Controls on dissolved organic carbon concentration and pH in an acid sensitive forested catchment of Southwest Scotland

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Supplementary Information

SI.1 Maps of forestry cover and soil type within the sample area

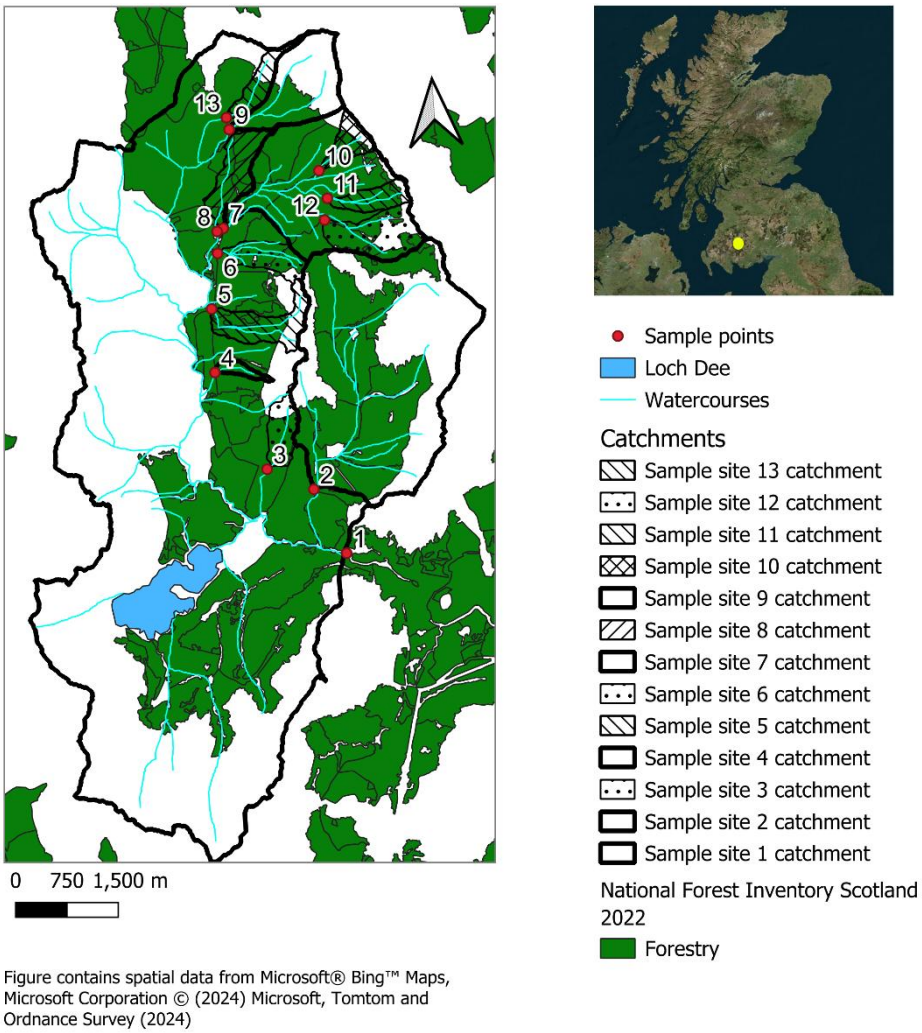

Figure S1. Forestry cover in the sampling area using data from the National Forestry Inventory Scotland 2022. This figure contains information supplied by the Forestry Commission. © Crown copyright and database right 2022 Ordnance Survey [AC0000814847]

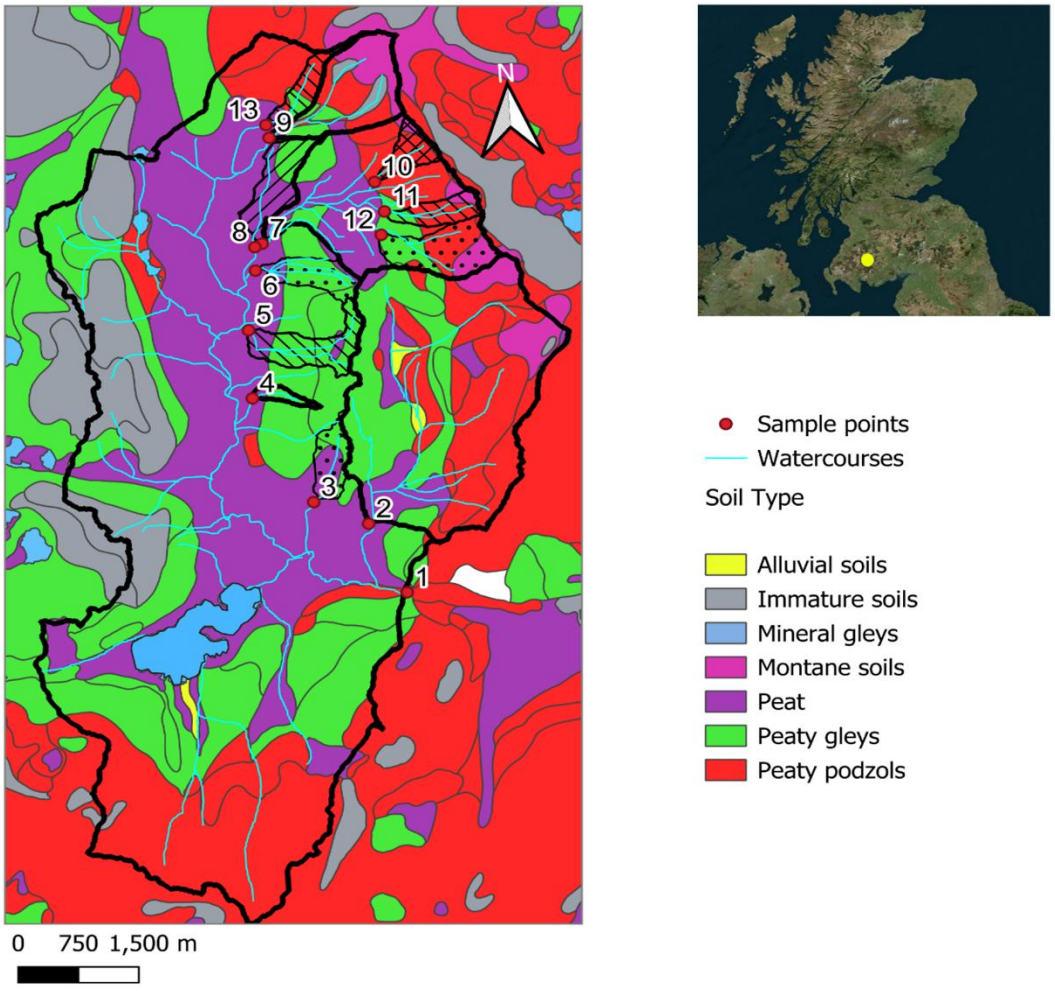

Figure contains spatial data from Microsoft® Bing™ Maps, Microsoft Corporation © (2024) Microsoft, Tomtom and Ordnance Survey (2024)

Figure S2. Map of soil type throughout the sampling area, with soils data from the 1:25,000 partial cover soil map of Scotland (Soil Survey of Scotland Staff, 2021).

The map of forestry cover (figure S1) was prepared in QGIS using data from the National Forestry Inventory Scotland 2022 (Forestry Commission, 2024). Forestry cover is extensive throughout the area sampled, with forestry stands of different ages, from young to mature trees (Forestry and Land Scotland, 2017), some of which were being felled during the sampling period (figure 1 in the main text and SI.2).

The map of soil type (figure S2) presents data from the soil map of Scotland (Soil Survey of Scotland Staff, 2021) and highlights the variability of soils within the sample area. Dystrophic blanket peat, peaty gleys, and peaty podzols are the three most dominant soil types, with alluvial, immature, montane and mineral gley soil types also present.

SI.2 Images of forestry operations

Figure S3. Images showing some of the forestry in the catchment of sample point 5 during the sampling period. These photographs were taken in August 2023.

The images in figure S3 were taken near sample point 5 in August 2023, and show the ongoing forestry operations as described in the Backhill of Bush land management plan (Forestry and Land Scotland, 2017). The operations commenced from around October 2022 for approximately one year, to harvest a section of mature forestry plantation around sample point 5.The images show overland flow of water into a drainage ditch in the peaty soil running adjacent to the gravel track which gives access to the site (n.b. the drainage ditch pictured was not directly connected to a watercourse).

SI.3 DOC quantification quality control

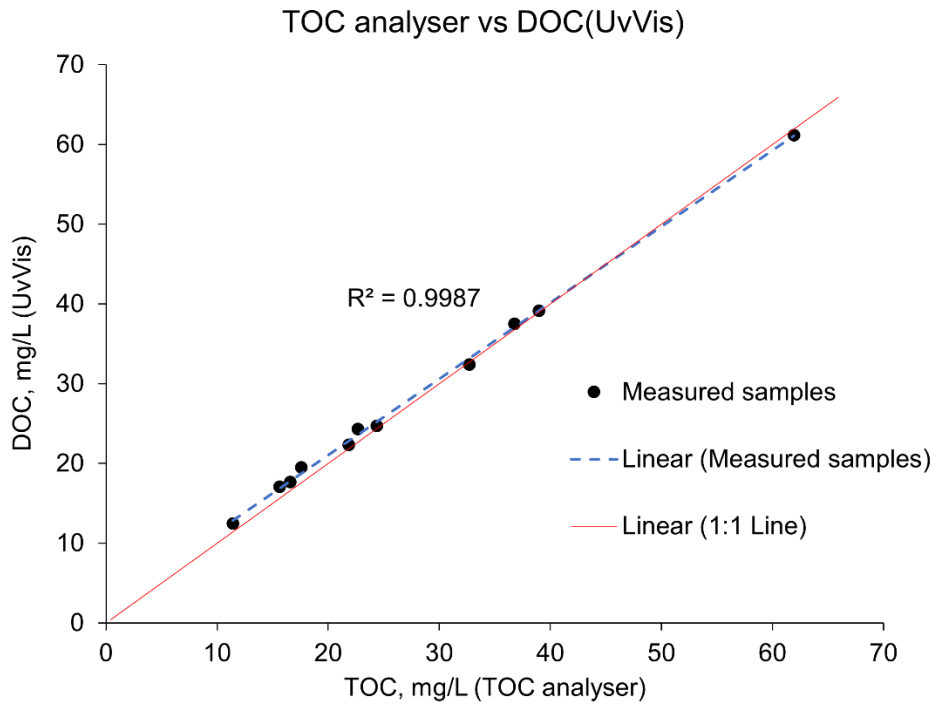

Figure S4. Scatter plot showing the comparison of the DOC concentration measured by the direct UV/Vis spectrophotometer method compared to the reference TOC analyser method. The 1:1 line is shown in red, and the blue dashed line shows the linear regression between the two methods.

Table S1. Results of the analysis of DOC by the UV/Vis and TOC analyser methods

TOC analyser (mg L^{-1})	**DOC, UV/vis (mg L^{-1})**	**Difference (mg L^{-1})**	**95 % CI from Carter et al., (2012)**	**Recovery (%)**
16.57	17.67	1.10	± 2 mg L^{-1}	106.61
11.41	12.48	1.07	± 2 mg L^{-1}	109.40
17.59	19.50	1.91	± 2 mg L^{-1}	110.88
21.84	22.35	0.52	± 4 mg L^{-1}	102.38
32.70	32.42	-0.28	± 4 mg L^{-1}	99.13
22.68	24.33	1.65	± 4 mg L^{-1}	107.26
15.64	17.05	1.42	± 2 mg L^{-1}	109.06
36.78	37.50	0.71	± 4 mg L^{-1}	101.94
38.99	39.16	0.17	± 4 mg L^{-1}	100.44
61.92	61.15	-0.77	± 4 mg L^{-1}	98.76
24.38	24.73	0.35	± 4 mg L^{-1}	101.44
			Average	**104.30 %**
			Standard deviation	**4.43 %**

The accuracy of the DOC concentrations calculated using the dual wavelength UV/visible spectrometry (UV/vis) method of Carter et al., (2012) was verified by comparison with a TOC analyser (Thermolox, Sercon). Eleven water samples collected in August were analysed by both the UV/vis and TOC analyser methods and compared in the scatter plot in figure S4 and in table S1. The results of the UV/Vis method showed excellent agreement with the TOC analyser, with a regression coefficient of $R^2 = 0.9987$ and Lin's Concordance Correlation Coefficient (CCC) of r_c=0.997 (Lin, 1989; Muir & Innes, 2024). The UV/vis method gave results which were slightly higher than those measured by TOC, with an average recovery of 104.30 %, however all the DOC concentrations measured by the UV/vis method were within the 95 % confidence intervals (CI) reported by Carter et al., (2012), of 2 mg L^{-1} for concentrations from 5 – 20 mg L^{-1}, and 4 mg L^{-1} for concentrations from 20 – 80 mg L^{-1}.

SI.4 Example images of filtered particulates

Around 500 ml of selected samples collected in January 2024 were filtered under vacuum using Buchner apparatus, and the images of particles retained on glass fibre filters (VWR) are shown in figure S5. The images were taken using a dissection microscope with 10x optical zoom and a microscope camera (MU1403, AmScope). A region near the centre of each filter (approx. 10 by 15 mm) was marked by making pinholes in the filter so the same region could be identified for comparison before and after combustion in the furnace. A ruler with mm graduations was photographed along with the samples at the top of each image. The filtered particulate material was examined under the microscope before and after combustion in a furnace at 450^{O}C for 4 hours to identify whether particles were of mineral or organic composition. Samples 5 and 8, which had the highest turbidity measurements (figure 4 iii of the main text), had a large amount of particulate matter present on the filters, while sample 4 had a lesser amount and sample 2 had no particles evident. The images of the same filters after being in the furnace shows that the particulate matter present has mostly completely disappeared due to the combustion process, while any remaining particles decreased in size. The filters were also carefully weighed to 4 decimal places before and after the being in the furnace, however any change in mass resulting from the combustion of particles was too small to be detected. The results of this analysis is taken as verification of the predominantly organic composition of particulate matter influencing the turbidity results, suggesting that the samples with higher turbidity measurements are subject to greater erosion of peat which is transported in particulate form.

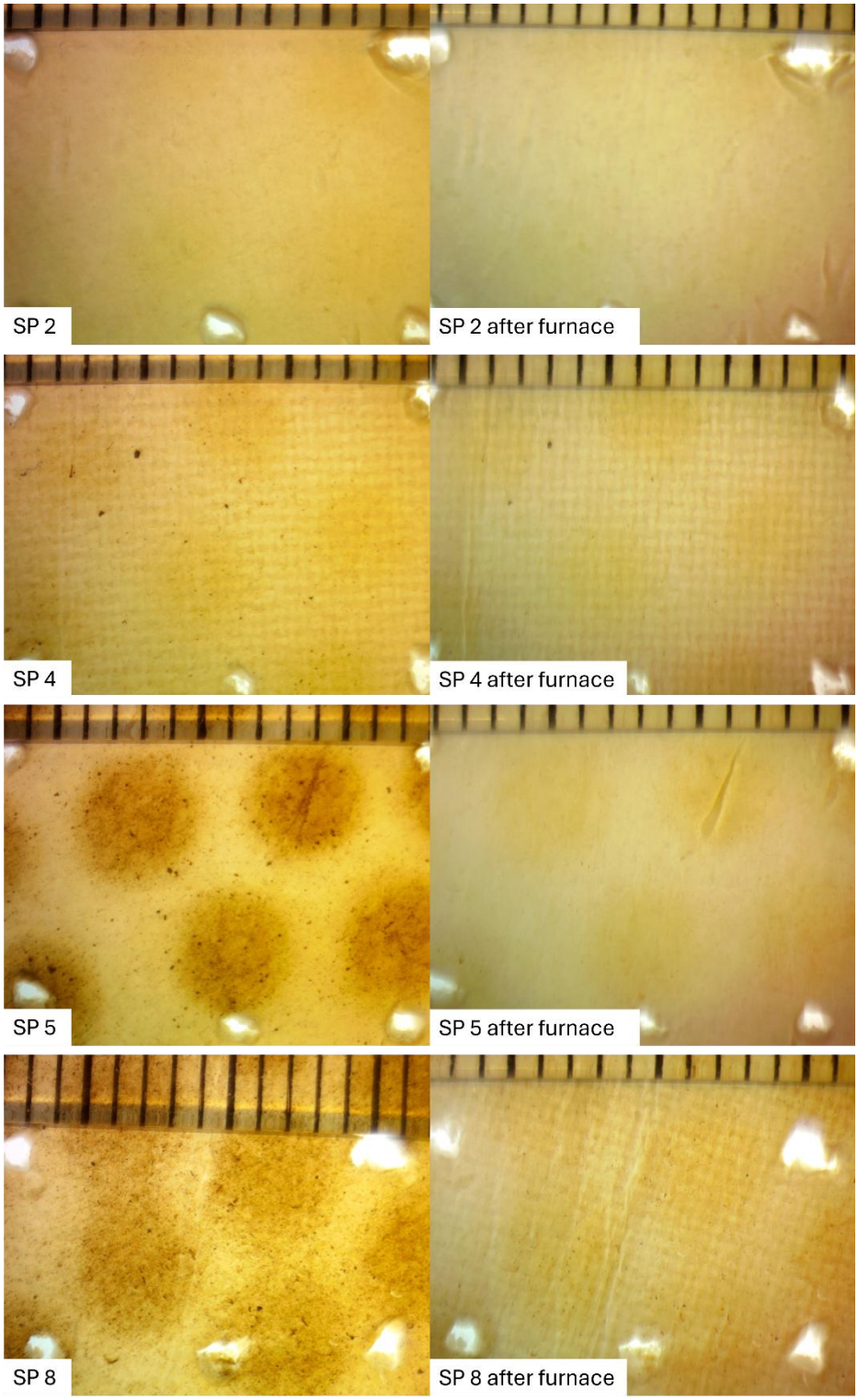

Figure S5. Images of particles retained on glass fiber filters before and after combustion in a furnace a 450^{O}C for 4 hours. The 4 pairs of images, from top to bottom, are for sample points (SP) 2, 4, 5, and 8 collected in January 2024. The scale bar at the top of each image shows 1 mm graduations.

SI.5 PCA results

Table S2. Eigenvalues showing the contribution of each principal component to the cumulative variance

Principal components	Eigenvalue	Variance, %	Cumulative variance, %
PC 1	5.44	49.46	49.46
PC 2	1.99	18.10	67.56
PC 3	0.99	9.02	76.58
PC 4	0.72	6.50	83.08
PC 5	0.57	5.17	88.25
PC 6	0.48	4.35	92.59
PC 7	0.38	3.50	96.09
PC 8	0.22	2.02	98.11
PC 9	0.14	1.29	99.40
PC 10	0.06	0.59	99.99
PC 11	<0.01	0.01	100

Table S3. The contribution of each variable to each principal component. The strength of correlation for each variable with each principal component is shown by colour coding from Blue (strongest correlation) to Red (weakest correlation).

	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8	PC 9	PC 10	PC 11
pH	9.317288	0.344476	1.648493	55.90428	2.91591	0.428407	3.07169	4.91E+00	19.028	2.43E+00	1.91E-03
DOC	15.68162	3.147478	0.706753	0.264298	1.024581	2.625302	0.07922	4.41E+00	0.013489	7.20E+01	2.02E-02
SUVA254	14.076	0.191013	3.58665	3.884421	0.635599	0.710432	3.080852	5.39E+01	19.8854	1.70E-04	4.47E-02
Nitrate	6.698316	2.006489	41.53342	1.224605	3.448811	0.901775	37.75765	5.89E-01	0.863895	4.97E+00	2.54E-03
Turbidity	11.74158	2.164554	8.829879	0.904314	2.18982	5.218834	39.48066	1.25E-04	20.38177	9.08E+00	7.22E-03
Rainfall_3day	2.315505	30.4431	6.312089	9.814738	5.572099	4.08906	7.630948	8.13E+00	25.68498	1.21E-02	4.24E-04
Temp_3day	1.864291	29.45373	13.3649	15.48096	0.090568	0.014811	0.079925	2.26E+01	8.575811	8.48E+00	9.85E-03
PeatyGley	10.68084	7.234508	0.486803	7.165278	32.17033	6.713946	0.075358	1.14E+00	0.495645	2.94E-02	3.38E+01
DystrophicBlanketPeat	7.659853	8.247105	16.59362	4.457244	34.06739	1.562894	4.260558	5.01E-01	2.154496	1.23E+00	1.93E+01
PeatyGleyedPodzol	11.16201	7.96729	0.200256	0.846396	2.679417	41.42011	0.152117	3.81E+00	2.338882	2.37E-01	2.92E+01
OtherMineralSoils	8.802696	8.80026	6.737135	0.053468	15.20548	36.31443	4.331019	1.44E-02	0.577635	1.51E+00	1.77E+01

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