Project no. **GOCE-CT-2003-505540**

Project acronym: **Euro-limpacs**

Project full name: **Integrated Project to evaluate the Impacts of Global Change on European Freshwater Ecosystems**

Instrument type: **Integrated Project**

Priority name: **Sustainable Development**

Deliverable No. 10
Report on DOC quantity and quality data collected at the Clocaenog climate manipulation experiment, Wales (Task 5.1)

Due date of deliverable: **31 January 2005**
Actual submission date: **31 January 2005**

Start date of project: **1 February 2002** Duration: **5 Years**

Organisation name of lead contractor for this deliverable: **NERC**

Version 1

Project co-funded by the European Commission within the Sixth Framework Programme (2002-2006)		
Dissemination Level (tick appropriate box)		
PU	Public	
PP	Restricted to other programme participants (including the Commission Services)	✓
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Report on DOC quantity and quality data collected at the Clocaenog climate manipulation experiment, Wales

Chris D. Evans

Centre for Ecology and Hydrology, Deiniol Rd, Bangor, LL57 2UP, United Kingdom

Introduction and background

This report provides an interim summary of results from a plot-scale manipulation experiment, which is being used to assess the potential impact of climate change on the release of dissolved organic carbon (DOC) from soils to surface waters. Surface water DOC concentrations have undergone dramatic increases since the 1980s, most clearly in the 22 lakes and streams of the UK Acid Waters Monitoring Network (Freeman et al., 2001a; Evans et al., in press) but also in other UK upland waters (Worrall et al., in press), and other areas of Europe and North America (Stoddard et al., 2003; Skjelkvåle et al., in press). The potential implications of rising DOC are wide-ranging, from local ecosystem impacts on freshwater acidity, light regime and energy supply, through increased water treatment costs and health risks, to issues relating to increased fluxes of carbon and heavy metals from terrestrial stores into more reactive, mobile aquatic reservoirs. At present, there is no consensus on the likely drivers of rising DOC concentrations, but a number of processes linked to climate change have been suggested including rising temperatures (e.g. Freeman et al., 2001a); increased soil aeration (e.g. Evans et al., 2002; Worrall et al., 2004); changes in water flowpath due to increased rainfall (e.g. Tranvik and Janssen, 2002) and increases in primary production linked to rising atmospheric CO_2 levels (Freeman et al., 2004). Other proposed drivers are linked to atmospheric deposition, notably to the major reduction in atmospheric S deposition that has occurred since the 1980s, and the recovery from acidification that this has led to in soils and waters. These and other possible drivers of rising DOC have been considered in detail in a recent review supported by Eurolimpacs (Evans et al., in press). It is clearly essential that the main drivers of rising DOC be identified, before their wider significance, and future trajectory, can be established. The experimental work described in this report is intended to assess the validity and significance of two key proposed climatic influences on DOC, rising temperature and increased drought frequency.

Experimental design and previous work at the site

The climate manipulation experiment at Clocaenog, in North Wales, UK, was initiated for the EU Climoor project, to examine the effects of climate change on ecosystem functioning in European heathlands. The site is one of a network of four locations established across Europe for Climoor, which was expanded to six sites in the subsequent EU Vulcan project. Two climate manipulations were applied using a novel system of retractable roofs. Firstly, night-time warming was induced by drawing aluminium insulating roofs across 20 m^2 plots at night, reducing heat-loss from the soil. Droughts were stimulated by drawing transparent polyethylene curtains across adjacent plots during rainfall events in the growing season. Three replicates were established for each of the warming, drought and control plots. The systems used have the advantage that they are non-intrusive, and artefacts associated with the manipulations are therefore minimised. The experimental design is described in detail by Beier et al. (2004). A wide range of physical, biological and chemical measurements have been taken at the sites, and are described in a special issue of Ecosystems (volume 7 (6)); results for Clocaenog are summarised below. Soil solution sampling began in October 1998, prior to the start of experimental manipulations in April

1999, with samples collected bi-weekly and bulked to monthly samples prior to analysis. There was a break in soil water analysis from February 2002 to January 2003.

The Clocaenog experimental site is located at 490m above sea level, in a hilltop location in North Wales (53° 03' N, 3° 28' W). The site has a mean annual air temperature of 8.2 °C and receives around 1700 mm of rain per year. Site vegetation is predominantly *calluna vulgaris*, and soils are humo-ferric podzols, with a thin (5cm) litter and peat layer overlying around 25 cm of mineral soil above Palaeozoic shales. The warming treatments at Clocaenog increased plot air temperature in the first two years by 1.0 °C relative to control plots, and temperature in the top 10cm of soil by 0.7 °C (Beier et al., 2004). The drought treatments reduced water inputs during the growing season by 64%, and by 9% on an annual basis. Annual mean soil moisture content was reduced by 33% during the first two years, and further monitoring suggests that repeated droughts have led to irreversible changes in soil properties within the drought plots, with soil moisture levels failing to return to pre-drought levels during the dormant season (Sowerby et al., in prep.). Vegetation data from Clocaenog for the first two years of manipulation showed a significant 15% increase in total above-ground plant biomass growth in response to warming, and a non-significant 5% reduction in the drought treatment (Peñuelas et al., 2004). Over the same period, increased rates of litter decomposition were observed in the warming treatment, and decreased soil respiration in the drought treatment (Emmett et al., 2004). Variations in respiration rate over time at the control plots do however suggest that respiration rates are highly temperature-sensitive at the site (Q_{10} = 7.0). Schmidt et al. (2004) report a small increase in DOC leaching from the warming plots through to January 2001, with a correlated response of DON. Comparable increases in DOC leaching were not, however found in the less organic soils of the other Climoor study sites.

Measurements for Eurolimpacs

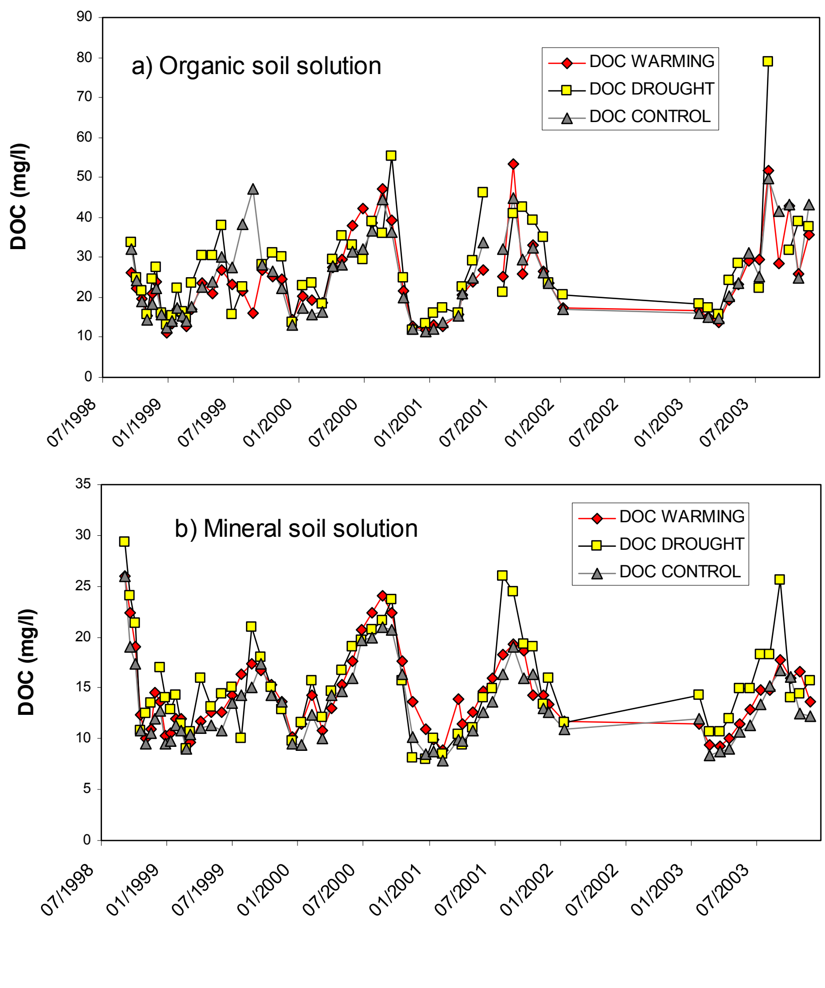
Measurements at the Clocaenog site for the Vulcan project ended in March 2004. Since this time, the experiment has continued with support from Eurolimpacs, in order to examine the effects of climate change on DOC. To maintain continuity, the drought and warming manipulation treatments have continued to operate as they did under Vulcan, with year-round night-time warming and summer drought. A range of meteorological measurements at the site, including ambient temperature, rainfall, wind speed, and air temperature, soil temperature and soil moisture within each experimental plot, have been maintained, while some vegetation and soil measurements are no longer funded and have been discontinued. The key measurements being made for Eurolimpacs are of DOC concentrations in the soil solution, within both the organic and mineral horizons. Samples are collected two-weekly, and bulked up to monthly composite samples for DOC analysis, consistent with previous measurements at the site. In addition, since June 2004, individual two-weekly samples have been analysed for absorbance at three wavelengths; 254 nm, 340 nm and 440 nm. Absorbance, i.e water colour, is strongly related to DOC concentration, in particular to the level of coloured humic substances with the DOM. The ratio of absorbance at 254nm to DOC is considered to provide an indicator of the level of recalcitrant, aromatic compounds within the DOM (Leenheer and Croué, 2003). Finally, a PhD studentship has been established to examine the effects of field climate manipulations on the enzymes (in particular the key phenol oxidase enzyme) that generate DOC from soil organic matter. Phenolic content of soil solution DOC will also be measured; phenolic compounds are refractory, and may inhibit further breakdown of DOC by extra-cellular enzymes (Freeman et al., 2001a). These measurements will begin in January 2005, and should aid understanding of the biological processes controlling DOC production.

Current status and results

At present, DOC data are available from the outset of the experiment in 1998 through to the end of 2003. Analytical results from 2004 are not yet available; nevertheless the current dataset collected over five years of climate manipulation allows a preliminary assessment of DOC response to climate changes to be undertaken.

Absolute DOC concentrations in the control, warming and drought plots are shown in Figure 1. These data show the seasonal nature of DOC variation, and suggest that neither warming nor drought treatments have fundamentally affected this seasonal pattern. Concentrations are consistently lower in the mineral soil for all plots. Differences between each of the treatments and the controls are shown in Figure 2, and mean data for each full year of sampling in Figure 3. Note that 1999 includes 8 samples collected before climate manipulations began, and 8 samples collected subsequently. Unfortunately a full year of pre-treatment data were not collected, and the earliest pre-treatment samples (in autumn 1998) may have been affected by sampler installation, and are not therefore considered here.

Figure 1. DOC concentrations (mean of 3 replicates) in warming, drought and control plots



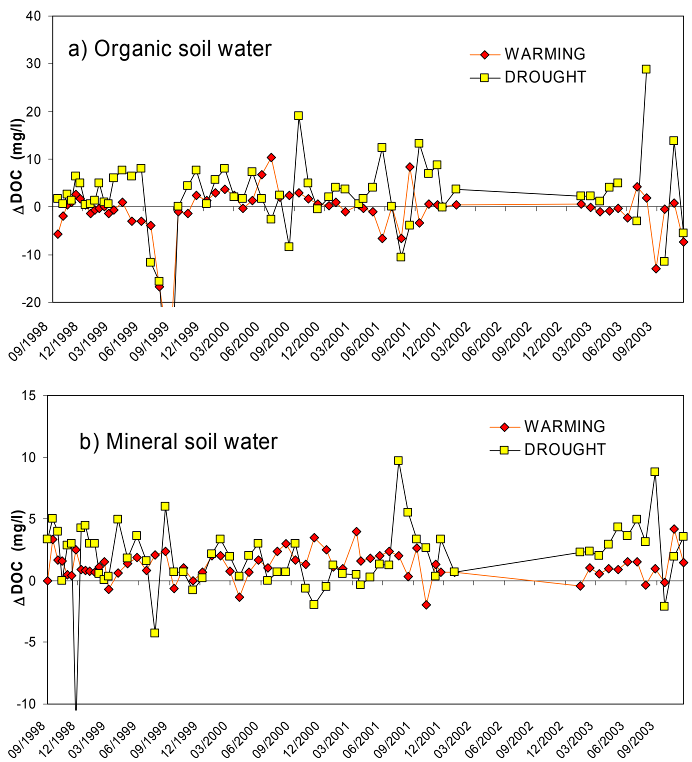
Warming treatment, organic soil solutions

DOC concentrations in the warming plots generally track those in the control plots, apart from a brief divergence in August and September 1999; these datapoints may be anomalous, since conditions were dry and no samples were obtained from several individual plots (both control and warming) in each month. There is little evidence of any longer-term deviation (Figure 2a), and although the annual mean data (Figure 3a,b) show that mean warming-plot concentrations from 2000 to 2003 were markedly higher than in 1999, this appears to be a consequence of the two possibly anomalous 1999 values.

Warming treatment, mineral soil solutions

Mineral layer DOC concentrations in the warming and control plots are closely correlated, both having a fairly stable seasonal cycle with higher concentrations in the summers of 2000 and 2001. There is a small but highly consistent difference between concentrations in the two treatments, with higher concentrations in the warming plots in 42 of 48 samples collected after the start of the manipulation. Unfortunately the short pre-treatment dataset is insufficient to determine whether this is a treatment effect, or simply a reflection of inherent differences between the two sets of plots. There is also some indication of a rising trend in $DOC_{warming}$-$DOC_{control}$ from 1998 through to 2001 (Figure 2b), but the 2003 data suggest that this was not sustained; the same pattern is evident in the annual mean data (Figure 3d).

Figure 2. Treatment minus control DOC concentrations (mean of 3 replicates)



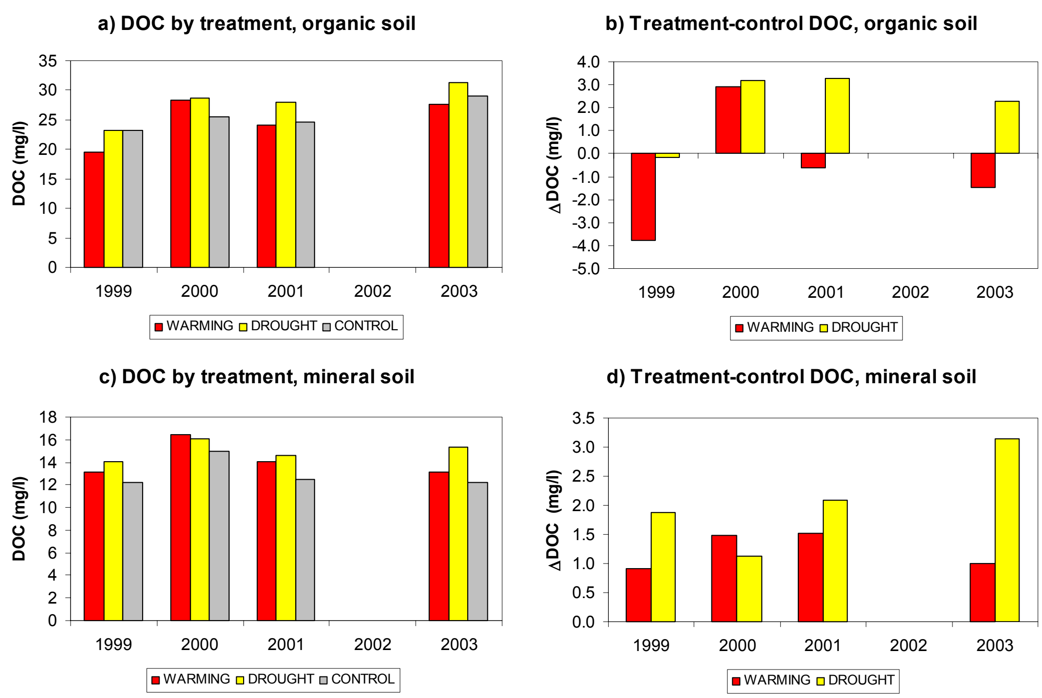
Drought treatment, organic soil solutions

Organic soil solution DOC concentrations are on average somewhat higher than those in either the control or warming plots. There is some suggestion that annual mean concentrations have increased over the study period (Figure 3a), although comparison with the annual means in the control plots is again hampered by the two outlying high-DOC values in 1999 at the control plots. Between 2000 and 2003, the mean difference between drought and control plots has been fairly stable (Figure 3b). It is therefore doubtful whether drought has caused an overall change in DOC concentrations in the organic soil solution. A clear treatment response is however seen over shorter timescales, as DOC levels in the drought plots show significantly greater short-term variability. Several clear 'spiked' in DOC are observed in the drought treatments, during or immediately after the drought periods in 2000, 2001 and 2003 (Figure 1a, Figure 2a). These may represent either elevated concentrations in very low water volumes (e.g. before 'missing values' where no sample was collected in any of the drought plots), or flushing of accumulated DOC as the soil rewets. There are also periods during the droughts where DOC concentrations appear reduced relative to the controls; possible reasons for this are discussed below.

Drought treatment, mineral soil solutions

Mineral soil solution data for the drought treatments show similar patterns to the organic soil solutions: DOC concentrations are on average higher than in the controls, both pre- and post-manipulation, with seemingly elevated short-term variability after the drought manipulation began. Periods of significantly elevated DOC were observed in 2001 and 2003. The most striking feature of the dataset is an apparent upward shift in DOC concentrations relative to the control plots since 2001. By 2003, levels were consistently higher in both the drought period itself, and in the dormant when no manipulation was applied. Consequently, there is an increasing trend in annual mean $DOC_{drought}$-$DOC_{control}$, which suggests that five years of repeated summer drought have been sufficient to generate a real response in DOC concentrations.

Figure 3. Mean DOC concentration by treatment for fully-sampled years



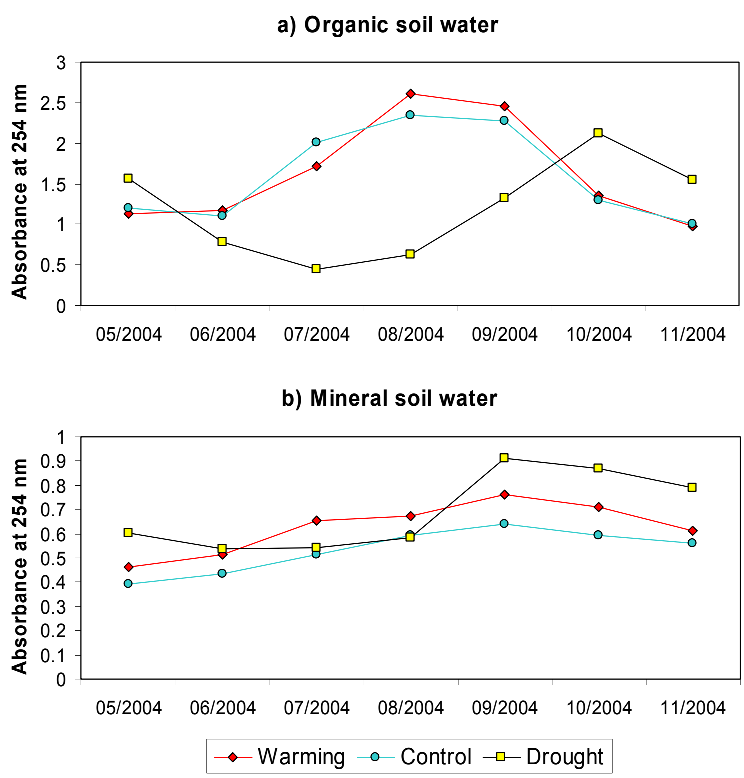
Absorbance data

Absorbance measurements have been made on samples collected from May 2004, covering the 2004 experiment drought period (applied from June 8th to September 1st). Absorbance data at the three wavelengths measured generally show similar patterns, therefore only the 254 nm data are presented here (Figure 4). Note that DOC measurements are not yet available for this period.

Although these data cover only a relatively short period, the patterns observed largely correspond to those observed for DOC over the longer period. Absorbance levels show very similar temporal patterns in the control and warming plots, peaking in late summer. In the organic horizon, absorbance levels in the warming plots appear slightly elevated during this peak, whilst in the mineral horizon, absorbances are consistently higher (on average, 17% above control). As noted for DOC, it is difficult to ascertain whether this represents a response to warming or inherent differences between plots.

Absorbance data for the drought plots show a strikingly different temporal pattern; during the early part of the drought, absorbance at 254 nm in the organic horizon fell to less than half that observed in the warming or control plots. This response is similar for all three individual plots, although only one drought plot yielded a sample at every time interval. Following the cessation of the drought, absorbance levels rose dramatically, exceeding those for the other treatments. A similar, albeit damped, pattern was observed in the mineral soil samples. Over the sampling period, the drought plots had the lowest mean absorbance levels in the organic horizon (25% less than control), but the higher levels in the mineral horizon (30% greater than control). This suggests that (coloured) DOC production in the organic horizon may not be increasing, but that a greater proportion of any DOC produced is reaching the mineral layer.

Figure 4. Soil water absorbance at 254 nm, 2004 data



Discussion

At present, data collected from the Clocaenog manipulation experiment do not show unequivocal evidence of a change in overall DOC production rates as a consequence of either warming or increased drought frequency. There is some indication that the warming treatment *may* have increased DOC (and associated absorbance) levels slightly in the mineral horizon, but it is also possible that the apparently higher levels in the warmed plots are due to existing differences between the two sets of experimental plots. If it were assumed that any differences between plots *did* represent a response to manipulation, this would imply that the (0.6 °C) experimental warming raised mineral soil DOC concentrations by around 10% (2000-2003 means). This is clearly much less than the large (90%) increase in streamwater DOC levels that has accompanied a similar temperature increase in the UK since the late 1980s (Evans et al., in press).

DOC responses to the drought manipulation are more pronounced in terms of altered temporal pattern. Results largely accord with previous observations of reduced DOC concentrations during periods of soil drying, followed by flushing of DOC upon soil rewetting (e.g. Mitchell and McDonald, 1992; Hughes et al., 1998; Tipping et al., 1999). It is possible that this simply reflects the physical entrapment of newly produced DOC in water within hydrologically isolated soil micropores, which is released as the soil matrix re-saturates. However recent work (Clark et al., in press) also suggests that sulphur oxidation in organic soils subject to drying may lead to short-term acidification, and to consequent suppression of DOC solubility over the drought period. In either case, these mechanisms suggest that drought may alter the timing of DOC release, rather than the overall rate of DOC export. The apparent recent increase in average DOC concentrations in the mineral horizons of drought versus control plots is therefore intriguing, in that it may indicate a climate-induced increase in DOC export. Previous work has suggested that soil aeration could increase the activity of the phenol oxidase enzyme (Freeman et al., 2001b), which could in turn contribute to increased DOC generation via decomposition. However the absence of a similar increase in the organic horizon suggests an alternative hypothesis, that drought-induced changes in soil structure, such as increased cracking, could be allowing more rapid infiltration of water to the mineral soil, and hence reduced retention of DOC within the organic horizon. Soil moisture data from the site, showing progressive long-term changes in thr drought treatments (Sowerby et al., in prep.) appear consistent with this hypothesis. Some evidence to support drought as a driver of rising DOC trends is provided by Watts et al. (2001), who noted step increases in water colour following each of a succession of droughts in reservoirs draining peats in Northern England. Data from a wetland manipulation experiment in mid-Wales also showed increased DOC after several years of induced drought (Hughes et al., 1998). However further data for the same site showed that the increase was not sustained, leading Freeman et al. (2004) to specifically discount drought as a driver of rising DOC levels in surface waters. This finding illustrates the importance of maintaining manipulation experiments over extended periods.

Overall, although the data suggest that climate does influence soil water DOC, neither warming nor drought manipulations have yet induced large increases in DOC production. Since the observed changes in surface water DOC have by contrast been dramatic (close to a doubling of concentrations over 15 years at the UK Acid Waters Monitoring Network sites) it seems doubtful on the current evidence whether climate change can be solely responsible for these changes. The most likely alternative drivers of increasing DOC are believed, on the basis of experimental data (Clark et al., in press) and analysis of monitoring data (Evans et al., in prep.) to be changes in the acidity and ionic strength of deposition; the focus of future work will therefore be on quantifying the relative importance of climate- and deposition-related drivers of changes in surface water DOC.

Plans for further work, and contribution to other Eurolimpacs tasks

The main aim of further work under this task will be the continuation of the climate manipulations at Clocaenog, and the extension of the current DOC dataset through to 2007. Absorbance measurements will be continued, and measurements of phenolic content of DOC, and soil enzyme activities, will be initiated shortly. The completed dataset will be analysed using a range of statistical techniques and results reported in a future deliverable. As part of this analysis, an attempt will be made to quantify the effect of climate manipulations on DOC flux as well as concentration.

Estimates of the relationship between soil DOC export and climate change from this experiment (along with other experimental data if relevant) will be used to develop climate-change forecasts of DOC concentrations within the catchment-scale model being developed under Task 5.2, and to inform the INCA-C model being developed in WP6. These relationships will also be used in WP4 to provide input data on organic acid concentrations to drive the site-based climate-change simulations of surface water acidity with the MAGIC model, which will in turn be upscaled to regional/large catchment-scale acidity simulations using the PEARLS model in WP6.

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