soil-solution collectors, especially for DOC. While previous field-based  
comparisons have been made, the scope of such studies has been limited with respect  
to soil types, replication and numbers of samples. In addition to the inherent  
differences in the nature of the collectors, the reported differences in the field  
observations may be linked to soil heterogeneity and the positioning of the collectors.  
125 It is necessary to be aware of the various problems and errors involved in sampling  
soil solutions in order to obtain environmentally representative data.

This paper presents the results of a field-based programme where DOC  
concentrations were monitored using replicated multiple collection methods in the  
topsoil over a range of soil types. The work is part of a wider project that is studying  
130 the factors controlling DOC fluxes in topsoils. The aims of this study were to  
determine:

(a) the performance of different collector types in obtaining a sample for subsequent DOC analysis.

135 (b) the extent to which DOC concentrations can vary with the use of different sampling methods, both locally within a soil and across a variety of soils with different DOC concentrations.

Three commonly used in-situ collectors were chosen for the study, namely a tension-free device and two contrasting tension collectors (Prenart and Rhizon). These are the same three collectors that were used by Reynolds *et al* (2004), allowing  
140 direct comparisons to be made between the two field studies.

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## **METHODS**

Soil solution collectors were deployed for one year at seven sites, having a range of soil and vegetation characteristics (Table 1). Each of the three collector types was deployed in triplicate and samples collected on a fortnightly basis. The  
165 nine collectors were randomly distributed at each site and the soil and organic horizon depths determined. To insert the collectors, small pits were excavated with care in the topsoils.

The tension-free collectors were constructed from PVC guttering and assembled using PVC conduit solvent cement. They had dimensions of  $7 \times 10 \times 5$  cm  
170 and a spigot to which tubing could be connected for water collection. The depth at which the collectors were positioned depended on the soil type (Table 1 and 2). For the ranker at Doe House Gill, they were placed near to the base of the fine soil, at a standard depth of 15cm. This was also the case for the mineral soils at Mask Hill, Cowdale Slack and Meathop Wood 1, and at a slightly shallower depth at Meathop  
175 Wood 2 because of the presence of large stones. At Ravenstonedale Common they were placed at the base of the organic layer, and in the peat at Moor House a depth of 10cm was chosen to represent a typical acrotelm depth. Each device was connected to a 1-litre bottle, buried at a lower depth to allow soil water to move freely.

Prenart soil-solution collectors (Prenart Equipment Aps, Denmark) are made  
180 of porous polytetrafluorethene (PTFE Teflon) and have a pore size of  $2 \mu\text{m}$ . The manufacturers state that they are robust and chemically inert. These collectors were installed horizontally at the midpoint between the soil surface and the depth of the tension-free collector (Table 2) and connected to a 1-litre collection bottle. For Prenart and tension-free collectors the pits were carefully backfilled with soil, with the  
185 bottles buried and retrieval tubes protruding from the soil. Tension was applied to the Prenart bottle by using a battery operated pump to 600mbar

The Rhizon collectors (Van Walt Ltd, UK) comprise a  $10 \times 0.25$  cm porous polymer tube, connected to a 10cm length of PVC tubing fitted to a luer-lock connector. The pore size of the porous polymer is  $0.15 \mu\text{m}$ . Each Rhizon collector  
190 was placed horizontally at the midpoint between the soil surface and the depth of the tension-free collector (Table 2) and connected to a  $20 \text{ cm}^3$  syringe, which was placed in a small buried plastic box that was readily accessible. Tension for the Rhizon collectors was achieved through drawing out the connected syringe and wedging it open with wooden sticks.

195 The water samples in the Prenart and tension-free collector bottles were removed in-situ by means of a battery operated pump, thus ensuring minimal disturbance to the collector and soil. The Prenarts were re-evacuated after sample removal. For the Rhizon collector, the syringe was disconnected, emptied into a clean bottle and replaced, with a vacuum being reapplied. The samples from the first  
200 collection were discarded to allow time for the collectors to adjust to the surrounding environment. Following the manufacturer's guidelines, the Rhizon collectors were replaced after six months.

Samples were stored in the laboratory at 5°C and filtered (Whatman GF/F) within 48 hours. The DOC concentration was determined, using a TOC-VCPH Total  
205 Organic Carbon Analyzer, along with the absorbance (340nm) and conductivity (25°C) for each individual sample. Extinction coefficients ( $\text{m}^2 \text{g}^{-1}$ ) at 340 nm were determined from the ratio of absorbance to DOC concentration.

Laboratory tests were undertaken, following the main field deployment, in order to investigate differences in DOC concentrations observed between tension and  
210 tension-free collectors. Raw samples from tension-free collectors were filtered through Whatman GF/F membranes as in the standard procedure, and then separately through 0.22  $\mu\text{m}$  and 0.1  $\mu\text{m}$  membranes. Additionally, Prenart collectors, recovered from the field sites, were cleaned with 0.1 M NaOH and thoroughly rinsed with deionised water before being placed in unfiltered tension-free collected samples in the  
215 laboratory, obtained from six of the field sites. Tension was applied to the Prenart collectors through a 20  $\text{cm}^3$  syringe, attached via PVC tubing. The syringes were pulled back and wedged open to hold the vacuum until each syringe was filled with soil solution. The resulting tension samples were then filtered (Whatman GF/F), as in the standard procedure. The same experiment was also conducted with Rhizon  
220 collectors but using new rather than cleaned devices. The DOC concentrations were determined in all the final test solutions. The finer filters used in the tests are carbon based, and so the "bleed" concentrations (average 0.45  $\text{g m}^{-3}$ ) were determined, and the DOC concentrations corrected.

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## RESULTS

The main results of the study are summarized in Table 2. To assess overall collector reliability, the total possible number of samples and the actual number of samples collected (classified as successes) were calculated. The maximum possible number of samples was 504 from each method, resulting in a total of 1176 samples. However the Rhizon samples were pooled due to the small volumes collected, resulting in a potential of 168 samples to be collected from 24 fortnightly visits. It can be seen from Table 2 that, with the exception of the Meathop Wood 2 site, the tension-free and Rhizon collectors were consistently more reliable in providing a sample for analysis, with success rates of between 32-76% and 8-88%, respectively. Prenart collectors performed relatively poorly, with success rates of 10 to 53%. All three collectors were generally less reliable in producing samples in Meathop Wood 2, compared to the other sites.

Mean annual averages from the three collectors were calculated using all available data, irrespective of success rates (Table 2). The average DOC concentrations for each site showed large differences, ranging from 1.3 g m<sup>-3</sup> at Doe House Gill (Prenart collector) to 34.7 g m<sup>-3</sup> at Moor House (tension-free collector). It is also clear from Table 2 that the average values differed between collector type. Overall, the means showed a trend of consistently higher DOC concentration from the tension-free collectors in comparison to those with tension applied. Some sites showed a wider range in DOC concentrations between collector types in comparison to other sites, in particular Cowdale Slack and Meathop Wood 2. Statistical comparisons of the data using the t-test showed that the tension-free collector concentrations were significantly ( $p < 0.05$ ) higher than the values from the Prenart and Rhizon collectors at four and six sites, respectively (Table 2). Only in two cases (Doe House Gill and Cowdale Slack) were there differences between the results from the Prenart and Rhizon collectors, and then in different directions.

Fig. 1 provides a more detailed comparison of the mean fortnightly DOC concentrations obtained by the three collector types. Here, the collectors were paired for comparison, i.e. the data points refer to successful collections from pairs of collector types. The measured concentrations were generally well correlated, with  $r^2$  values ranging from 0.6 to 0.8, but with an indication of bias as the best fit lines differ from the 1:1 line. The tension-free collectors have consistently higher DOC concentrations than the two tension-based collectors, except at very low values (Doe

House Gill site). The two tension collectors gave similar concentrations, reflected in the best-fit line lying closer to 1:1 (Fig. 1). Considerable variability is apparent in the concentrations measured at each site, which is also reflected in the annual standard deviations given in Table 2.

Concentrations of DOC were normalised by dividing mean values for each sampling period by the overall mean, for each collector type (Fig. 2). This revealed seasonal variations, with higher values in the summer and lower ones in the winter. The trend is clearest for the tension-free collector data. These results probably reflect either the temperature dependence of DOC production and / or greater evaporative concentration during the warmer period (Tipping et al., 2007).

The extinction coefficient provides a simple measure of DOC quality. The observed coefficients, along with paired t-tests between collector types, show little evidence of any consistent variation, either between sites or between collector types (Table 3). In only two cases were the extinction coefficients for tension-free collectors significantly different to Prenart collectors, and once for tension-free against Rhizon collectors. There was no significant difference between Prenart and Rhizon collector samples. The conductivity data also showed no evidence of significant differences between collector types, suggesting that the major ion contents of the soil solutions were not greatly dependent upon the sampling method.

The results of the laboratory tests to assess possible sampling artefacts are shown in Table 4 and Fig 3. The tension-free collector solution that was subsequently drawn through Rhizon and Prenart collectors produced the same trend as was observed in the field (Table 4). Compared to the initial tension-free collector solution, the DOC concentration was lower in the solution from the Rhizon collector and lower still in the Prenart collector solution, indicating DOC removal or rejection by the tension devices. However, the test involving additional filtration of tension-free collector solution through fine membranes showed no notable difference in the DOC concentration (Fig. 3), indicating that the loss of DOC is due to a mechanism other than simple filtration.

## **DISCUSSION**

This study has shown that there were significant differences in DOC concentrations from the use of the three different sampling methods. Concentrations of DOC obtained with the tension-free collector were significantly higher than those with the tension collectors at the majority of the sites monitored. The differences between collector types were evident whether all available data were used, or just pairs where there were missing data, showing that differences amongst collectors are not simply due to the ability of tension-free and Rhizon collectors to sample water, when the Prenart collector does not. In addition to the concentration differences and the variable degree of seasonality obtained with the three sampling methods, there also appeared to be a random scatter in the DOC concentrations at each site (Fig. 1). The most likely reasons are soil heterogeneity and variability in the performance of each collector type. Clearly the diverse sources of variability in DOC pose some problems in obtaining representative field concentrations. Despite being able to account for some of the observed variability, it is uncertain which factor has the most influence upon the results as soil heterogeneity and collector performance cannot be separately quantified. Neff and Asner (2001) similarly concluded that different collection methods are likely to affect DOC concentrations and flux estimates, and that it is difficult to assess these impacts separately from the underlying variation, resulting from soil and vegetation differences. It is evident that a large quantity of field data is required in order to identify trends and to average out the various types of variability observed.

The following factors might contribute to the higher DOC concentrations obtained with the tension-free collector.

(1) The laboratory tests, run subsequently to the field deployments, showed that some direct loss of DOC occurs with the tension collectors (Table 4). It seems unlikely that this is due simply to filtration, because when solutions collected with tension-free lysimeters are passed through 0.1 or 0.22  $\mu\text{m}$  pore size filters, no significant loss occurs (Fig. 3). The losses of DOC observed with the tension lysimeters may be due to sorption effects (Grossmann and Udluft, 1991), for example linked to electric charge or hydrophobicity. In order to minimise interaction with the soil solution, tension devices are generally constructed from inert materials, such as nylon, polyethylene or polytetrafluorethene (PTFE). An additional filtration effect on DOC

330 may also occur under field conditions due to the compaction of soil surrounding the tension collectors, resulting from the installation and/or the applied vacuum.

(2) The DOC concentration naturally varies with soil depth due to variations in pedological conditions, especially between the organic and mineral layers (Michalzik *et al* 2003, Kalbitz and Park 2000) . The vacuum applied to a tension collector  
335 inevitably creates a sphere of influence and consequently soil water can be drawn from both above and below the collector. It is possible that when placing tension collectors close to or at the base of the organic layer (for non-peat sites) soil water is sampled from the underlying mineral material. The tension-free collectors sample water that has passed through the material above, providing more certainty concerning  
340 the source of the soil water collected. In the present study an effort was made to circumvent this issue, by placing the tension-free device at the base of the topsoil and the tension devices at its midpoint.

(3) Water is held at different tensions in a soil, according mainly to its physical characteristics (e.g. pore sizes) and their spatial distribution, described by Warrick  
345 (2002). The sampled water will therefore depend not only on the distribution of water under different tensions, but also on the tension applied to the collector, and on the variation in the soil moisture content over the sampling period. Liator (1988) suggested that having a continuous vacuum applied can increase the variability of leachate volume, especially within soil horizons having different tensions and flow  
350 patterns. Applying tension to a sampler will therefore extract water (and DOC) from different sized soil pores. It is more likely that tension-free collectors sample larger pores, which wet and dry more often with more oxygen and therefore microbial activity and possibly DOC production. Tension samplers can draw water from smaller pores which remain water filled which may not contain as much DOC.  
355 Increasing the tension can lead to water being extracted from smaller soil pores described by Marshall and Holmes (1988). Tension collectors therefore collect a mixture of soil water from small and large pores leading to a possible dilution effect from the small pore water and so less DOC. In this study there was no evidence of the collectors extracting significantly different dissolved organic matter, as judged by  
360 the similar extinction coefficients (Table 3)

(4) The time period over which the applied vacuum is dissipated, and hence the sample collected, in the tension devices is unknown. The Rhizon collectors are assumed to fill relatively quickly from observations in the field, possibly within 24

hours, and hence the associated samples are probably closer to a point sample than a  
365 fortnightly average. The Prenart collectors filled more slowly, seen in the laboratory  
filtration experiment, possibly collecting over the entire 2-week deployment in the  
field. The tension collectors may therefore sample over different hydrological events  
to each other, and to the tension-free device. Although the timing of sampling is  
likely to vary with collector type, it is more difficult to see how this would produce a  
370 systematic difference in DOC concentration.

In contrast to our findings, Reynolds *et al* (2004) found that Prenart collectors  
gave higher DOC concentration than tension-free devices in peat soil. In both studies,  
tension-free collectors were placed at 10cm depth. However Reynolds *et al* (2004)  
placed the tension collectors at 10cm depth, whereas in the present study they were  
375 installed at the topsoil midpoint (5cm). There may be larger stores of DOC in the  
deeper, more humified material of the peat (and in other soils), causing higher DOC  
concentrations to be sampled with the tension collectors deployed at greater depth,  
especially due to their extended downward sphere of influence. Another difference  
between the two studies is in the orientation of deployment. Tension collectors in the  
380 present study were installed horizontally, whereas Reynolds *et al* (2004) inserted the  
tension Prenart collectors vertically. If the DOC concentration varies with depth, then  
the vertical deployment may also have contributed to the higher DOC concentrations  
found by Reynolds *et al* (2004) with the tension collectors. Alternatively, the  
difference in results found between the two studies may be due to site-specific or  
385 collector-specific characteristics, which may preclude generalising about how  
collector type influences the measured DOC concentration. The study by Reynolds *et al*  
(2004) was based on a single peat site therefore how representative these results are  
on a wider scale is questionable.

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## **CONCLUSIONS**

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The study has shown that DOC concentrations in soil solutions were significantly higher with tension-free collectors than with tension devices at six out of seven sites. The most likely explanation for the lower concentrations obtained with the tension devices are artefacts, associated with sorptive removal of DOC by the collector or with localised soil compaction induced by the applied vacuum, as well as the influence of tension upon the source of soil water from different pores. It is concluded that tension-free collectors are more likely to be representative of free flowing water through the organic horizon, which is key to representing DOC fluxes through topsoils. Other advantages of tension-free collectors are that they can be custom-made to suit the project requirements, they can provide a larger volume of soil water, and in this study were successful more frequently. Our results raise several issues concerning the DOC concentrations obtained with different collectors over a broad range of soil types. In many studies only one collection method is used, therefore hampering comparisons with the results of studies based on a different sampling method.

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Table 1. General characteristics of the sampling sites.

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<b>Site name</b>	<b>Longitude / Latitude</b>	<b>Altitude (m)</b>	<b>Soil Type</b>	<b>Vegetation Type</b>
Doe House Gill	54° 24 N 3° 9W	1172	acid ranker	grassland
Mask Hill	54° 27N 2° 29W	987	cambic stagnohumic gley	moorland
Cowdale Slack	54° 29N 2° 29W	1148	typical brown earth	grassland
Meathop Wood 1	54° 13N 2° 52W	42	brown earth	deciduous woodland
Meathop Wood 2	54° 13N 2° 52W	42	calcareous brown earth	deciduous woodland
Ravenstonedale Common	54° 24N 2° 26W	1331	ferric stagnopodzol	grassland
Moor House	54° 41N 2° 23W	1893	peat	moorland

Table 2. Summary of the sampling results.

	Collector <sup>1</sup>	Sampling depth, cm	No. of samples	Success %	[DOC] g m <sup>-3</sup>			Sig. diffs. <sup>2</sup>
					mean	SD	RSD %	
Doe House Gill	TFC	20	54	75	2.0	1.1	54	<i>a,b,c</i>
	PC	8	37	51	1.3	0.6	47	
	RC	9	15	63	3.3	1.8	55	
Mask Hill	TFC	15	52	72	11.7	4.0	34	<i>b</i>
	PC	7.5	38	53	9.8	12.3	126	
	RC	7.5	21	88	7.3	2.6	36	
Cowdale Slack	TFC	15	50	69	13.4	7.2	54	<i>a,b,c</i>
	PC	7.5	23	32	6.4	2.1	33	
	RC	7.5	18	75	4.8	0.8	17	
Meathop Wood 1	TFC	15	45	63	15.2	4.8	32	<i>b</i>
	PC	7.5	23	32	13.6	6.3	46	
	RC	7.5	7	29	11.6	3.1	27	
Meathop Wood 2	TFC	12	23	32	21.1	9.4	45	<i>a</i>
	PC	7.5	12	17	8.3	1.8	22	
	RC	7.5	2	8	10.2	0.0	0	
Ravenstonedale Common	TFC	15	55	76	25.1	6.8	27	<i>a,b</i>
	PC	7	25	35	17.8	4.8	27	
	RC	7.5	20	83	17.0	5.1	30	
Moor House	TFC	10	48	67	34.7	11.1	32	<i>b</i>
	PC	5	7	10	30.7	8.5	28	
	RC	5	16	67	25.7	5.6	22	

<sup>1</sup> TFC tension-free collector, PC Prenart collector, RC Rhizon collector.<sup>2</sup> Differences between means ( $p < 0.05$ ); *a* TFC  $\neq$  PC, *b* TFC  $\neq$  RC, *c* PC  $\neq$  RC

Table 3. Mean extinction coefficients ( $\text{m}^2 \text{g}^{-1}$ ) at 340 nm for each collector type, with standard deviations in brackets. The final column indicates where differences were significant at the 5% level; *a* TFC  $\neq$  PC, *b* TFC  $\neq$  RC, *c* PC  $\neq$  RC

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Site	TFC	PC	RC	differences
Doe House Gill	1.0 (0.5)	0.9 (0.6)	0.8 (0.4)	
Mask Hill	1.3 (0.7)	0.8 (0.4)	0.8 (0.3)	<i>a,b</i>
Cowdale Slack	0.9 (0.4)	1.2 (2.1)	0.7 (0.6)	
Meathop Wood 1	0.9 (0.4)	0.5 (0.2)	0.7 (0.5)	<i>a</i>
Meathop Wood 2	1.1 (0.6)	0.8 (0.7)	0.4 (0.1)	
Ravenstonedale Common	1.1 (0.5)	1.5 (1.1)	1.0 (0.4)	
Moor House	1.3 (0.8)	1.8 (0.6)	1.5 (0.7)	

520 Table 4. Laboratory collector test results. Average DOC concentrations ( $\text{g m}^{-3}$ ) are shown for solutions collected with tension-free collectors (TFC), and then subsequently drawn through Rhizon collectors (RC) or Prenart collectors (PC). Values in brackets are standard deviations of triplicate determinations.

Site	TFC	RC	PC
Mask Hill	12.7 (0.1)	11.0 (0.6)	9.1 (0.9)
Cowdale Slack	22.2 (0.1)	19.2 (0.6)	14.3 (2.2)
Meathop Wood 1	21.1 (0.1)	20.3 (0.2)	16.6 (0.6)
Meathop Wood 2	25.6 (0.1)	24.0 (0.9)	19.8 (1.1)
Ravenstonedale Common	22.9 (0.5)	16.0 (1.2)	13.7 (1.3)
Moor House	30.1 (0.2)	19.5 (1.0)	20.7 (0.4)

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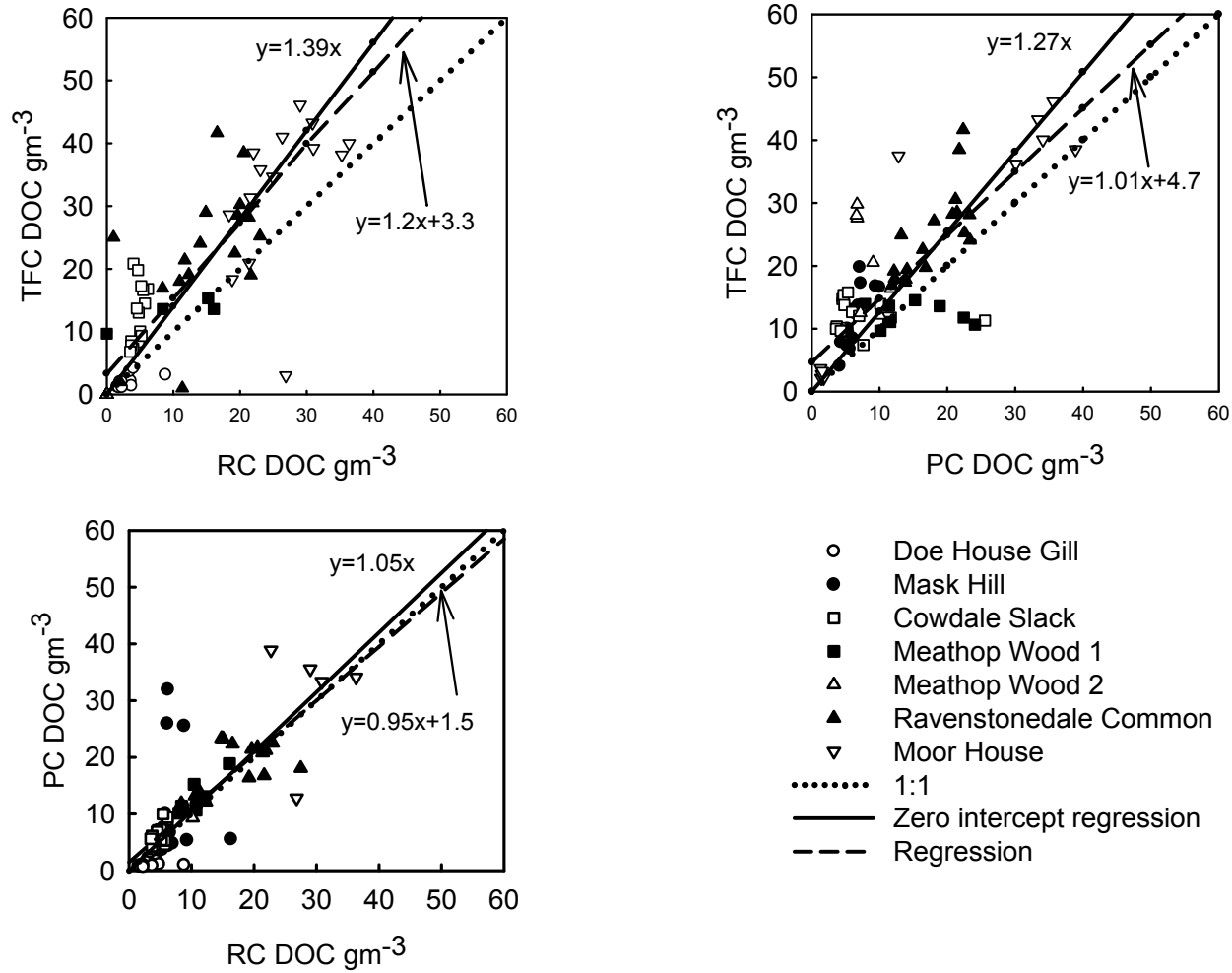
### **LEGENDS TO FIGURES**

530 Figure 1. A comparison of the fortnightly mean DOC concentrations between  
collectors, for occasions when at least one of the triplicated deployments was  
successful for each collector.

Figure 2. Seasonal variations in the ratio of fortnightly DOC concentration to the  
535 overall mean concentration, for all sites. The dotted line provides a reference. For  
key to symbols, see Fig. 1.

Figure 3. Comparison of DOC concentrations in samples that had been filtered with a  
GF/F filter only (x-axis) and then subsequently with a 0.22 $\mu$ m membrane. The  
540 regression line with a forced intercept of zero is shown..

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550 Figure 1

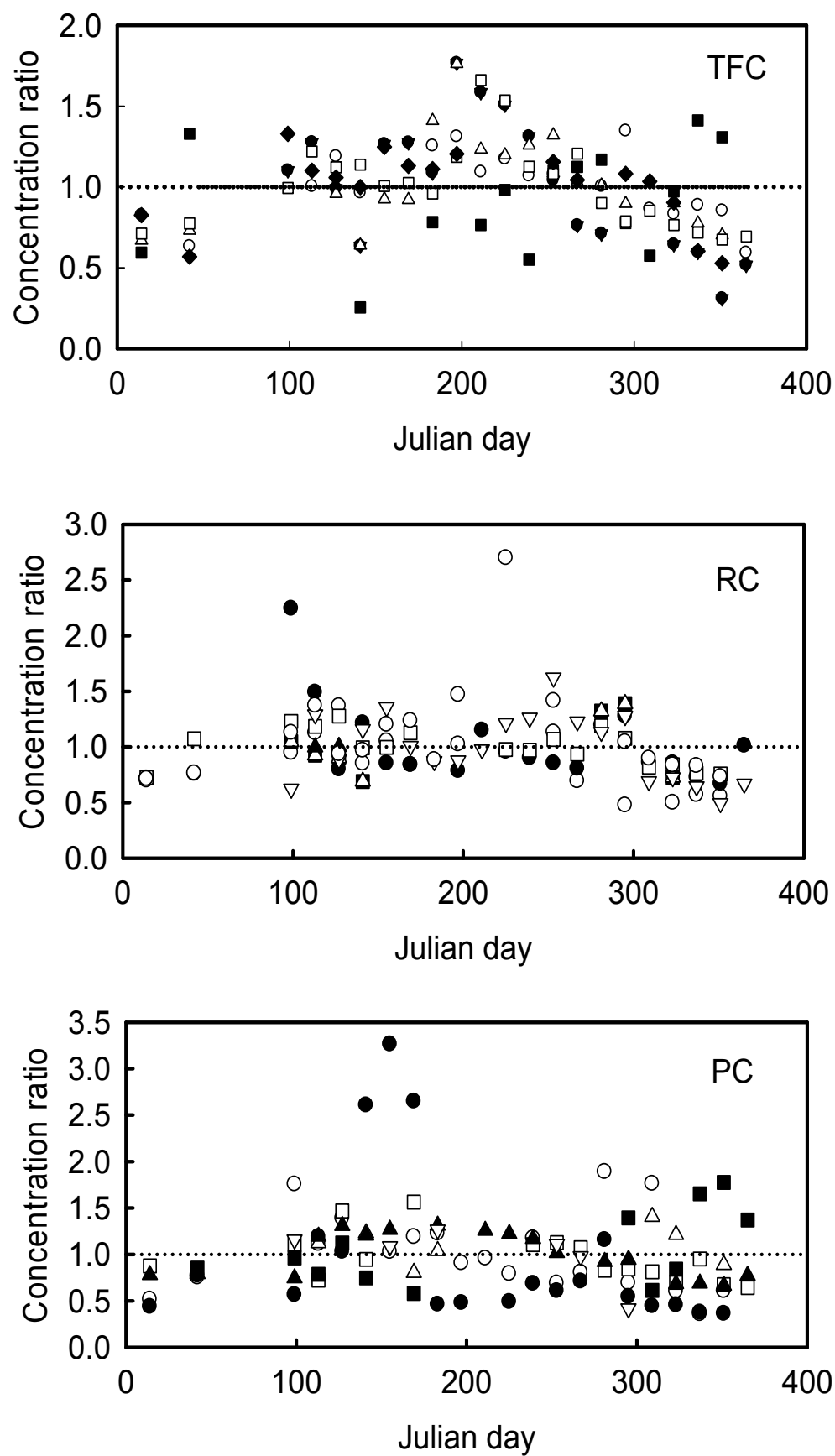
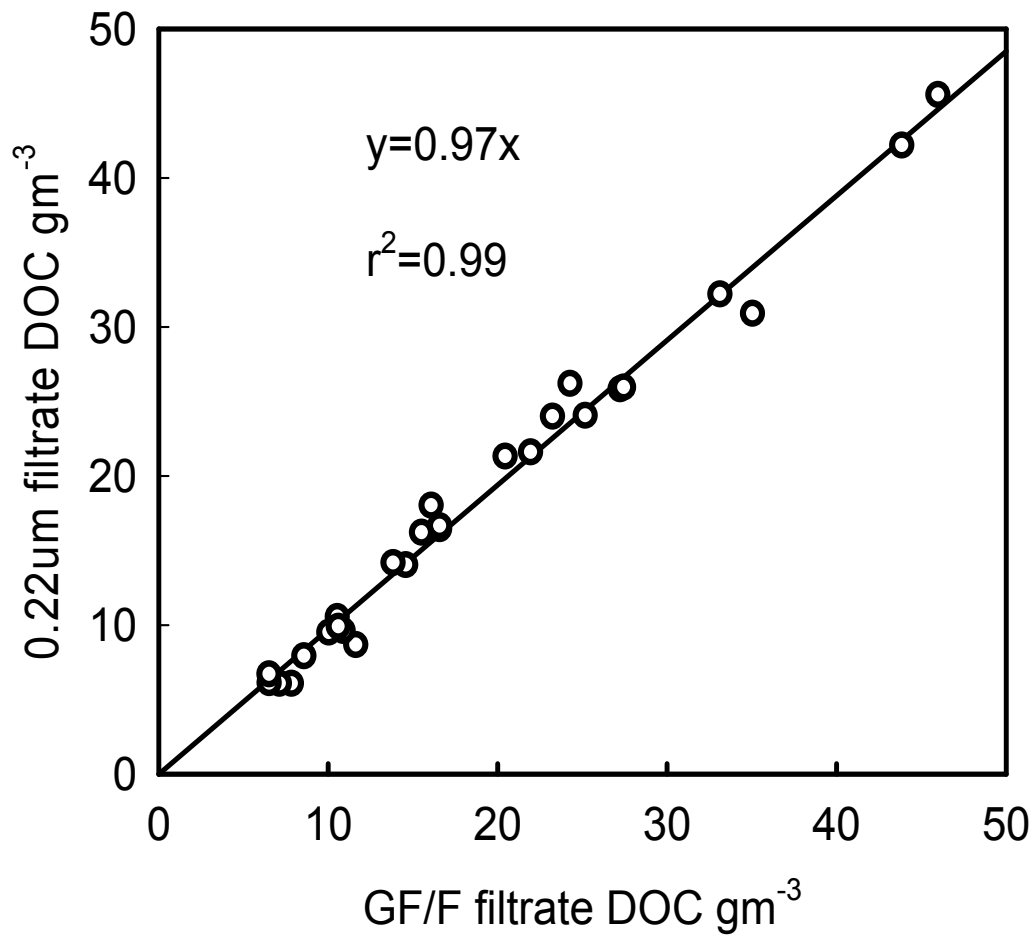


Figure 2





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Figure 3

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