

Sedimentary organic matter geochemistry of Clayoquot Sound, Vancouver Island, British Columbia

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Abstract

Surface sediment samples from three interconnected fjords of Clayoquot Sound, British Columbia, were density fractionated (1.6 g cm^{-3}) to isolate discrete organic debris (OD) from mineral-associated organic matter (MOM). Total organic carbon (OC) values varied greatly, ranging from $<0.1\%$ to 8.8% by weight, with a general decreasing trend from fjord head to the continental shelf. Within the sediment, terrestrial OM was present either as vascular plant debris or soil MOM. Down-fjord, the woody vascular plant material in the OD fraction acquires nitrogen, which is hypothesized to be due to the bacterial incorporation of nitrogen from the water. Terrestrial OC in the MOM is incompletely replaced by marine OC within the fjords, resulting in a 65% net loss of MOM. Sediments deposited under oxic and intermittently anoxic water column conditions have organic carbon to surface area ratios (OC:SA) ranging from 0.4 to 1.2 mg C m^{-2} , similar to that of typical continental margin sediments. Given that temperate fjords contain an estimated 12% of the continental margin sediment deposited during the last 100,000 yr, and that they bury at least a margin-equivalent amount of OC (either weight or surface area normalized), we hypothesize that temperate fjords may contain 12% or more of the sedimentary OC buried during this time.

Temperate fjords contain less than 0.1% of the total volume of continental margin sediments, yet they hold 12% of the total volume of margin sediment deposited during the last 100,000 yr (calculated from Syvitski et al. 1987). Because understanding the preservation of organic carbon (OC) in continental margin sediments is essential for balancing the global carbon budget (Bernier 1989; Hedges and Keil 1995), determining carbon storage in fjords is of interest. While enough terrestrial particulate OC is discharged by rivers to account for all the OC currently buried in marine sediments (Bernier 1989; Hedges and Keil 1995), only a small fraction appears to be preserved there (Hedges et al. 1997). Questions persist as to the fate of terrestrial OC in marine sediments because this relatively refractory form of reduced carbon must either be mineralized or structurally unrecognizable (Hedges et al. 1997). Temperate fjords receiving a large flux of terrestrial OC are thus ideal for studying the transport and diagenesis of this material in situ.

The term fjord applies to high-latitude, coastal estuaries created through glacial erosion and sea-level fluctuations that have occurred since the last glacial maximum approximately 17,000 B.P. (Syvitski et al. 1987). Several features are characteristic of most fjords: they are long compared with their width, are steep-sided and deep, typically possess one or more submarine sills that may be remnant moraines, and usually have a river draining into the head (Farmer and Free-land 1983). All silled fjords are immature estuaries and hence sites of net sediment accumulation. Unusually high marine sediment OC contents in excess of 10% by weight

have been recorded from many fjord basins (Skei 1983). It has been hypothesized that temperate fjords are globally significant carbon sinks because of the high influx of terrestrial, refractory OC (Burrell 1988). However, to our knowledge, no studies have been conducted within fjords to specifically examine the mixture of terrestrial (derived from the watershed) and marine (produced in the saline estuarine waters) sedimentary material.

Sedimentary organic matter (OM) can exist as discrete particles or be associated with inorganic minerals in a number of ways (Keil et al. 1994; Arnarson and Keil 2001). The importance of organic/mineral interactions is supported by the strong correlation between OC concentration and mineral surface area (SA) in sediments of different size and density fractions regardless of mineralogy (Keil et al. 1994; Mayer 1994*a,b*). The organic carbon to surface area ratio (OC:SA) is a powerful means for determining sites with unusually high or low preservation potential. However, depositional environments with large amounts of distinct organic debris can compromise the utility of the OC:SA measurement by causing an overestimate of OC that is truly mineral associated.

In this study, density fractionations of surface sediment from three interconnected, temperate fjords were performed in order to physically separate minerals and their associated organic matter from distinct organic fragments. Terrestrial and marine contributions to, and diagenetic alterations of, sedimentary OC are assessed by elemental (C and N) and isotopic ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) analyses of these fractions. The SAs of sedimentary minerals were determined in order to evaluate spatial sedimentation patterns and to normalize the concentration of OC by attenuating artifacts due to grain-size variations (Keil et al. 1997).

Study site—The Pacific coastline of British Columbia's Vancouver Island is indented with numerous long, narrow fjords with shallow, glacially formed sills at their mouths. Clayoquot Sound consists of a series of interconnected fjords

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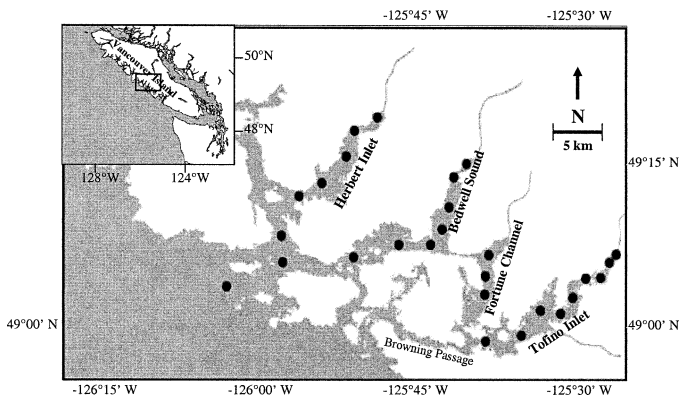


Fig. 1. Map of the Clayoquot Sound fjord system. Surface sediment sampling locations are noted. Streambed samples were collected along Tofino Creek at the head of Tofino Inlet.

whose sills are among the shallowest of Vancouver Island (Fig. 1). Of all the west coast inlets of Vancouver Island, the fjords of Clayoquot Sound exhibit the greatest difference from open ocean water characteristics, possibly because of their extremely shallow sills (Pickard 1963). Although these fjords are relatively similar, they have been unsystematically named “inlet,” “sound,” and “channel.” The three fjord systems to be discussed, Herbert Inlet, Bedwell Sound, and Fortune Channel/Tofino Inlet, all share a common sill. In addition to its connection through Fortune Channel, Tofino Inlet is connected to the outer sill by Browning Passage (Fig. 1). Both Herbert and Tofino are believed to be intermittently anoxic, with a small, permanently anoxic basin at the head of Tofino. Bedwell is shallower than the other inlets and is likely to be permanently oxygenated as determined by water column surveys (Pickard 1963; Greengrove et al. 2004).

The dominant sources of sediment to the fjords are from rivers that flow into their heads. The Kennedy River, which drains a lake of comparable size to the fjords, is also a significant source of freshwater to Tofino Inlet's central basin. However, because the lake allows for the settling of particulates, the Kennedy River is unlikely to be a major source of sediment. Unlike many mainland British Columbian fjords whose rivers are fed mainly by glacial melt during the summer, the temperate fjords of Vancouver Island do not drain significant ice fields and thus experience their maximum river discharge during the winter peak in precipitation (Pickard 1963). During this time, the freshwater transport of particulate OC to fjords is greatest, and two-layer circulation within fjords is best developed (Syvitski et al. 1987). While sediment at fjord heads is river derived, the coarse surficial sediments found on the sill and lower fjord most likely do not have a modern river source. Instead these minerals are either relict sediments deposited during maximum glacial extent or are being placed there by alongshore transport outside of the fjords.

The temperate rainforest that borders Clayoquot Sound supports lush vegetation composed almost exclusively of C_3 trees, including western hemlock, amabilis fir, western red cedar, and Douglas fir. Only on the subaerial and intertidal deltaic deposits at the fjord heads are C_4 grasses likely to be present.

Methods

All samples were collected aboard the R/V *Clifford A. Barnes* during cruises in September 2001 and 2003. Surface sediments, approximately the top 20 cm, were collected using a Van Veen grab sampler. Marine organic matter end members were collected by surface plankton net tows within Bedwell and at the outer sill. Terrestrial plant materials and streambed sediments were hand picked in the Tofino Creek watershed at the head of Tofino Inlet and identified aboard ship. Although the streambed samples are composed predominantly of sand, they also include smaller amounts of silt and clay that winnow to the fjords. All samples were immediately frozen for transport.

After thawing, the surface sediment samples were homogenized and then sieved through a 385- μm sieve in order to remove any coarse debris and fauna that would interfere with OC and surface area measurements. Samples were washed three times with distilled water to remove salts and then freeze dried. Bulk sediment samples were divided into two density fractions, mineral containing and mineral free, using heavy liquid floatation in a sodium polytungstate solution of density 1.6 g cm^{-3} (Arnarson and Keil 2005). After adding the dense solution to the sediment, the samples were sonicated in a water bath for 10 min in order to break up macroaggregates and unstable microaggregates (Golchin et al. 1994; Arnarson and Keil 2001). Samples were then centrifuged at 24,000 $\times g$ for 20 min. A pipette was used to remove the low-density material suspended in the supernatant after centrifugation. These steps were repeated until no additional material remained in the supernatant. The low-density organic debris (OD) fraction consists of all of the material of density $<1.6 \text{ g cm}^{-3}$, while the high-density mineral-associated organic matter (MOM) fraction contains all material $>1.6 \text{ g cm}^{-3}$. Both fractions were rinsed with distilled water, centrifuged, and decanted four times to remove the polytungstate salt and then freeze dried.

Weight percentages of organic carbon (OC) and total nitrogen (TN) were measured in triplicate for bulk samples, density fractions, and marine and terrestrial end members. The elemental compositions were measured with a Carlo Erba model 1106 CHN analyzer after vapor-phase acidification to remove inorganic carbon (Hedges and Stern 1984). Stable carbon and nitrogen isotopic compositions were determined in duplicate on a Finnigan Delta XL continuous flow isotope ratio mass spectrometer (IR-MS) interfaced with a Carlo Erba NC 2500. The SAs of the inorganic mineral matrices, normalized per unit mass, were measured by nitrogen adsorption using a five-point BET method on a Micromeritics ASAP 2010 surface area analyzer (Lowell and Shields 1991; Arnarson and Keil 2001). Before SA analysis the bulk sediment samples were gently ground with a mortar and pestle in order to break up the pellet formed during freeze drying, baked at 350°C for 12 h to remove organic matter, and degassed for 24 h to remove water. A scanning electron microscope (SEM) was used to visually inspect sediment composition.

Results

Bulk sediments—Sediment samples were collected as fjord transects (Fig. 2a). The percentage organic carbon by weight (%OC) of the bulk sediments covered a large range from 0.06% on the continental shelf just outside the sill to 8.8% at the head of Tofino Inlet (Table 1; Fig. 2b). When bulk organic carbon content was normalized to mineral SA (OC:SA), the samples ranged between 0.5 and 9.0 mg C m⁻². The majority of the sites have OC:SA ratios far in excess of those typically measured in continental margin sediments (0.5–1.1 mg C m⁻²) (Keil et al. 1994).

Mineral SA ranged from 1.2 m² g⁻¹ for shelf samples to 75 m² g⁻¹ in a deep fjord basin (Table 1; Fig. 2c). These values correspond to a range in particle size from >250 μm (coarse sand) to <1 μm (fine clay) (Keil et al. 1994). Low SA minerals are found adjacent to the river deltas at the heads of the fjords. Moving seaward, the minerals generally increase in SA until a maximum is reached 8–12 km seaward of the rivers. From these maxima, SA then decreases seaward (Fig. 2c). Low SA minerals are also found where Browning Passage meets Tofino Inlet.

Fractionated sediment and end members—The organic debris (OD) fraction always constituted a minority of the bulk sediment mass, but was occasionally the dominant form of OC found at a station (0–75% of total OC) (Table 1; Fig. 2b). In Bedwell and Tofino the sites in closest proximity to the head rivers were found to have the greatest amount of OD, with decreasing amounts found seaward. It was not possible to isolate any OD from stations seaward of the outer sill. In Herbert the three sites closest to the head river contain the greatest amount of OD (Fig. 2b).

For most of the stations MOM constitutes the majority of the sedimentary OC, up to 100% for sill stations (Table 1; Fig. 2b), with %OC values that range from 0.06% to 4.7%. This fraction's OC:SA values average 0.8 ± 0.2 mg C m⁻² and range between 0.4 and 1.2 mg C m⁻², similar to the range generally measured along continental margins (0.5–1.1 mg C m⁻²) (Keil et al. 1994) (Fig. 2d). Streambed MOM has an average OC:SA of 1.5 ± 0.07 mg C m⁻². The permanently anoxic basin at the head of Tofino Inlet has the highest OC:SA of 2.4 mg C m⁻² (Fig. 2d).

Density fractionation of bulk sediment highlights compositional differences between OD and MOM. Atomic C:N ratios of OD and MOM fractions ranged from 13.5 to 49.7 and from 8.3 to 18.8, respectively (Table 1; Fig. 2e). OD found at a particular station always has a higher C:N than MOM at the site. For all of the fjords, the C:N values of both fractions decrease with increasing distance from the fjord head. The C:N of MOM is consistent (9.47 ± 1.2) from within approximately 10 km of the fjord heads to the shelf. Compared with most fjord samples, MOM isolated from streambed samples have high C:N ratios (~17) (Table 1). Terrestrial end member C:N ranged from 37 to 300, with leafy material having lower C:N than woody material (Table 2), and marine plankton samples having the lowest measured C:N values (~8.6).

Fjord sediment δ¹³C values ranged from -27.0‰ to -22.6‰ for OD and from -24.9‰ to -19.0‰ for MOM

(Table 1; Fig. 2f). While OD of both Herbert and Tofino have similar δ¹³C values throughout, there is an increase in δ¹³C with distance down-fjord in Bedwell (Fig. 2f). δ¹³C of MOM generally increased down-fjord. δ¹³C of streambed MOM (-26.8‰) is depleted relative to all fjord MOM samples (Fig. 2f). Terrestrial end members ranged from -34.4‰ to -25.0‰, with woody material being more enriched than leafy (Table 2), and marine plankton having the lowest measured δ¹³C (-17‰).

Fjord sediment δ¹⁵N values ranged from -0.15‰ to 8.7‰ for OD and from 4.8‰ to 9.0‰ for MOM (Table 1; Fig. 2g). Both fractions show a general down-fjord increase in δ¹⁵N with similar values close to the sill (Fig. 2g). δ¹⁵N of terrestrial end members ranged from -1.6‰ to 0.25‰ (Table 2), and marine plankton had a high δ¹⁵N value of 9.0‰.

Discussion

Organic debris—Visual identification by SEM and the nearly constant δ¹³C of the OD fraction in both Herbert and Tofino (Fig. 2f) indicate that woody terrestrial material is the source of the OD throughout these fjords (Fig. 3a). Similarly, wood fragments have been found to be the dominant form of particulate OM in Howe Sound, British Columbia (Adams and Bustin 2001). However, the δ¹³C of the OD in Bedwell becomes more enriched down-fjord from -27.0‰ to a value similar to that found in Herbert and Tofino. This difference is likely due to a considerable amount of leafy terrestrial material deposited at Bedwell's head that becomes less significant down-fjord (Fig. 3a). This was confirmed using SEM.

The C:N ratio and δ¹³C of fractionated sediments have previously been used as a means of identifying the origin of sedimentary OM (e.g., Keil et al. 1994), while δ¹⁵N is often used to distinguish trophic levels and understand OM alteration during early diagenesis (Fogel and Tuross 1999; Lehmann et al. 2002). Differences in δ¹⁵N values of terrestrial and marine end members (Table 2) are due to their different mechanisms for acquiring nitrogen. While terrestrial plants rely on nitrogen-fixers to convert atmospheric N₂ (δ¹⁵N = 0‰) to usable forms, marine microorganisms assimilate dissolved nitrogen. Pacific Ocean dissolved nitrate has an average δ¹⁵N of 6‰ (Brandes 1996), but has been shown to be higher (7–9‰) within such Pacific estuaries as Puget Sound (Kassakian unpubl. data). The down-fjord decrease in C:N is accompanied by a 9‰ increase in the δ¹⁵N of the OD within all of the inlets (Tables 1, 2; Fig. 3b). These trends are consistent with the down-fjord addition of a marine end member to a terrestrially derived source material. It has been shown that vascular plant materials gain nitrogen (decrease C:N) while submerged (Hernes 1999). This accumulation of nitrogen occurs as carbon-rich polysaccharides and lignins from vascular plant tissues are converted to microbial biomass (Hedges and Oades 1997). While an increase in δ¹⁵N is usually attributed to the fractionation of OM through a series of trophic levels, the amount of fractionation per trophic level is small (<2‰) (Peterson et al. 1985). To account for the dramatic 9‰ down-fjord increase in OD δ¹⁵N, the terrestrial source material would have to

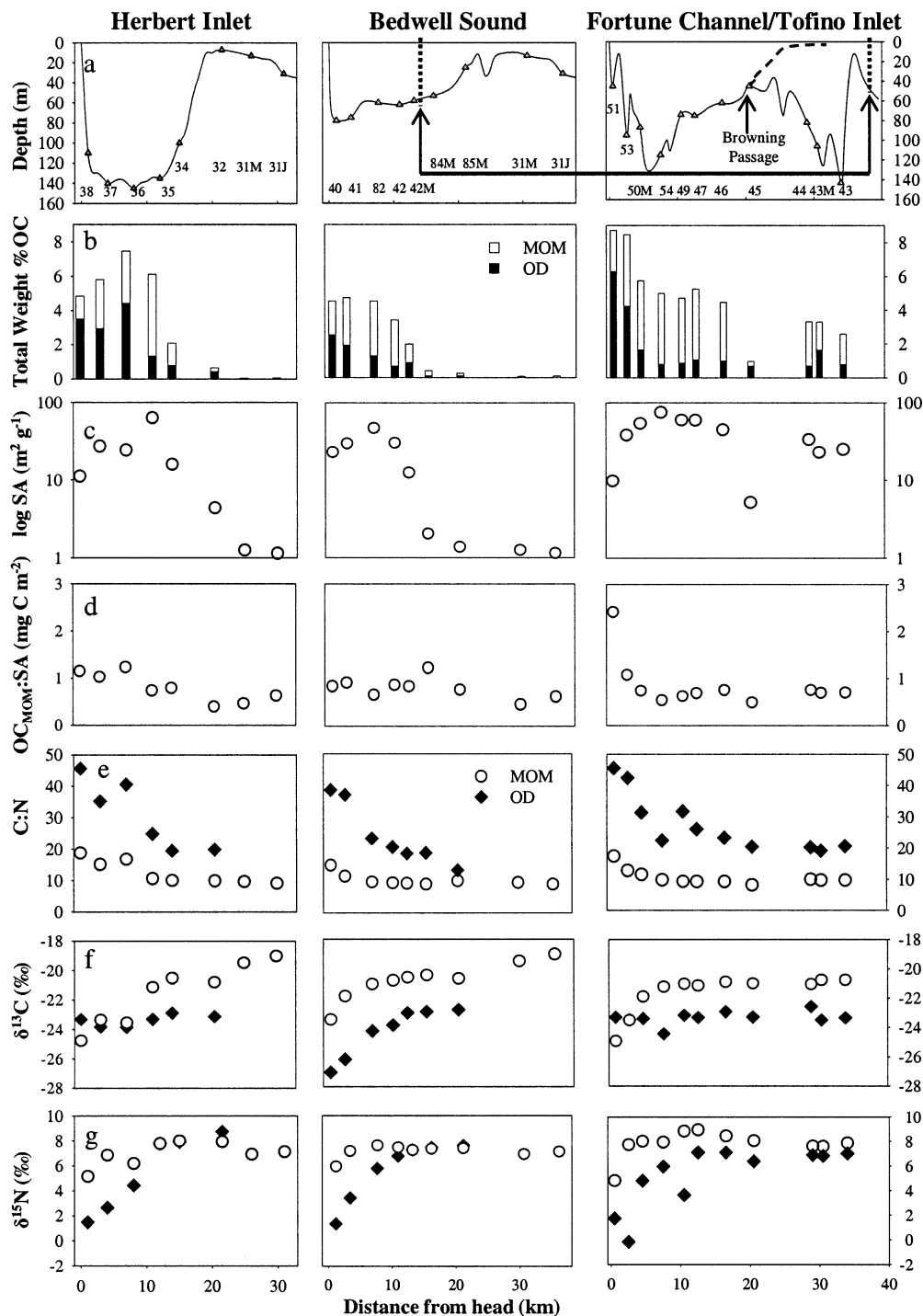


Fig. 2. Surface sediment characteristics from transects of Herbert Inlet, Bedwell Sound, and Fortune Channel/Tofino Inlet. Values for the MOM (white) and organic debris (black) density fractions are shown. (a) Station depth, with vertical dotted lines indicating the junction of Bedwell Sound and Fortune Channel, and a dashed line indicating Tofino Inlet's connection to the outer sill through Browning Passage, (b) contributions of density-fractionated sediment to the weight percentage organic carbon of the bulk sediment, (c) mineral surface area of the heavy fraction, (d) mineral-associated organic carbon to surface area ratio, (e) organic carbon to total nitrogen ratio (atomic), (f) organic $\delta^{13}C$, and (g) organic $\delta^{15}N$.

Table 1. Organic and mineral data for bulk and density-fractionated sediments.

Location	Station	Latitude	Longitude	Depth (m)	Bulk				Mineral-associated organic matter				Organic debris					
					Mineral		OC:SA		wt		OC:SA		wt		C:N		δ ¹³ C	
					SA (m ² g ⁻¹)	wt (%)	OC:SA (mgC m ⁻²)	wt (%)	OC:SA (mgC m ⁻²)	wt (%)	OC:SA (mgC m ⁻²)	C:N	δ ¹³ C (‰)	δ ¹⁵ N (‰)	wt (%)	OC:SA (mgC m ⁻²)	C:N	δ ¹³ C (‰)
Sill	31J	49.117	-126.065	31	1.15	0.07	0.63	0.07	0.63	9.16	-19.00	7.15						
Herbert Inlet	31M	49.137	-126.020	13	1.26	0.06	0.47	0.06	0.47	9.71	-19.47	6.95						
	32	49.156	-126.022	7	4.40	0.64	1.45	0.18	0.40	9.93	-20.78	7.97						
	34	49.187	-126.008	100	16.00	2.09	1.31	1.27	0.79	10.08	-20.51	8.01						
	35	49.197	-125.588	135	63.87	6.10	0.96	4.73	0.74	10.66	-21.12	7.81						
	36	49.217	-125.569	145	24.33	7.45	3.06	3.00	1.23	16.84	-23.55	6.21						
Bedwell Sound	37	49.236	-125.562	140	27.35	5.80	2.12	2.82	1.03	15.18	-23.34	6.87						
	38	49.247	-125.545	110	11.20	4.83	4.31	1.29	1.15	18.82	-24.77	5.16						
	85M	49.140	-125.564	25	1.39	0.24	1.72	0.11	0.78	10.20	-20.65	7.41						
	84M	49.150	-125.527	53	2.06	0.39	1.87	0.26	1.24	9.14	-20.42	6.36						
	42M	49.151	-125.502	58	12.50	1.96	1.57	1.06	0.85	9.41	-20.58	7.26						
Fortune Channel	42	49.161	-125.493	62	30.53	3.39	1.11	2.69	0.88	9.55	-20.78	7.48						
	82	49.179	-125.487	60	47.42	4.49	0.95	3.19	0.67	9.84	-21.03	7.64						
	41	49.201	-125.483	75	29.95	4.71	1.57	2.77	0.93	11.68	-21.86	7.18						
	40	49.212	-125.473	78	23.15	4.51	1.95	1.97	0.85	15.08	-23.44	5.96						
	43	49.142	-125.455	143	25.10	2.59	1.03	1.78	0.71	9.81	-21.41	7.90						
Tofino Inlet	43M	49.127	-125.458	106	23.00	3.29	1.43	1.63	0.71	9.77	-20.76	7.62						
	44	49.112	-125.459	82	33.66	3.31	0.98	2.57	0.76	10.08	-21.05	7.64						
	45	49.075	-125.459	45	5.19	0.97	1.87	0.26	0.50	8.27	-21.00	8.08						
	46	49.081	-125.430	62	45.10	4.46	0.99	3.44	0.76	9.33	-20.89	8.48						
	47	49.099	-125.414	75	59.82	5.25	0.88	4.16	0.70	9.34	-21.13	8.96						
Streambed	49	49.097	-125.399	74	60.08	4.71	0.78	3.81	0.63	9.37	-21.03	8.86						
	54	49.109	-125.389	115	75.78	4.99	0.66	4.16	0.55	9.87	-21.21	7.96						
	50M	49.124	-125.378	87	54.34	5.76	1.06	4.06	0.75	11.61	-21.89	8.03						
	53	49.125	-125.366	95	38.56	8.46	2.19	4.19	1.09	12.90	-23.50	7.75						
	51	49.137	-125.359	45	9.82	8.81	8.97	2.38	2.42	17.48	-24.92	4.82						
	49.142	-125.355		4.37	2.56	5.86	0.62	1.43	16.75	-27.88	1.81							
	49.142	-125.355		7.28	1.85	2.54	1.12	1.53	17.58	-25.74	1.60							

Table 2. Elemental and isotopic compositions of terrestrial materials and marine plankton.

Sample	C:N	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)
Plankton (fjord)	7.89	-17.21	8.81
Plankton (sill)	9.38	-16.76	9.28
Cedar wood	300.10	-25.05	-1.37
Hemlock needles	46.35	-28.97	-1.56
Fern leaf	41.96	-34.42	-1.55
Maple leaf	41.11	-29.51	0.25
Alder leaf	36.59	-26.39	-1.36

cycle through approximately three to five trophic levels before being deposited at down-fjord sites. However this seems unlikely, and we favor the hypothesis that the 9‰ increase in $\delta^{15}\text{N}$ is due to the addition of heavy marine nitrogen to a terrestrial source material.

Neither the simple addition of marine plankton nor marine bacteria (both containing marine carbon and nitrogen) to terrestrial end members can account for both the observed $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ trends (Fig. 4). Instead the addition of marine nitrogen occurs without the significant addition of marine OC, allowing the OD to retain its terrestrial $\delta^{13}\text{C}$ signature. Because bacterial $\delta^{13}\text{C}$ compositions reflect their dominant food source (Fry and Sherr 1984), it is likely that upon entering the fjords the terrestrial material is used as a carbon source by colonizing bacteria. The overall $\delta^{13}\text{C}$ signature of the terrestrial material is conserved by carbon incorporation into bacterial biomass. Because the microorganisms themselves are nitrogen-rich compared with the terrestrial substrate, generally with C:N ratios between 4 and 5 (Müller 1977), they assimilate dissolved nitrogen to produce proteins. Assuming that bacteria, like marine phytoplankton, incorporate nitrate with little isotopic fractionation (Lui and Kaplan 1989), it is expected that bacteria within the fjords would have $\delta^{15}\text{N}$ values similar to the measured plankton ($\sim 9\text{‰}$).

Two-end member isotopic mixing models (Prahl et al.

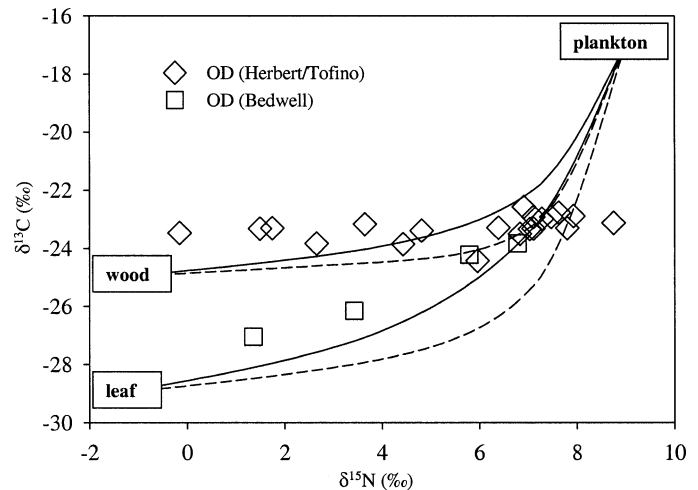


Fig. 4. Trends in $\delta^{13}\text{C}$ versus $\delta^{15}\text{N}$ for organic debris. End member mixing of a terrestrial source material with marine plankton (solid line) and marine bacterial biomass (dashed line).

1994) were used in order to quantify the proportions of terrestrial nitrogen (%Terr N_{OD}) and carbon (%Terr C_{OD}) in the OD. While similar models generally use C:N and $\delta^{13}\text{C}$ values to delineate terrestrial/marine contributions, the inclusion of bacterial OM without a definitive $\delta^{13}\text{C}$ value prevents such modeling. Instead the $\delta^{15}\text{N}$ of a theoretical marine bacteria ($C:N_{\text{bac}} = 4\text{‰}$; $\delta^{15}\text{N}_{\text{bac}} = 9\text{‰}$) and the average of the terrestrial materials ($\delta^{15}\text{N}_{\text{terr}} = -1.1\text{‰}$) were used as end members for %Terr N_{OD} (Fig. 3b).

$$\% \text{Terr } N_{\text{OD}} = \left[\frac{(\delta^{15}\text{N}_{\text{OD}} - \delta^{15}\text{N}_{\text{bac}})}{(\delta^{15}\text{N}_{\text{terr}} - \delta^{15}\text{N}_{\text{bac}})} \right] \times 100$$

Results of the $\delta^{15}\text{N}$ end member mixing model indicate that the %Terr N_{OD} decreases down-fjord from 88% to 3% (Fig. 5a), suggesting that up to 97% of the OD nitrogen is derived from estuarine or marine sources.

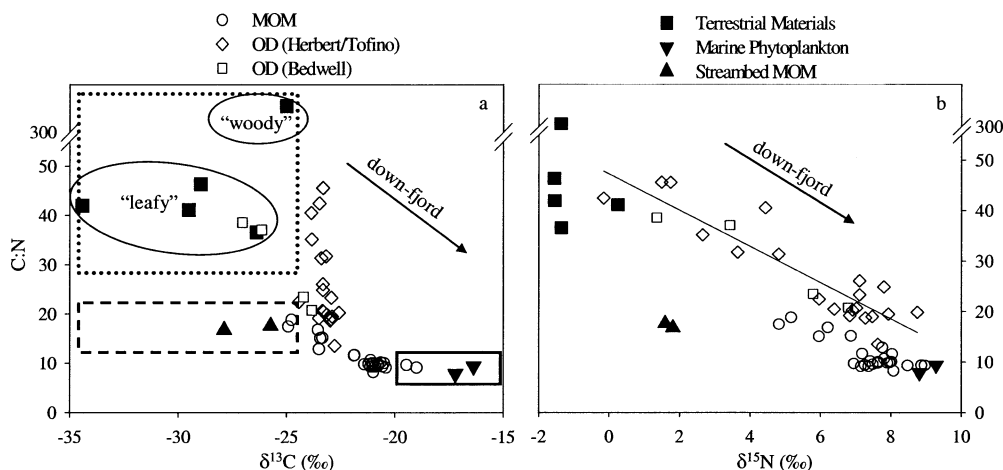


Fig. 3. Trends in atomic C:N ratio versus (a) $\delta^{13}\text{C}$, and (b) $\delta^{15}\text{N}$, for MOM, organic debris, terrestrial materials, marine plankton, and streambed MOM. Marine plankton and streambed OM act as end members for the fjord MOM fraction. Typical ranges for vascular plant detritus (dotted box), soil OM (dashed box), and marine OM (solid box) are estimated from analyzed samples and references cited in the text. Typical values for "woody" and "leafy" terrestrial materials are noted.

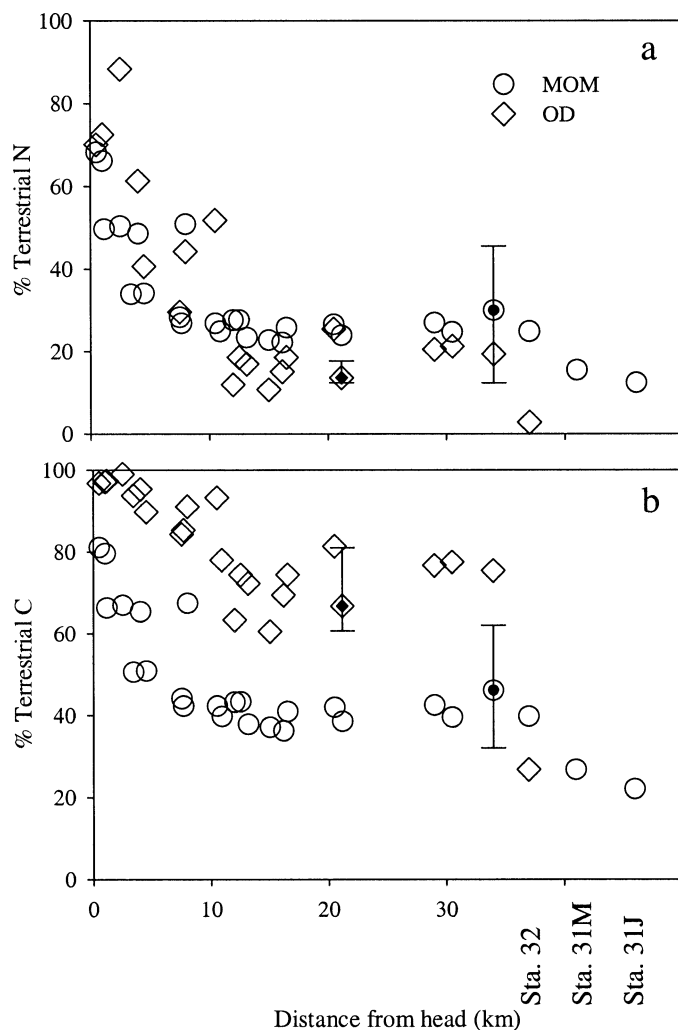


Fig. 5. Modeled percentage terrestrial (a) nitrogen and (b) carbon versus distance from the fjord heads for organic debris and MOM. Sampling stations on the outer sill are noted. Error bars indicate deviations from the modeled values when a range of alternative terrestrial end members are employed.

Before it is possible to calculate %Terr C_{OD} , it is necessary to pinpoint the C:N ratio of the terrestrial source material. While the majority of the OD appears to be derived from wood (Fig. 3a), the sedimentary OD is substantially enriched in $\delta^{13}C$ and depleted in C:N compared with this end member. Because the terrestrial materials analyzed were collected from live plants, these differences may be due to early diagenesis of the OD either on the forest floor or after being introduced to the marine environment. Small enrichments of $\delta^{13}C$ have been observed during early diagenesis in both soils (Baisden et al. 2002) and marine sediments (Freudenthal et al. 2001). Soil OM has also been shown to have lower C:N values than fresh terrestrial plant materials (Hedges and Oades 1997). Therefore we suspect the predominant source of the OD to be terrestrially degraded wood. Assuming no diagenetic alteration of end member $\delta^{15}N$ values, the linear fit of the OD C:N and $\delta^{15}N$ data results in a terrestrial source

material with $C:N_{terr} = 51$ (Fig. 3b). This calculated end member was then used to determine the %Terr C_{OD} :

$$\%Terr C_{OD} = \left\{ (C:N_{terr} \times \%Terr N_{OD}) \div [C:N_{terr} \times \%Terr N_{OD} + C:N_{bac} \times (100 - \%Terr N_{OD})] \right\} \times 100$$

There is a gradual down-fjord decrease in %Terr C_{OD} from >95% at the fjord heads to ~70% within the fjords, with <30% Terr C found at the only sill site where OD was able to be isolated (Fig. 5b). This indicates that the vast majority of the OD is buried as partially degraded wood, again confirmed by SEM. As a check, model calculations using plankton and wood as end members result in a planktonic $\delta^{13}C$ range of -21‰ to -24‰, depleted relative to true planktonic values. This verifies that the nitrogen being entrained in the OD is not due to planktonic OM sorbed to the wood particles. It is generally thought that due to the refractory nature of terrestrial OC, phytodetritus is the major source of energy to the subeuphotic benthos (Burrell 1988). Although our results suggest that terrestrial OC could be partially remineralized in surface sediments, some woody debris is likely to survive oxic respiration and sulfate reduction and eventually drive methanogenesis (Schlesinger 1991).

Mineral-associated organic matter—MOM most likely consists of a mixture of degraded terrestrial OC (derived from soils) and marine OC (e.g., Keil et al. 1994) (Figs. 3a, 4). At sites closest to the fjord heads the C:N and $\delta^{13}C$ of MOM is similar in character to that of the streambed sediment analyzed and of typical soil OM. Similar results have been observed for other river deltas (Showers and Angle 1986; Prahl et al. 1994). This streambed sediment OC is likely derived from soil, where carbon-rich compounds are preferentially used causing low C:N ratios compared with fresh terrestrial OM (Hedges and Oades 1997). Down-fjord stations have progressively lower C:N and enriched $\delta^{13}C$ values, consistent with the addition of marine OC, possibly replacing the mineral-bound soil OC (Fig. 3a). We are unable to determine whether the marine component of the MOM is derived from plankton and/or bacteria.

Similar to the OD fraction, end member isotopic mixing models were used to determine the contribution of terrestrial carbon (%Terr C_{MOM}) and nitrogen (%Terr N_{MOM}) to the MOM. $\delta^{13}C$ of plankton ($\delta^{13}C_{mar}$) and streambed MOM ($\delta^{13}C_{str}$) were used as end members for %Terr C_{MOM} (Fig. 3a):

$$\%Terr C_{MOM} = \frac{(\delta^{13}C_{MOM}) - (\delta^{13}C_{mar})}{(\delta^{13}C_{str}) - (\delta^{13}C_{mar})} \times 100$$

With the relative contributions of marine and terrestrial OM calculated, N:C values of the end members were then used to determine the %Terr N_{MOM} .

$$\begin{aligned} \%Terr N_{MOM} &= \frac{N:C_{str} \times \%Terr C_{MOM}}{N:C_{str} \times \%Terr C_{MOM} + N:C_{mar} (100 - \%Terr C_{MOM})} \\ &\times 100 \end{aligned}$$

These models suggest that the %Terr C_{MOM} decreases from a maximum of 81% at the head of Tofino to as low as 22% outside the sill (Fig. 5b). Along with the 78% loss of terrestrial OC down-fjord, up to 88% of terrestrial nitrogen is lost from sedimentary minerals (Fig. 5a). Similarly, MOM exported by the Amazon and Columbia Rivers has been shown to experience replacement of soil OC by marine OC upon deposition on the delta (Keil et al. 1997). Leithold and Blair (2001) hypothesized that the rates of reloading of particles with marine OC should depend on their exposure time to the water column in the surface mixed layer of the seabed and hence on sediment accumulation rate. Our results strengthen this hypothesis by showing a progressive decrease in the %Terr C_{MOM} as assumed sedimentation rates decrease down-fjord (*see also* Syvitski and Murray 1981).

Rock-derived OC, such as kerogen and graphite, is an additional component of MOM that has been shown to be a significant fraction of marine and terrestrial sediments (Blair et al. 2003; Dickens et al. 2004). Despite the low sedimentation rates and high degree of soil OM replacement, the MOM found at sill stations does not appear to be entirely marine (22% Terr C). This may be due to the persistence of mineral-bound kerogen, which, unlike the modern terrestrial component of soil OM, cannot be easily mineralized and replaced. Although rapidly eroding watersheds of tectonically active margins have been shown to promote the preservation and reburial of kerogen (Blair et al. 2003), this has not been systematically evaluated in our system.

Only after the removal of OD from MOM by density fractionation do OC:SA measurements accurately reflect the amount of OC influenced by mineral interaction. Without removal, large amounts of debris cause bulk sediments to have elevated OC:SA values (Keil and Hedges 1993). Before density fractionation, our bulk sediment samples had OC:SA values up to 360% higher than after fractionation. With the exception of the single anoxic station, streambed MOM has the highest carbon loading with an OC:SA of $1.5 \pm 0.07 \text{ mg C m}^{-2}$ (Fig. 6). Although fjord sites that are either oxic or intermittently anoxic have OC:SA values that fall within the range typical of oxygenated continental margin sediment, stations with the greatest amount of mineral-bound terrestrial OC have the greatest carbon loadings. Although such trends could be caused by the dilution of fluvial materials by the addition of low OC:SA marine inorganic surfaces such as calcite and opal biogenic debris, acidification of the sediments revealed no significant amounts of inorganic carbon, and sediments of nearby fjords contain little opal (Adams and Bustin 2001; Grocock et al. unpubl. data).

The down-fjord decrease in OC:SA is consistent with the net loss of MOM during replacement of terrestrial OC by marine OC (Fig. 6), as observed in the Amazon, Fly, and Columbia River deltas (Keil et al. 1997). Whether or not the terrestrial MOM being replaced is directly mineralized or released as dissolved OC remains unknown. The observed ~65% drop in OC:SA as marine replacement occurs suggests that a mineral's carrying capacity is lower for marine OC than terrestrial OC, or that replacement is incomplete.

Numerous studies have shown that suboxic and anoxic bottom water enhances organic matter preservation in marine sediments (Hartnett et al. 1998; Keil and Cowie 1999),

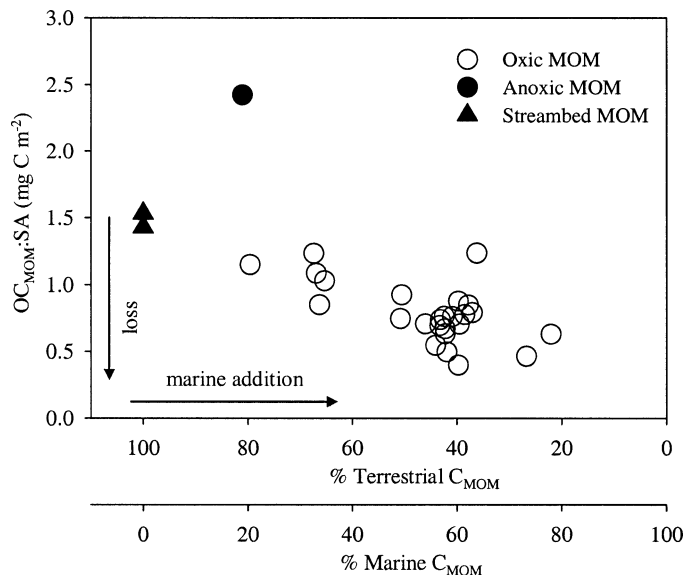


Fig. 6. Trends in OC:SA versus modeled %Terr C of marine oxic/intermittently anoxic MOM, marine anoxic MOM, and streambed MOM. OC:SA ratios for continental margin sediments typically range from 0.5 to 1.1 mg C m^{-2} . A downward shift in OC:SA denotes a net loss of MOM, while decrease in %Terr C indicates the addition of marine OC (Keil et al. 1997).

possibly by decreasing the efficiency of microbial oxidation of organic matter (Demaison and Moore 1980). As a result, sediments underlying oxygen-deficient water masses have OC:SA ratios in excess of those found in fully oxygenated regions (Keil and Cowie 1999). Based on the density and apparent oxygen use structure of the water column within Clayoquot Sound (Greengrove et al. 2004), we theorize that bottom water in both Herbert and Tofino are anoxic during the winter and then become replaced by upwelled, oxygenated water in late summer. The only site we know to be continually anoxic (Sta. 51, at the head of Tofino) displays the greatest relative preservation of MOM, possessing more than double the typical OC:SA (Fig. 6). Stations at the heads of Herbert and Bedwell do not display this excess loading, indicating that a high sedimentation rate is not likely responsible for the high OC:SA. Because the OC:SA values of all stations besides the anoxic site are close to the typical range, we hypothesize that intermittently anoxic bottom-water conditions are insufficient to cause elevated surface carbon loadings. Similar results have been documented in nearby Effingham Inlet (Grocock et al. unpubl. data).

Despite the differing morphology and annual water column conditions, the fjords of Clayoquot Sound display remarkably similar spatial trends in surface sediment characteristics. The greatest amount of terrestrial OC preservation occurs in close proximity to the fjord heads where fluvial sediment is rapidly buried, resulting in the preservation of relatively fresh woody debris and mineral-associated soil OM. The down-fjord increase of exposure time in the surface mixed layer due to lower sedimentation rates allows for (1) replacement of soil MOM by marine OM and (2) incorporation of bacterially derived OC into the distinct woody debris. The relative amount of carbon preserved by mineral

protection decreases as marine OM replaces terrestrial OM, resulting in a net loss of MOM. Intermittently anoxic stations have similar carbon loadings as oxic stations, with enhanced preservation of mineral-bound OC occurring only under permanently anoxic conditions. Because these processes have been observed previously along continental margins, studies within the fjords of Clayoquot Sound serve as a microcosm for continental margin processes.

The efficient trapping of both terrestrial OC and fine-grain clay minerals suggests that these fjords, and all temperate fjords, may be globally significant carbon sinks. Assuming that 12% of continental margin sediment deposited in the last 100,000 yr is within temperate fjords (Syvitski et al. 1987) and that these sediments have typical margin sediment OC:SA ratios and wt% OC values, then 12% of OC burial occurs in temperate fjords. However, if these sediments contain more than a shelf-equivalent quantity of OC, which is caused by the preservation of soil MOM and terrestrial debris, then burial may exceed 12% of OC in the last 100,000 yr. This implies that OC burial in temperate fjords may be a much larger component of the OC cycle than has previously been appreciated.

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