Biogeochemistry **19**: 27–50, 1993

Concentration and composition of dissolved organic carbon in streams in relation to catchment soil properties

P. N. NELSON, J. A. BALDOCK & J. M. OADES
Australian Centre for Water Treatment and Water Quality Research, Department of Soil Science, Waite Agricultural Research Institute, The University of Adelaide, Glen Osmond, South Australia, 5064

Received 7 January 1992; accepted 27 October 1992

Key words: dissolved organic carbon, forest floor leachate, adsorption onto soils, catchment processes, soil properties, humic streams

Abstract. Two adjacent catchments in the Otway Ranges of Victoria, Australia (Redwater and Clearwater) produce water with markedly different concentrations of dissolved organic carbon (DOC) during summer. Water from Redwater Creek had a DOC concentration of 32 mg L^{-1}, while water from Clearwater Creek had a DOC concentration of 3.8 mg L^{-1}. Examination of the catchments revealed that while climate, topography, vegetation and land use were similar, the soils were different. The objective of this study was to examine the relationship between the concentration and chemical composition of DOC in stream waters and the nature of soils in the two catchments. Soil mapping determined that clayey soils formed on Cretaceous sediments (Cretaceous soils) occurred throughout both catchments, but that Redwater Catchment also contained a large area (39%) of sandy soils formed on Tertiary sediments (Tertiary soils). The concentration of DOC in forest floor leachate was high in both the Tertiary and Cretaceous areas; however, the concentration of DOC in water draining areas dominated by Tertiary soils was greater than that in water draining areas dominated by Cretaceous soils. Laboratory experiments showed that the Cretaceous soils had higher adsorption capacities for forest floor leachate DOC than the Tertiary soils. The difference in DOC concentrations of the streams was therefore attributed to the difference in adsorption capacity of catchment soils for DOC. Adsorption capacities of the soils were found to be a function of their clay contents and specific surface areas.

Solid-state ^{13}C nuclear magnetic resonance spectroscopy and pyrolysis-mass spectrometry were used to determine the chemical structure of DOC found in streams and forest floor leachate samples and that remaining in solution after interaction with soil. Chemistry of DOC in forest floor leachate was similar before and after interaction with soil, indicating no preferential adsorption of a particular type of carbon. Thus, differences between the chemical structure of stream DOC and forest floor leachate DOC could be attributed to microbial modifications during its movement through soils and into the streams, rather than losses by adsorption.

Introduction

Dissolved organic carbon (DOC) is of major importance in the ecology of freshwater bodies (Thurman 1985; Meyer 1990). It also causes problems with water treatment which are difficult and expensive to control (Hine & Bursill 1987). DOC concentrations in streams may be influenced by many environmental factors such as soils, geology, topography, vegetation, and land use and management, and the effects of these factors are difficult to distinguish in catchment studies.

As water moves from the atmosphere to the stream, contact with organic materials present. as vegetation, litter, or organic soil horizons leads to a high DOC concentration. The DOC concentration may subsequently be reduced when the water comes in contact with adsorptive materials having high specific surface area and/or reactive surfaces. Thus, stream DOC concentrations are high where (a) water moves directly from being in intimate contact with plant or organic material into the streams, such as in marshy areas (e.g. Grieve 1984), or where (b) water moves through soil in zones which have a low adsorption capacity for DOC (e.g. Meyer 1986; Reeve & Fergus 1982). Areas which have permeable and adsorptive soil horizons produce stream water with low DOC concentrations. Losses by adsorption have also been implicated in changes to the nature of the DOC as it moves through catchments (McDowell & Likens 1988; Leenheer 1980). Adsorption capacity of catchment soils has been related to Fe and Al oxide content (Moore 1989; Moore & Jackson 1989; McDowell & Wood 1984; Reeve & Fergus 1982) and clay content (Nelson et al. 1990; Meyer 1986; St. John & Anderson 1982; Dawson et al. 1981; Leenheer 1980).

Although stream DOC concentrations are also affected by stream-side and in-stream processes (Thurman 1985; Meyer 1990), and vary with time as hydrologic pathways change (Sedell & Dahm 1990; Kramer et al. 1990; Cronan 1990), any model of DOC movement into streams needs to consider the adsorption capacity of catchment soils. However, it is not yet possible to predict such adsorptive capacity by measuring all of the reactive constituents implicated (Tipping 1990), especially in pedologically distinct areas. Furthermore, given the many and varied mechanisms by which DOC can be adsorbed on soil surfaces (Greenland 1970; Schulthess & Huang 1991; Jardine et al. 1989; Tipping 1990), and the ubiquity of the reactive constituents in soils, it is perhaps strange that the total amount of surface available for adsorption reactions, which could be considered a primary factor of importance, is often overlooked. Surface area could be measured by direct methods such as N_2 adsorption, or indirectly by measures of particle size, such as clay content.

In this study, the existence of two adjacent forested catchments with similar topography, stream channel morphology, landuse, vegetation and climate, but which produce stream water with markedly different DOC concentrations (Hart & McKelvie 1986; Fisher 1982) was exploited to study the relationship between soil properties and stream DOC concentrations. The catchments, named Clearwater and Redwater, are situated in the Otway Ranges of Victoria, Australia (Fig. 1). According to existing information, the only apparent difference between the catchments was geology and presumably soils (Pitt 1977), although no detailed information was available as to the nature and distribution of soil types within the catchments. The goal of this work was to test the hypothesis that when a wide variety of soils are examined, soil adsorption capacity and hence stream DOC concentration are related to the amount of surface area available. We also set out to examine the effect of adsorption losses on the nature of DOC.

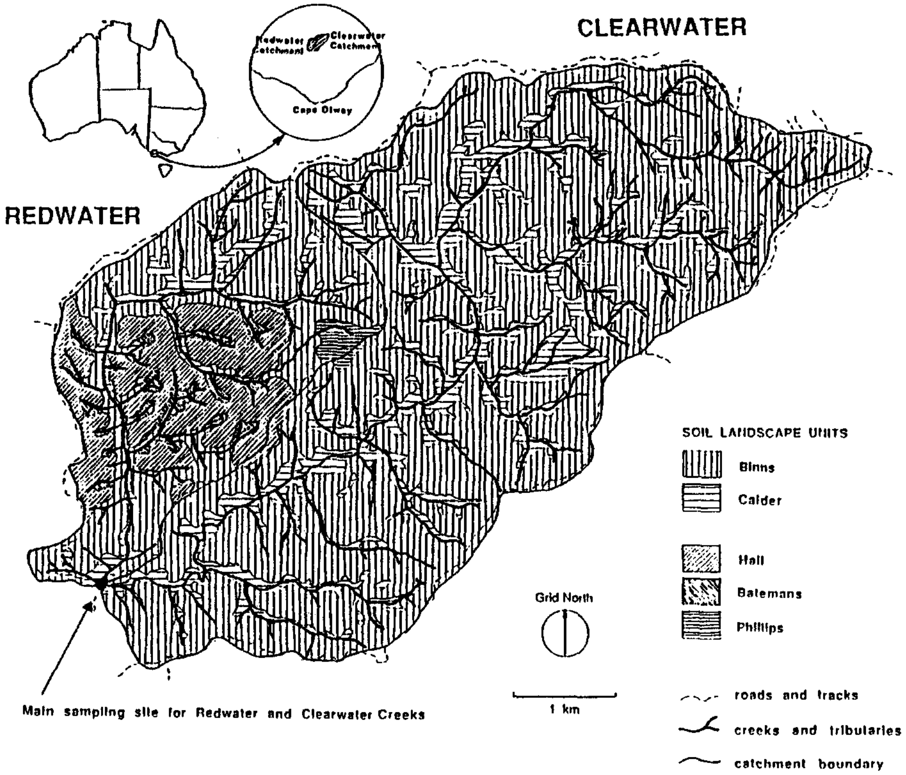
Materials and methods

Catchment location, climate and geology

Redwater and Clearwater catchments lie adjacent to each other on the southern side of the main Otway ridge in south eastern Australia (Fig. 1). Redwater catchment is 7.1 km^2 in area and Clearwater catchment is 19.1 km^2.

The climate of the study area is temperate. Average annual rainfall ranges from approximately 1400 mm yr^{-1} at the lowest elevations to approximately 1800 mm yr^{-1} at the highest elevations. August is the wettest month and January is the driest month. Monthly average temperatures range from 7 °C in July to 16 °C in February (Linforth 1977).

The geological history of the study area is one of sediment deposition, uplift and subsequent dissection (Douglas 1977; Pitt 1977). Fine to medium grained feldspathic sandstones and mudstones were laid down during the Lower Cretaceous period, and were subsequently covered with deposits of quartz sands and gravels during the early Tertiary period. Uplift of the Otway Range has been continuous since the Cretaceous period, with major movements along faults resulting in rapid downcutting and the removal of hundreds of metres of unconsolidated Tertiary sediments and Lower Cretaceous sandstones and mudstones (Douglas 1977; Pitt 1977). The landscape now consists of deep, steep sided valleys (slopes 10—80%) and ridges. Elevation ranges from approximately 200 to 500 m. Tertiary sediments remain only as pockets capping some of the hills in Redwater catchment, and have a relatively even depth of approximately 6 m. The geology of all of Clearwater catchment and 61% of Redwater catchment is Cretaceous, while the remaining 39% of Redwater catchment is Tertiary (Fig. 1 and 2). Stream channel morphology is similar in the two



UNIT	GEOLOGY	TOPOGRAPHY	SOIL TYPES[1]	VEG.: DOMINANT OVERSTOREY
Binns	Cretaceous	slopes, ridges	GD(vc), GS(c)	*Eucalyptus regnans* and associated species
Calder	Cretaceous	valleys, slopes	GS(c), GD(e)	*Nothofagus cunninghamii, Acacia melanoxylon*
Hall	Tertiary	slopes, ridges	S(vc), SG(c), SC(m), SI(m)	mixed eucalypts, *Leptospermum juniperinum*
Batemans	Tertiary	valleys	S(c), SC(c), SI(c), SG(l)	*Eucalyptus regnans* and associated species
Phillips	Tertiary	slopes	L(d)	mixed eucalypts, *Leptospermum juniperinum*

[1] The extent of each soil type in the units is described as follows: d= dominant (90-100%), vc= very extensive (60-90%), e= extensive (30-60%), c= common (20-30%), l= limited (10-20%), m= minor (0-10%)

Fig. 1. Soil landscape map produced for Redwater and Clearwater catchments.

catchments. The main stream channels are in Cretaceous sediments, and have no associated wetland or floodplain zones.

Soil landscape mapping and soil sampling

Soil landscape mapping was completed using aerial photo interpretation, a vegetation map (Conservation, Forests and Lands 1984) and field obser-

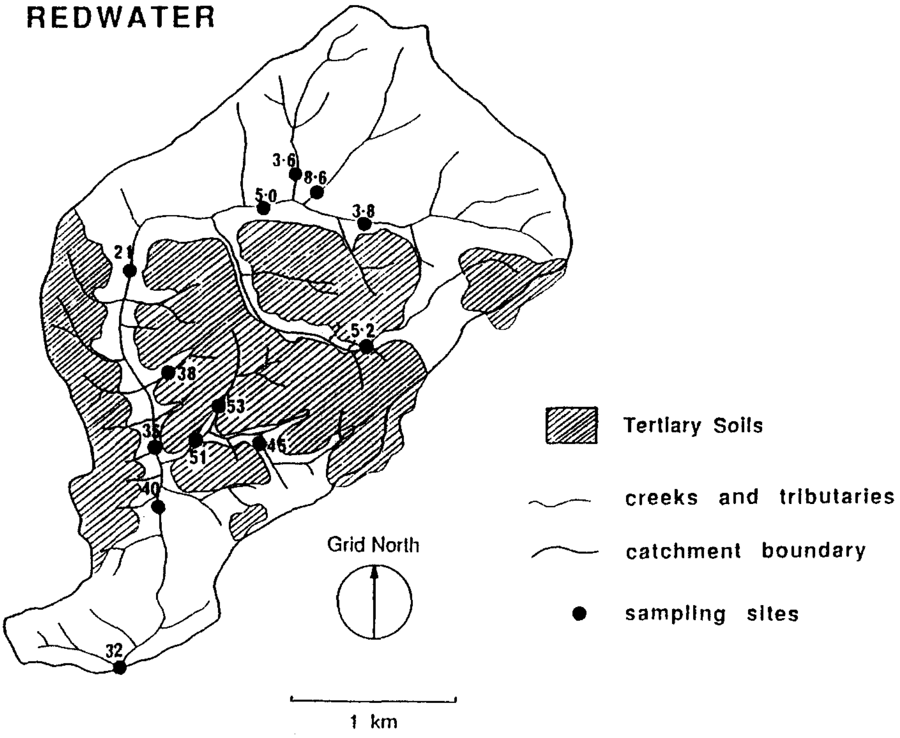


Fig. 2. Concentrations of DOC (mg L^{-1}) in Redwater Creek and its tributaries and the distribution of Tertiary soil in Redwater catchment.

vations. The field observations consisted of a description of soil profiles at 100 sites using the methods and descriptive terms defined by McDonald et al. (1990). The sites were located throughout the catchments, and consisted of auger holes (7 cm diameter) dug to 1.5 m positioned along transects which took in major landform elements. At each profile, samples were taken at 0—10 cm, 60—70 cm and 120—130 cm depths. The sampling depths are hereafter referred to as 5 cm, 65 cm and 125 cm respectively. At some sites dry sand or bedrock halted augering and the deeper samples could not be obtained. The soil samples were air-dried, ground to <2 mm, and used in the experiments described below. The gravimetric water content of each sample was determined so that all analyses could be expressed on the basis of equivalent oven dry weight.

Five soil landscape units were delineated on the basis of vegetation, topography and soil characteristics. They were each given a name, and are mapped and defined in Fig. 1. Binns and Calder units were associated with Cretaceous lithology. The upslope positions were allocated to Binns, and the wetter downslope positions were allocated to Calder. Hall and

Batemans units were associated with Tertiary geology and occupy the upslope and downslope positions, respectively. Phillips unit was associated with a small area of finer textured Tertiary sediments.

The soil profiles were divided into seven groups or soil types which were named according to their main distinguishing characteristics. Soils developed on Cretaceous sediments are hereafter referred to as "Cretaceous soils", and soils developed on Tertiary sediments are hereafter referred to as "Tertiary soils". Their occurrence within the soil landscape map units is shown in Fig. 1. General characteristics of the soil types are as follows:

a) Cretaceous soils
   1) The "deep brown gradational soils" (GD) consist of a brown loam A horizon grading into a yellow clay B horizon overlying weathered parent material at > 1 m depth. The reaction trend is acidic. Nutrient levels are relatively high and permeability is moderate.
   2) The "shallow brown gradational soils" (GS) are similar to the "deep brown gradational soils", except that weathered parent material is encountered at < 1 m depth. Rock floaters and surface boulders are common.

b) Tertiary soils
   1) The "black sand" (S) soils consist of black, highly organic sand or sandy loam near the surface, over bleached greyish sand which extends at least to 150 cm depth. The boundary between the black sand and grey sand horizons may be abrupt to very diffuse. The soils have < 30% gravel (quartz) and no illuvial iron or clay rich horizons within 150 cm of the surface. Many areas remain moist throughout the year however, suggesting the presence of impeding layers at > 150 cm depth. The reaction trend is acidic and severe nutrient deficiencies occur. Water holding capacity is low and permeability is high.
   2) The "black sand with gravel" (SG) soils are similar to the "black sand" soils except that at least one horizon contains > 30% gravel (2—6 mm sub-angular to sub-rounded quartz).
   3) The "black sand with clay" (SC) soils are similar to the "black sand" soils except that a clayey horizon occurs within 150 cm of the surface. Permeability is low and soils remain waterlogged for most of the year.
   4) The "black sand with iron oxide horizon" (SI) soils are similar to the "black sand" soils except that they have an iron oxide rich horizon within 150 cm of the surface. The iron rich horizon may be soft and permeable or a ferricrete hardpan. Hardpans restrict drainage and root penetration.

5) The "black loams" (L) consist of black loam over whitish weathered Paleocene (Tertiary) sandy siltstone.

All soils are covered by a 1—10 cm thick litter layer.

Catchment vegetation

The vegetation of the study area consists mostly of wet sclerophyll forests (Conservation, Forests and Lands 1984; Parsons et al. 1977). A similar range of species of tall trees is present in the geologically different areas, because in the Tertiary areas tree roots can penetrate through the less fertile Tertiary soils into the Cretaceous sediments below (Pitt 1977).

In the Cretaceous areas, tall (30 m) closed forests dominated by *Nothofagus cunninghamii* and often including *Acacia melanoxylon* occur in the drainage lines and valley floors. These communities sometimes spread to the sheltered middle and lower slopes in the wettest areas, preferring sites that are permanently moist, and define the extent of Calder unit. On the slopes and ridges of Cretaceous areas (Binns unit) are tall (>40 m) open forests with a canopy of *E. regnans* and occasionally *Acacia melanoxylon.*

At the margins of the Tertiary soils, where the sand is shallow and conditions are moist due to the downslope position, the dominant vegetation is tall open forests of *E. regnans*. Upslope of the *E. regnans* forests, the vegetation consists of mixed stands of eucalypts containing *E. obliqua.*, *E. regnans, E. viminalis* and *E. cypellocarpa*. The hilltop communities, where the sand is deepest, are dominated by either open forests (<40 m high) of *E. baxterii* or pure stands of *Leptospermum juniperinum. L. juniperinum* continues as a second tree stratum below the eucalypt forest throughout the Tertiary areas.

Most of the forest in the study area originates from the late 1930's when widespread wildfires stimulated intense regeneration.

Experimental

Carbon in streams, forest floor leachate and soils

Water samples were collected from Redwater and Clearwater Creeks during summer under base flow conditions on 9 and 26 January, 1990. The stream sampling points (38°44′S, 134°32′E) were just upstream from their confluence (Fig. 1). Water samples were also collected from flowing tributaries of Redwater Creek during January 1990 at the locations indicated in Fig. 2. The concentration of DOC in all samples was measured according to the method outlined by Hine et al. (1986) in which the DOC in a filtered (0.45 μm pore size) sample is converted to carbon dioxide by an ultraviolet-catalysed persulphate oxidation, reduced to methane, and detected by flame ionization. Filtration of all samples was carried out with either nylon (Whatman Polycap) or polyvinyl flouride (Millipore Durapore) membranes which were rinsed with deionized water and then sample before use.

The chemical structure of the stream DOC was characterized by solid-state cross polarization/magic angle spinning ^{13}C nuclear magnetic resonance (CP/MAS ^{13}C NMR) spectroscopy (Oades et al. 1987) and pyrolysis-mass spectrometry (pyrolysis-MS) (Baldock et al. 1991). The samples used for these analyses were prepared by evaporating 43 L of filtered (0.45 μm) stream water to 2 L at $< 30\,^{\circ}$C under vacuum and freeze-drying. The signal intensity acquired from the CP/MAS ^{13}C NMR analysis of each sample was divided into the following seven chemical shift regions: alkyl (10—45 ppm), O-alkyl (45—90 ppm), acetal (90—110 ppm), aromatic (110—140 ppm), phenolic (140—160 ppm), carboxyl (160—190 ppm) and carbonyl (190—210 ppm). The labels given to each spectral region are thought to be indicative of the dominant type of C resonating in the regions.

In this study, forest floor leachate was defined as the water which had passed through the canopy and litter layer, but had not yet come in contact with the highly modified organic or mineral portions of the soil. Forest floor leachate collectors were set up as follows at 3 locations in Binns unit, 1 in Calder and 1 in Hall. The litter layer was removed from a 2 × 1.5 m area, and a plastic sheet was lain on the soil surface. A 5 L container was placed under a hole made in the plastic sheet at its lowest point. The litter layer was then replaced. A separate trial indicated no significant leaching of DOC from the plastic sheets and containers. Rainfall during the period 20—23 January led to 0.4—1.3 mm of leachate being collected. The samples (one for each site) were analysed for DOC and then combined into one sample.

Total carbon (TC) contents of soil samples from 37 Cretaceous sites and 31 Tertiary sites (3 depths for each site) were measured using a Leco CR12 Carbon Analyser. As no carbonate was detected in any of the soils, it was assumed that the values obtained for total carbon content were equivalent to total organic carbon content. Water soluble organic carbon (WSC) contents of the same soil samples were determined by measuring the amount of DOC in filtered (0.45 μm) extracts produced by shaking deionized water (50 ml) with soil samples (10 g) for 16 hours on an end-over-end shaker operating at 15 revolutions per minute.

Adsorption capacity of soils

Soil samples used for the adsorption experiment (12 Cretaceous sites and 13 Tertiary sites, with 3 depths for each site) were chosen to cover the variation within both the Cretaceous and Tertiary areas. The relative capacity of the soils to adsorb organic matter was determined by measuring the net amount of DOC adsorbed from a solution with an initially high DOC concentration. 50 ml of the combined forest floor leachate sample (with a DOC concentration of 182 mg L^{-1}) was added to each 10 g soil sample. The suspension was shaken for 16 hours on an end-over-end shaker operating at 15 revolutions per minute. Temperature was kept at 4 °C to minimize microbial activity. The DOC concentration of the centrifuged and filtered (0.45 μm) supernatant was then measured, and the amount of carbon adsorbed was calculated from the difference between the DOC concentration of the solution before and after mixing with the soil.

The clay content of each soil sample was measured by the pipette method (Gee & Bauder 1986) omitting the H_2O_2 pretreatment. The specific surface area (SSA) of each soil sample was determined by N_2 adsorption (Zarcinas et al. 1982).

Chemical structure of adsorbed DOC

The chemical structure of organic materials which were adsorbed onto soils was investigated in a separate experiment from that used to study DOC adsorption. A DOC solution was prepared by combining forest floor leachate with a litter extract. Addition of the litter extract was necessary because the amount of forest floor leachate collected was insufficient for the analyses required. The litter extract was prepared by covering litter samples collected from each of the 5 forest floor sites with 8 L of deionized water in bins and allowing the mixture to stand for 2 d at 25 °C. The extract was filtered (5 μm), evaporated under vacuum at <30 °C to approximately half the original volume, and filtered again (0.45 μm). Four litres of litter extract (262 mg L^{-1} DOC) was added to the combined forest floor leachate sample (10.5 L at 182 mg L^{-1} DOC), evaporated (<35 °C, under vacuum) to 7 L, and sterilized by filtration (0.2 μm). The resultant solution had a DOC concentration of 387 mg L^{-1} and was kept at 4 °C in sterile conditions.

The soil sample used in this experiment was obtained by combining subsamples collected from the 65-cm depth of thirteen of the Cretaceous sites, and had a clay content of 50.0%, specific surface area of 43.4 m^2g^{-1}, TC content of 1.09% and WSC content of 38.9 $\mu g\ g^{-1}$. The combined sample was placed in six 1-L centrifuge bottles (160 g soil in each), and sterilized by gamma-irradiation (50 kGy from a ^{60}Co source). In order to bring the DOC solution in contact with the soil, 800 mL was added to each bottle under sterile conditions. The resulting suspensions were shaken for 16 hours on an end-over-end shaker at 20 °C. They were then centrifuged and the supernatants filtered (0.2 μm). The concentration of DOC in the solution before and after adsorption was measured, and the remainder of each solution was freeze-dried. The chemical composition of the carbon contained in the before and after adsorption solutions was determined by CP/MAS ^{13}C NMR and pyrolysis-MS analysis of the freeze-dried samples.

Statistical analyses

All statistical analyses were performed using the Genstat 5.0 program. In several instances the data was transformed prior to analysis to ensure that adequate distribution of residuals was obtained which confirmed the validity of using the analysis of variance procedures.

Results and discussion

DOC concentration in streams and forest floor leachate

Measured during base flow conditions in summer, the concentration of DOC in Redwater Creek (32.0 mg L^{-1}) was much greater than that in Clearwater Creek (3.8 mg L^{-1}). The concentrations were comparable to those measured previously in different studies (Hart & McKelvie 1986; Fisher 1982). Concentrations of DOC in tributaries draining Tertiary soils, 38—53 mg L^{-1}, were greater than in those draining Cretaceous soils, 3.6—8.6 mg L^{-1} (Fig. 2), indicating that the areas containing Tertiary soils were responsible for the high final DOC concentration of Redwater Creek.

The DOC concentration of forest floor leachate in Cretaceous areas was 105 mg L^{-1} in the Calder unit site, and 105, 108 and 205 mg L^{-1} in the Binns unit sites. At the Tertiary site (Hall unit), the forest floor leachate DOC concentration (148 mg L^{-1}) fell within the range measured for the Cretaceous areas. However, due to the small number of samples taken, temporal and spatial variability were not accounted for, and thus no conclusion could be drawn as to whether or not DOC concentrations in forest floor leachate were significantly different in the two areas. DOC concentrations of forest floor leachate collected in this study were high compared to those measured in North American catchments (Cronan 1990), perhaps partly because sampling occurred in the summer during the period of high temperature, low rainfall and maximum leaf senescence.

Organic carbon in soils

Total organic carbon content of the Tertiary soils was significantly higher than that of the Cretaceous soils (Fig. 3a) and decreased significantly with

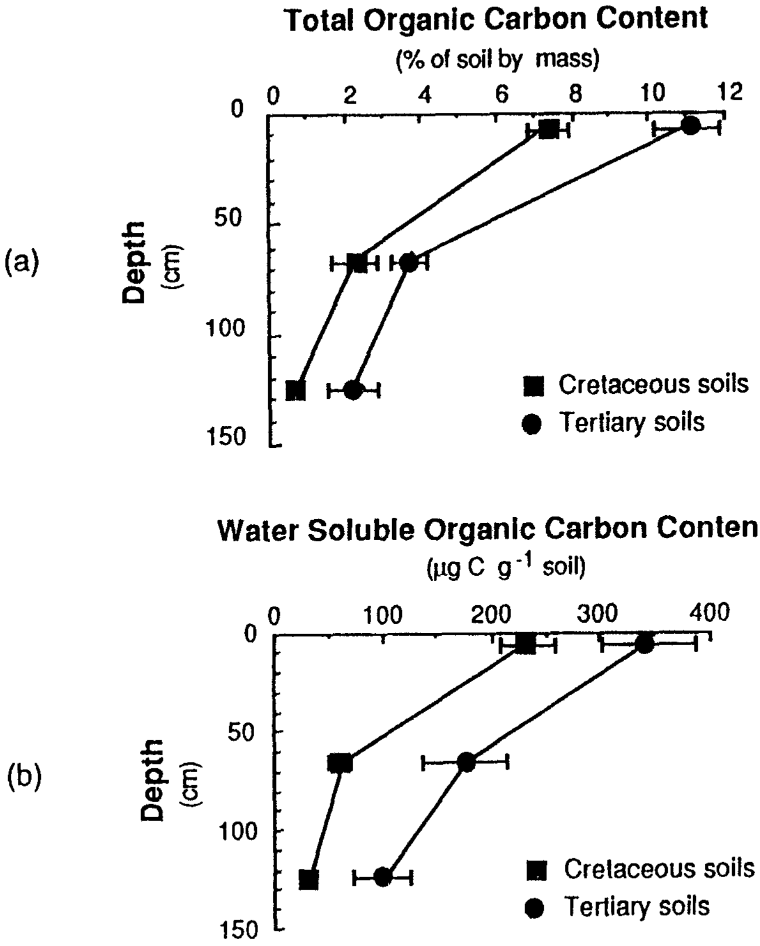


Fig. 3. (a) Total organic carbon content of the catchment soils. Analysis of variance showed that the effects of geology and depth were significant at $p < 0.001$, while their interaction was not significant. (b) Water soluble organic carbon of the catchment soils. The effects of geology and depth were significant at $p < 0.001$, while their interaction was significant at $p < 0.05$. Error bars in all figures represent the means plus or minus their standard deviations.

depth for both soil groups. Assuming that inputs of carbon were similar in the two soil groups, the difference suggested that the breakdown or turnover rate of organic material was slower in the Tertiary soils. The low pH of the Tertiary soils would inhibit faunal activity and hence the incorporation and breakdown of organic matter. Also, although the Tertiary soils are generally very well drained, in many areas gravel layers or impermeable clay or ferricrete layers may prolong the duration of waterlogging in the A horizon and thus decrease turnover rates of organic matter. In the Cretaceous soils, total carbon content gradually decreased with depth; however, in the Tertiary soils there was often a distinct break between a highly organic A_1 horizon and a highly leached gravelly or sandy A_2 or E horizon with a low total carbon content.

Water soluble organic carbon content of the Tertiary soils was greater than that of the Cretaceous soils at all depths (Fig. 3b). Although the Tertiary soils contained almost twice as much water soluble organic carbon, the difference was not large enough to explain the 8-fold difference in DOC concentration of the streams, especially when it was considered that the Tertiary soils occupied only 39% of the Redwater catchment.

Sources of stream DOC and adsorption capacity of soils

Although Meyer (1990) suggested stream channels and the riparian zone as a major source and sink of DOC, the similar stream morphology, stream-bed materials and stream-side vegetation in the two catchments precluded stream-side effects as a major factor influencing the measured stream DOC concentrations. On the other hand, differences between the upland soils were marked. The net amount of forest floor leachate DOC which was adsorbed by the soils in the adsorption experiment is given in Fig. 4. The nature and concentration of DOC added in this experiment was the same as that added naturally from forest floor leachate. The proportion of the added DOC that was adsorbed varied from −5% (net desorption) in the Tertiary samples from 5 cm depth to 53% in the Cretaceous samples from 125 cm depth. The Cretaceous soils had a greater adsorption capacity than the Tertiary soils at all depths, and the increase in adsorption capacity of the Cretaceous soils with depth was greater than that of the Tertiary soils. The small amount of adsorption which occurred in the Tertiary soils suggested that much of the DOC entering the soil which is not sequestered by microorganisms would be leached. On the other hand, a large proportion of the DOC moving through the Cretaceous soils would be adsorbed and potentially available to be mineralized.

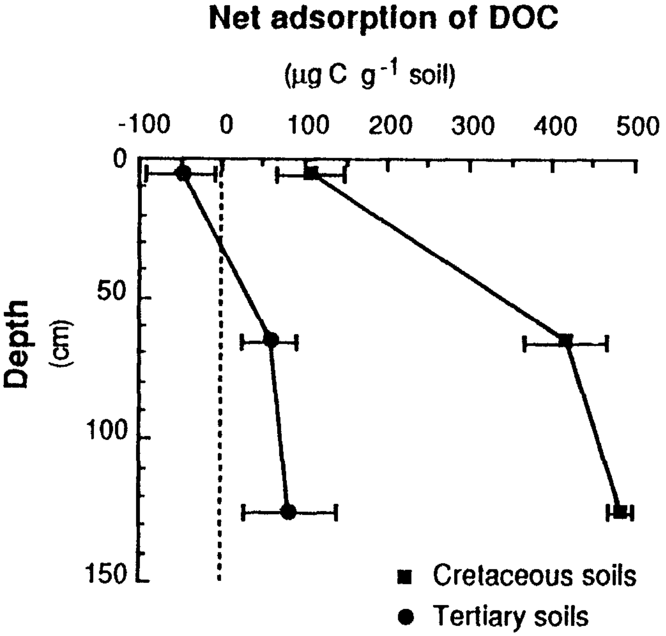


Fig. 4. Net adsorption of forest floor leachate DOC by the catchment soils. The effects of geology, depth and their interaction were all significant at $p < 0.001$.

The Cretaceous soils had a significantly greater clay content than the Tertiary soils at all depths (Fig. 5a). Most Tertiary soils had clay contents <5% throughout the profile, but some contained clay horizons. In the Cretaceous soils, clay content decreased below 65 cm depth as relatively unweathered sandstone and siltstone were encountered. Specific surface area (SSA) of the soils followed similar trends to those observed for clay content, with the exception that the changes noted with increasing depth were larger for the Cretaceous soils (Fig. 5b).

The adsorption capacity of all samples included in this study and those of a similar study which used soils collected from the Mount Lofty Ranges of South Australia (Nelson et al. 1990) were plotted as a function of their respective clay contents and SSA values (Fig. 6). The soils used included surface soils and subsoils and showed a wide range of properties. Clay contents ranged from 0.4 to 67.1% and carbon contents ranged from 0.1 to 18.2%. Linear regressions of adsorption capacity on clay content and on SSA were both found to be significant and are shown in Fig. 6. SSA described more of the variation in adsorption capacity than clay content, presumably because one factor controlling the extent of adsorption reactions was the extent of surface area available for adsorption. Using either clay content or SSA, the major proportion of the variation in adsorption

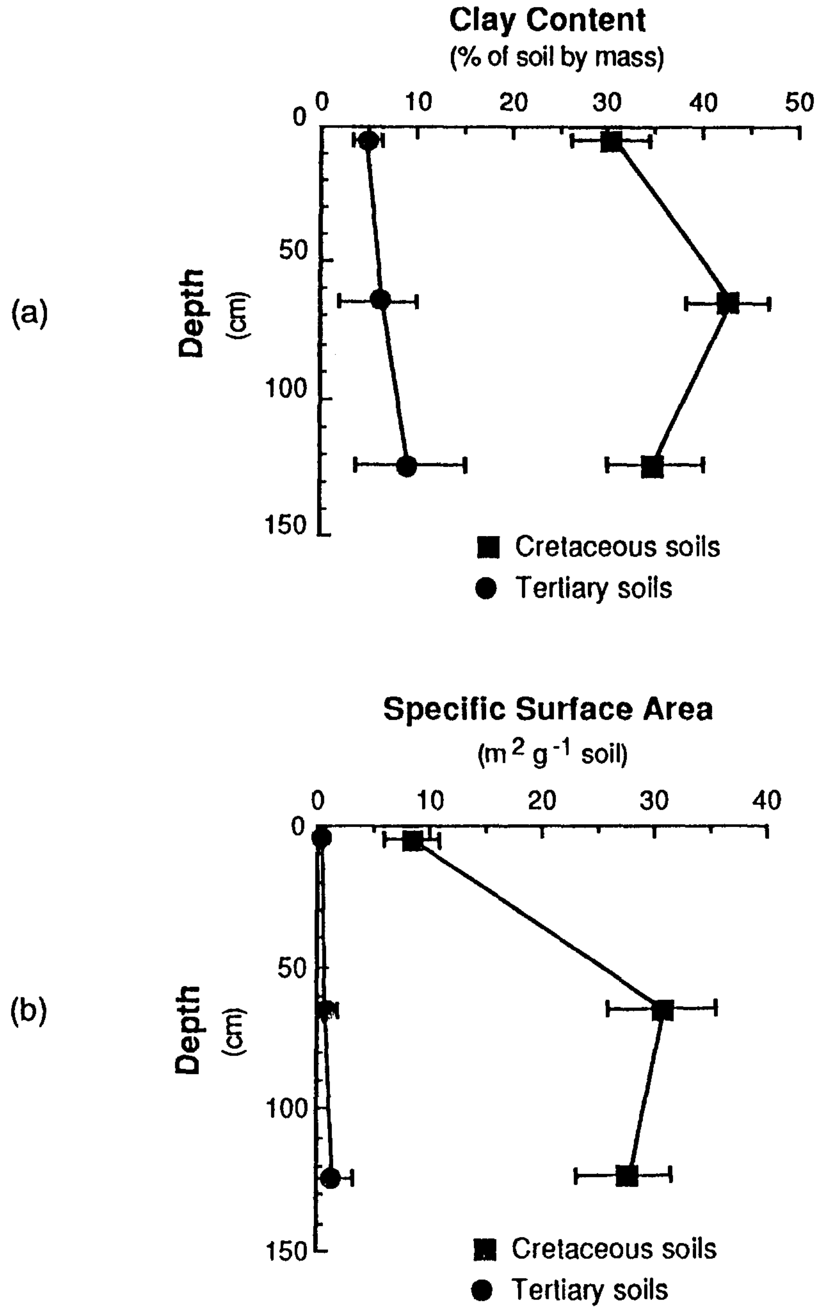


Fig. 5. (a) Clay content of the catchment soils. The effects of geology, depth and their interaction were significant at $p < 0.001$, significant at $p < 0.05$, and non-significant respectively. (b) Specific surface area of the catchment soils. The effects of geology, depth and their interaction were all significant at $p < 0.001$.

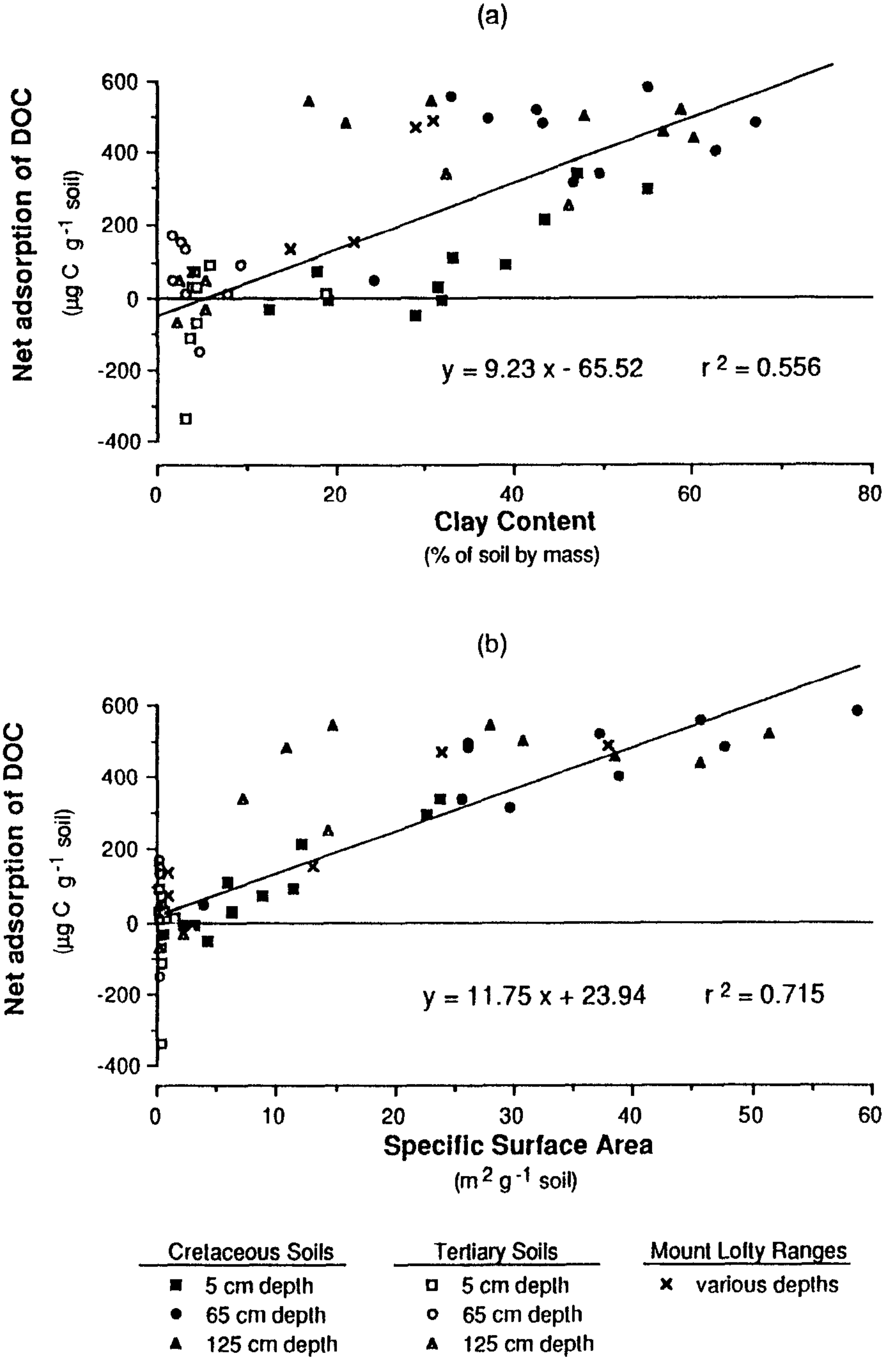


Fig. 6. Adsorption capacity of the soils for forest floor leachate DOC expressed as a function of their respective (a) clay content and (b) specific surface area.

capacity was accounted for, irrespective of the nature of the surfaces. Residual variation was probably due to the nature of the surfaces available; e.g. the quantity and form of Fe and Al oxides, clay mineralogy, nature of the exchange cations, and organic matter content. The similar behaviour of the samples collected from the Mount Lofty Ranges and the Otway Ranges, despite the fact that their chemical and mineralogical properties differed, suggests that the relationship between adsorption capacity and SSA may be applicable to all soils.

Adsorption capacity measured in mixed slurry experiments can only be seen as an index of relative behaviour of soils, rather than in a mechanistic way, because no account is taken of the pore systems through which the water moves. However, Qualls & Haines (1992) found that adsorption isotherms established using mixed soil slurries were comparable to isotherms established using unsaturated flow through undisturbed soil cores.

Assuming that the initial mass isotherms (amount of DOC adsorbed versus the amount initially added) were linear (Nodvin et al. 1986; Nelson et al. 1990), they could be estimated for each soil sample by joining the two points, WSC (amount desorbed with no added DOC) and net adsorption (net amount adsorbed/desorbed at an initial added DOC concentration of 910 μg C g^{-1} soil). Nodvin et al. (1986) suggested that the slope of the isotherm, m, represents the fraction of DOC which is retained by the soil, and provides a measure of the affinity of the soils for DOC. They also suggested that the "reactive soil pool" (RSP) of DOC could be calculated by RSP = intercept/$(1 - m)$. In this work, m was found to be significantly related to net adsorption (at an initial added DOC concentration of 910 μg C g^{-1} soil), with the linear regression equations shown in Table 1. The relationship was particularly good for samples with a net adsorption greater than 50 μg C g^{-1} soil. The affinity of the soils for DOC, m, was significantly related to clay content and SSA (Table 1), but the correlation

Table 1. Linear regression equations of estimated initial mass isotherm parameters, m (slope) and RSP (reactive soil pool) as a function of measured soil properties.

Est. parameter	Measured parameter	Slope	Intercept	r^2
m	net adsorption[1]	6.81×10^{-4}	0.214	0.658
m	net adsorption[2]	8.95×10^{-4}	0.125	0.955
RSP	WSC	1.68	−17.22	0.904
m	clay content	7.01×10^{-3}	0.150	0.455
m	SSA	8.62×10^{-3}	0.219	0.538

[1] all samples;
[2] samples with adsorption > 50 μg C g^{-1} soil.

coefficients were lower than for net adsorption, possibly due to errors involved in estimating *m* from only two points on the isotherm. RSP was closely related to, and slightly higher than WSC (Table 1).

Chemical structure of adsorbed DOC and stream DOC

Of the 1858 mg DOC added to the soil sample in this experiment, 958 mg net was adsorbed, resulting in a final DOC concentration of 187 mg L^{-1}. The loss of DOC from the solution was assumed to be due to adsorption onto soil surfaces, as the employment of sterile conditions precluded significant microbial assimilation or breakdown.

The sample before adsorption consisted of the DOC leached from plant materials which had undergone some microbial modification but had not come in contact with soil. CP/MAS ^{13}C NMR analyses indicated that the DOC before adsorption was dominated by O-alkyl carbon and contained a significant proportion of alkyl and carboxyl carbon as well as minor amounts of all the remaining types of carbon (Fig. 7, Table 2). The composition of the sample after adsorption was similar to that of the sample before adsorption (Fig. 7, Table 2). A decrease in the proportion of O-alkyl carbon was evident which suggested that a small amount of carbohydrate carbon may have been preferentially adsorbed; however, the difference was not large enough to make a conclusive statement. The origin of the large peak at 169 ppm in the sample after adsorption (Fig. 7b) is not known, but it would appear that this form of carbon was adsorbed less readily than the other forms of carbon and accounted for the increased proportion of carboxyl carbon in the DOC after adsorption (Table 2). The occurrence of a weakly adsorbed structure in the carboxyl

Table 2. Quantification of the CP/MAS ^{13}C NMR spectra by integration of the signal intensity contained in each spectral region (expressed as percentage of total signal).

		Forest floor leachate		Creeks	
Chemical shift (ppm)	Dominant group	Before adsorption	After adsorption	Redwater	Clearwater
10—45	alkyl	23.2	21.9	15.8	15.9
45—90	O-alkyl	37.5	33.6	28.1	29.3
90—110	acetal	8.5	7.6	10.4	7.7
110—140	aromatic	9.7	9.7	15.8	12.6
140—160	phenol	6.4	6.4	7.9	7.2
160—190	carboxyl	12.5	18.3	19.0	24.6
190—210	carbonyl	2.6	2.1	3.1	2.5

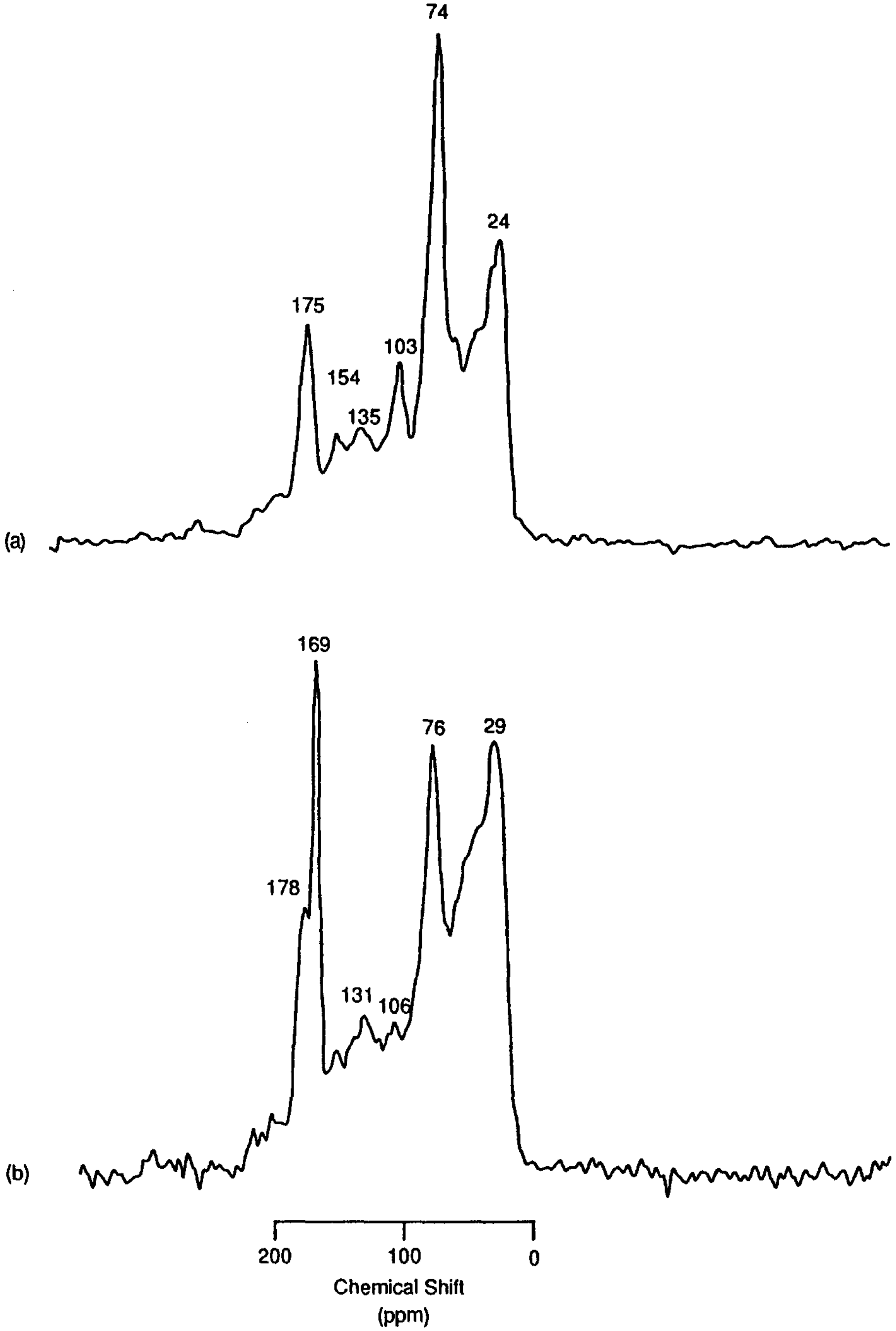


Fig. 7. Solid state CP/MAS ^{13}C NMR spectra acquired for DOC in forest floor leachate (a) before adsorption, and (b) after adsorption.

region seems unusual because of the many mechanisms through which carboxyl structures can be adsorbed on soil surfaces. A similar chemical structure of the DOC before adsorption and after adsorption was supported by the pyrolysis-MS results (Fig. 9a). The CP/MAS ^{13}C NMR and pyrolysis-MS results therefore indicated that there was little if any selective adsorption of specific types of carbon during the adsorption process despite the fact that 52% of the added carbon had been adsorbed onto soil particles. Hydrophobic components of DOC have been found to be preferentially adsorbed (Dunnivant et al. 1992; Leenheer 1980), but it is not clear how the hydrophobic/hydrophilic classification corresponds with chemical structures.

The chemical structure of DOC contained in Redwater and Clearwater Creeks was found to be similar (Fig. 8 and 9b and Table 2); however, as noted for the DOC after adsorption, a strong resonance near 169 ppm was observed for DOC in Clearwater Creek. Since there was little evidence that the chemical structure of DOC in forest floor leachate was altered by adsorption, differences noted in chemical nature of DOC in forest floor leachate and stream samples were presumably due to microbial modification of forest floor leachate DOC as it passed through the soil and into the streams.

Stream DOC samples had less alkyl and O-alkyl and more aromatic and carboxyl C than forest floor leachate DOC samples. The decrease in the proportion of O-alkyl C from the forest floor leachate to the stream was expected, as microorganisms readily break down carbohydrates. A decrease in the saccharide signal in the pyrolysis-MS results corroborated the NMR results. The increase in aromatic C was also expected, as the recalcitrant nature of aromatic structures is known to lead to their preservation relative to other C types. The relative decrease in alkyl C was mainly due to the loss of C resonating at 24—30 ppm suggesting that the alkyl C in streams was more highly branched or closely associated with carboxyl groups than the alkyl carbon in forest floor leachate (Duncan 1987). The increase in the carboxyl signal may have been due to the synthesis of low molecular weight organic acids by micro-organisms during decomposition processes or by algae in the streams (Thurman 1985).

Conclusions

Redwater and Clearwater are adjacent catchments which yield water with markedly different concentrations of DOC. Climate, vegetation, topography, stream channel characteristics and land use are similar in the two

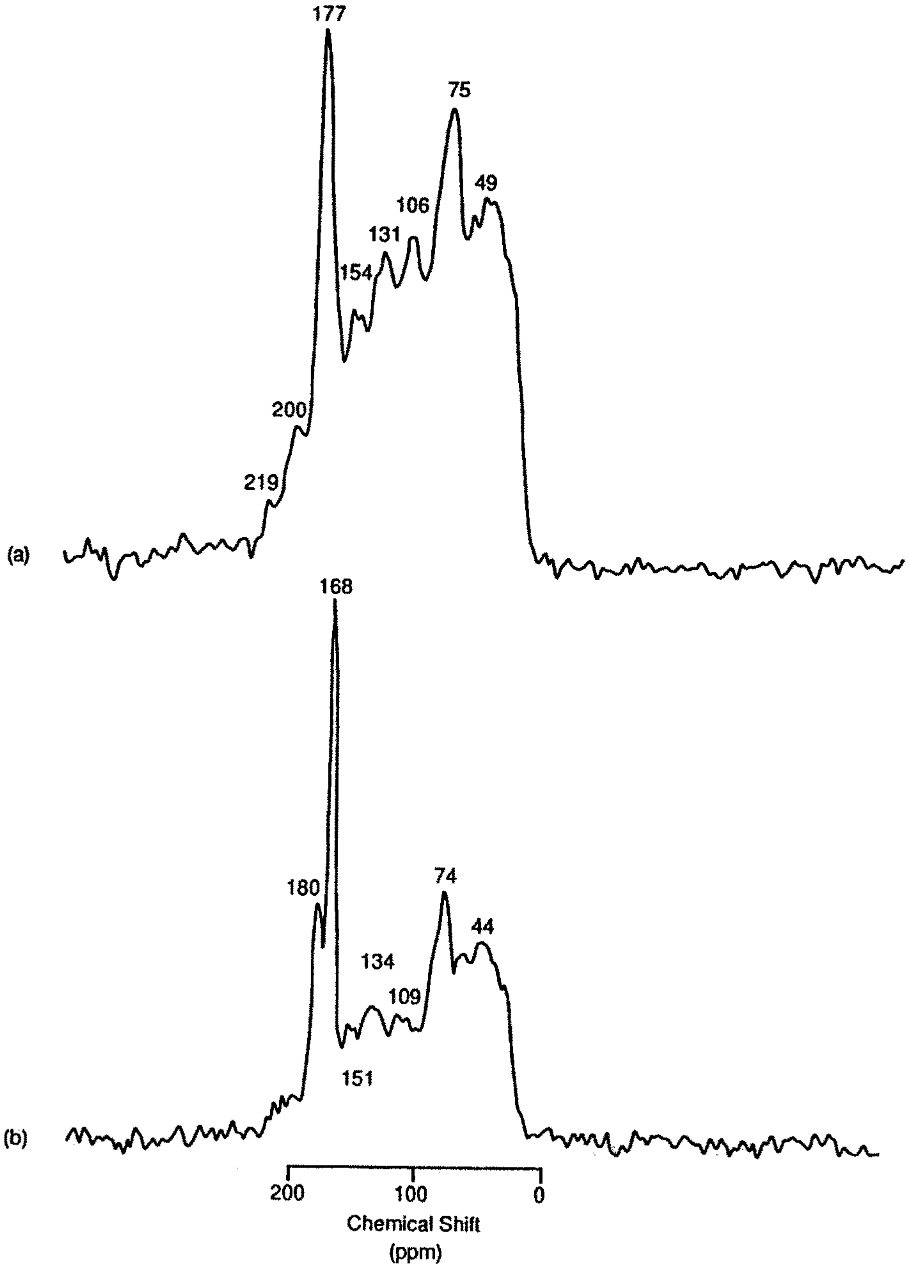


Fig. 8. Solid state CP/MAS ^{13}C NMR spectra acquired for DOC in (a) Redwater Creek and (b) Clearwater Creek.

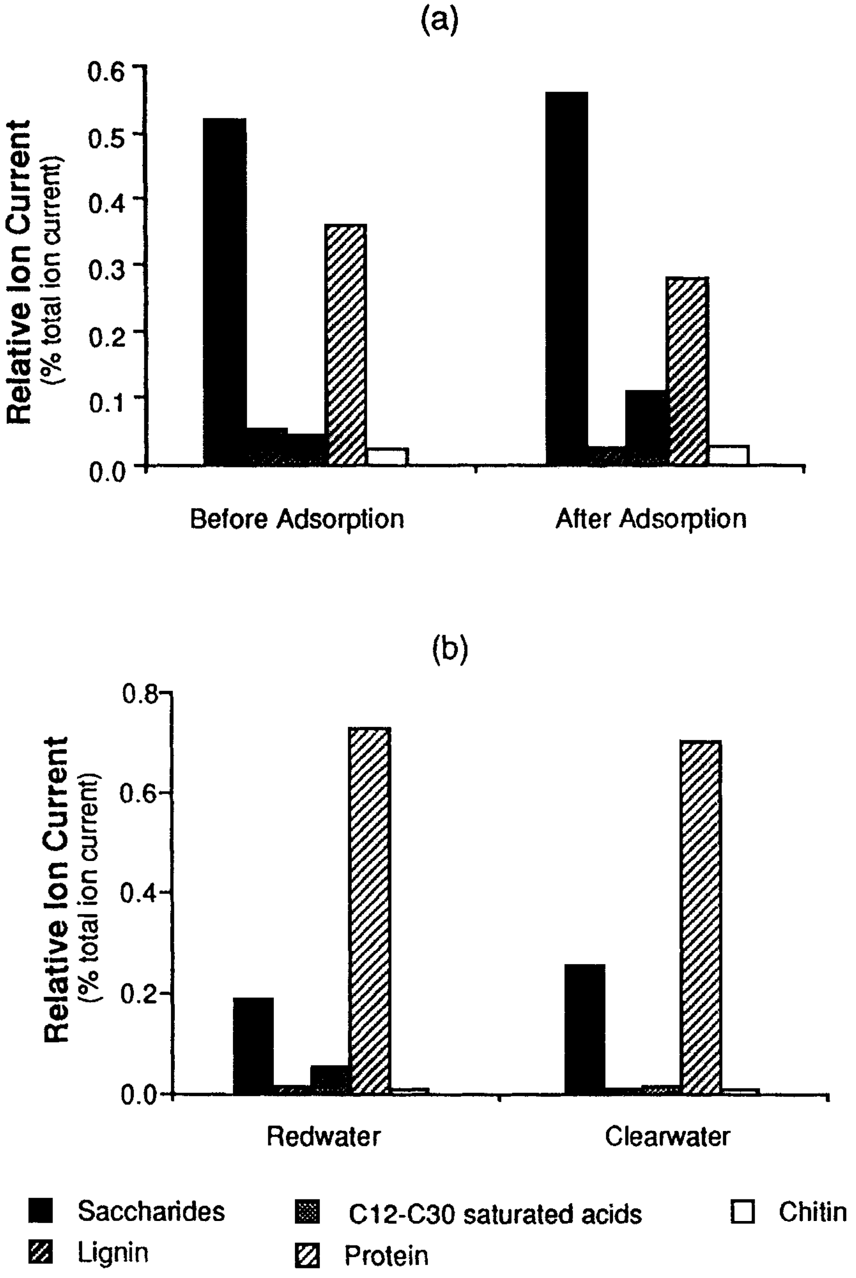


Fig. 9. Pyrolysis-MS results obtained for DOC in (a) forest floor leachate before adsorption and after adsorption and (b) Redwater and Clearwater Creeks.

catchments. Geology is very uniform throughout the catchments (Lower Cretaceous shales and siltstones), except for a large portion (39%) of Redwater catchment, which contans Tertiary deposits of quartz sand. A distinct difference in the concentration of DOC in the streams draining areas of Tertiary and Cretaceous geology made it clear that the different concentration of DOC noted in Redwater and Clearwater Creeks was a function of the distribution of soils derived from Tertiary and Cretaceous sediments within the two catchments.

The concentration of DOC in water decreased during its passage through the soil, more so in Cretaceous soils than Tertiary soils. In the laboratory, Cretaceous soils were found to have much higher adsorption capacities for DOC than Tertiary soils. Specific surface area accounted for the major proportion of variation in adsorption capacity of soils with a wide range of properties, irrespective of the nature of the surfaces.

The chemical character of DOC in Redwater and Clearwater creeks was similar but differed from that of forest floor leachate. Loss of DOC by adsorption did not change the chemical characteristics of forest floor leachate DOC indicating that the different chemical nature of DOC in forest floor leachate from that in streams was a result of microbial activity, probably in the soils.

Acknowledgements

Financial support for this work was provided by the Australian Centre for Water Treatment and Water Quality Research and the Waite Institute Research Committee.

We are grateful to Erik Lock, Jennifer Beer, Craig Allen, Geoff Fraser, Paul Knight, Michelle Sexton and Angela Waters for their technical assistance. Evangelo Cotsaris (State Water Laboratory, S.A. Engineering and Water Supply Department) made the DOC measurements, Lynne Giles (Biometry Section, Waite Agricultural Research Institute) performed the statistical analyses, Dr. John Hanna (CSIRO Division of Fuel Technology) obtained the CP/MAS ^{13}C-NMR spectra and Dr. Graeme Currie obtained the pyrolysis-MS spectra. The help and cooperation provided by the Victorian Department of Conservation and Environment (Colac Region) is also acknowledged with thanks.

References

Baldock JA, Currie GJ & Oades JM (1991) Organic matter as seen by solid state ^{13}C NMR and pyrolysis mass spectrometry. In: Wilson WS (Ed) Advances in Soil Organic Matter

Research: The Impact on Agriculture and the Environment. The Royal Society of Chemistry, Cambridge

Conservation, Forests and Lands, Victorian Department of (1984) Vegetation map of the Otway Ranges (unpublished)

Cronan CS (1990) Patterns of organic acid transport from forested watersheds to aquatic ecosystems, pp 245—260. In: Perdue EM & Gjessing ET (Eds) Organic Acids in Aquatic Ecosystems. John Wiley and Sons, London

Dawson HJ, Hrutfiord BF, Zasoski RFJ & Ugolini FC (1981) The molecular weight and origin of yellow organic acids. Soil Sci. 132: 191—199

Douglas JG (1977) The geology of the Otway Region, southern Victoria. Proc. Roy. Soc. Vic. 89: 19—25

Duncan TM (1987) ^{13}C chemical shielding in solids. J. Phys. Chem. Ref. Data 16: 125—151

Dunnivant FM, Jardine PM, Taylor DL & MacCarthy JF (1992) Transport of naturally occurring dissolved organic carbon in laboratory columns containing aquifer material. Soil Sci. Soc. Am. J. 56: 437—444

Fisher RK (1982) Investigations of the natural organic compounds in some Australian freshwater streams. M. App. Sc. Thesis, Chisholm Institute of Technology

Gee GW & Bauder JW (1986) Particle-size analysis, pp 383—411. In: Klute A (Ed) Methods of Soil Analysis. Part I. Physical and Mineralogical Methods. 2nd Edition. American Society of Agronomy/Soil Science Society of America, Madison, Wisconsin

Greenland DJ (1970) Sorption of organic compounds by clays and soils. Monograph 37 Soc. Chem. Ind

Grieve IC (1984) Concentrations and annual loading of dissolved organic matter in a small moorland stream. Freshwater Biol. 14: 533—537

Hart BT & McKelvie ID (1986) Chemical Limnology in Australia. In: DeDekker P & Williams WD (Eds) Limnology in Australia. Dr. W. Junk Publishers, Dordrecht

Hine PT & Bursill DB (1987) Seasonal trends in natural organics in South Australian waters and their effects on water treatment. AWRAC Research Project 84/167

Hine PT, Couche DJ, Bursill DB & Summer A (1986) Analytical method for dissolved organic carbon. State Water Laboratory Technical Report No. 9. Engineering and Water Supply Department, South Australia

Jardine PM, Weber ML & MacCarthy JF (1989) Mechanisms of dissolved organic carbon adsorption on soil. Soil Sci. Soc. Am. J. 53: 1378—1385

Kramer JR, Brassard P, Collins P, Clair TA & Takats P (1990) Variability of organic acids in watersheds, pp 127—139. In: Perdue EM & Gjessing ET (Eds) Organic Acids in Aquatic Ecosystems. John Wiley and Sons, London

Leenheer JA (1980) Origin and nature of humic substances in the waters of the Amazon River Basin. Acta Amazonica 10: 513—526

Linforth DJ (1977) The climate of the Otway Region. Proc. Roy. Soc. Vic. 89: 61—68

McDonald RC, Isbell TF, Speight JG, Walker J & Hopkins MS (1990) Australian Soil and Land Survey: Field Handbook. 2nd Edition (Inkata Press: Melbourne)

McDowell WH & Likens GE (1988) Origin, composition and flux of dissolved organic carbon in the Hubbard Brook Valley. Ecological Monographs 58: 177—195

McDowell WH & Wood T (1984) Podzolization: soil processes control dissolved organic carbon concentrations in stream water. Soil Sci. 137: 23—32

Meyer JL (1986) Dissolved organic carbon dynamics in two subtropical blackwater rivers. Archiv. füer Hydrobiologia 108: 119—134

Meyer JL (1990) Production and utilization of dissolved organic carbon in riverine ecosystems. In: Perdue EM & Gjessing ET (Eds) Organic Acids in Aquatic Ecosystems (pp 281—299). John Wiley and Sons, London

Moore TR (1989) Dynamics of dissolved organic carbon in forested and disturbed catchments, Westland, New Zealand. 1. Maimai. Water Resources Res. 25: 1321—1330

Moore TR & Jackson RJ (1989) Dynamics of dissolved organic carbon in forested and disturbed catchments, Westland, New Zealand. 2. Larry River. Water Resources Res. 25: 1331—1339

Nelson PN, Cotsaris E, Oades JM & Bursill DB (1990) Influence of soil clay content on dissolved organic matter in stream waters. Aust. J. Mar. Freshwater Res. 41: 761—774

Oades JM, Vassallo AM, Waters AG & Wilson MA (1987) Characterization of organic matter in particle size and density fractions from a red-brown earth by solid-state ^{13}C NMR. Aust. J. Soil Res. 25: 71—82

Parsons RF, Kirkpatrick JB & Carr GW (1977) Native vegetation of the Otway Region, Victoria. Proc. Roy. Soc. Vic. 89: 77—88

Pitt A (1977) Soils of the Otway Ranges and surrounding coastal plain. Proc. Roy. Soc. Vic. 89: 69—75

Reeve R & Fergus IF (1982) Black and white waters and their possible relationship to the podzolization proces. Aust. J. Soil Res. 21: 59—66

Schulthess CP & Huang CP (1991) Humic and fulvic acid adsorption by silicon and aluminium oxide surfaces on clay minerals. Soil Sci. Soc. Am. J. 55: 34—42

Sedell JR & Dahm CN (1990) Spatial and temporal scales of dissolved organic carbon in streams and rivers. In: Perdue EM & Gjessing ET (Eds) Organic Acids in Aquatic Ecosystems (pp 261—279). John Wiley and Sons, London

St. John TV & Anderson AB (1982) A re-examination of plant phenolics as a source of tropical black water rivers. Tropical Ecology 23: 151—154

Thurman EM (1985) Organic Geochemistry of Natural Waters. Martinus Nijhoff/Dr. W. Junk Publishers: Dordrecht

Tipping E (1990) Interactions of organic acids with inorganic and organ surfaces. In: Perdue EM & Gjessing ET (Eds) Organic Acids in Aquatic Ecosystems (pp 209—221). John Wiley and Sons, London

Zarcinas BA, Smith LH & Stace HCT (1982) Instructions for surface areas analyses and calculations. Notes on Soil Techniques No. 4. Commonwealth Scientific and Industrial Research Organisation, Division of Soils, Australia