

## ASSESSING 'QUALITY' FROM A MICROBIAL PERSPECTIVE: CONTRASTS BETWEEN ORGANIC MATTER CHARACTERISTICS AND REMINERALIZATION RATES AND PATHWAYS

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### Introduction

Organic matter 'quality' has long been recognized to affect rates of microbial remineralization of organic matter (e. g. WESTRICH & BERNER, 1984), but factors determining 'quality' remain elusive. WESTRICH & BERNER (1984) defined organic matter components of their multi-G model empirically. 'Quality' has also been associated with specific characteristics of sedimentary POC (particulate organic carbon) such as C/N ratio, amino acid composition or contribution to sedimentary N, or carbohydrate and amino acid contribution to total organic carbon (e. g. COWIE & HEDGES, 1994; DAUWE *et al.*, 1999).

The extent to which bulk composition of sedimentary POC reflects the substrates actually used by sedimentary microbial communities is unclear, however, since a small, rapidly cycled fraction of POC – whose identity is obscured by a background of bulk POC – may fuel microbial metabolism. Furthermore, the methods typically used (e. g. COWIE & HEDGES, 1994; WAKEHAM *et al.*, 1997; DAUWE *et al.*, 1999) to measure POC composition provide no information on the manner in which these components are linked in macromolecular structures. Macromolecular structure is an important consideration since heterotrophic microbes must use extracellular enzymes to hydrolyze substrates to sizes sufficiently small (600 daltons; WEISS *et al.*, 1991) for transport across the membrane. The types of substrates accessible to a sedimentary microbial community therefore depend also on the activities and substrate specificities of the extracellular enzymes of the organisms.

We sought to measure carbon flow between the initial (enzymatic hydrolysis) and terminal steps in the carbon remineralization pathway in sediments dominated by different terminal remineralization processes: sulfate, iron, and manganese reduction. We also compared specific components of POC and DOC inventories with rates of remineralization processes. Do sediments dominated by different pathways differ from one another in bulk POC characteristics?

### Study site and methods

Sediment cores were collected from Stations S4, S6, and S9 in the Skagerrak (map in CANFIELD *et al.*, 1993) by multicorer and box corers. Sulfate, iron, and manganese reduction rates were measured in intact cores (SRR) and bags (FeR, MnR) as described in JØRGENSEN (1978), THAMDRUP & DALSGAARD (2000), and THOMSEN (2001). Total hydrolyzable amino acids (THAA) and carbohydrates (TCHO) were measured according to LINDROTH & MOPPER (1979) and PAKULSKI & BENNER (1992). DOC was measured by high-temperature combustion (SHARP, 1997); POC and PON were quantified by elemental analyzer (KRISTENSEN & ANDERSEN, 1987).  $\text{SCO}_2$  production and oxygen uptake were measured in intact cores incubated for 8 h at bottom water temperature, using flow injection/diffusion (HALL & ALLER, 1992) and Winkler titration, respectively. Extracellular enzymatic hydrolysis was measured (ARNOSTI, 1995) using pullulan as a substrate.

### Results and discussion

Bulk sediment characteristics (C/N, POC, PON) showed little variation with depth or between stations; C/N ratios were close to 12 for all stations (Fig. 1).

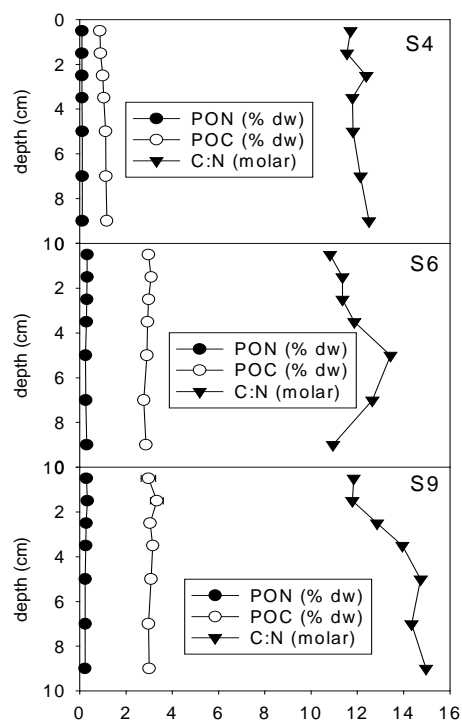


Fig. 1. Bulk sediment characteristics (C/N, POC, PON) at three stations in the Skagerrak.

Depth profiles of TCHO and THAA, the two compound classes that typically comprise most of marine plankton biomass (WAKEHAM *et al.*, 1997), were also relatively invariant (Fig. 2).

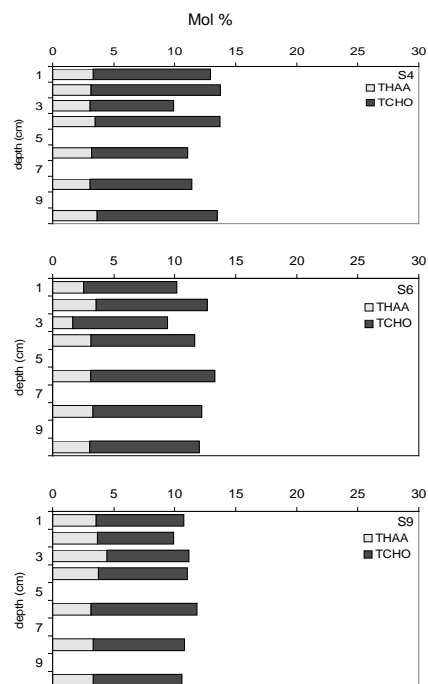


Fig. 2. Depth profiles of total carbohydrates (TCHO) and total hydrolyzable amino acids (THAA) at three stations in the Skagerrak.

Overall, an average of just 12% of POC could be attributed to TCHO and THAA. By comparison, WAKEHAM *et al.* (1997) identified, at a molecular level, approximately 20% of surface sediment TOC at a station in the equatorial Pacific. Stations S4, S6, and S9 therefore exhibit bulk sediment characteristics that could be considered consistent with 'low quality' organic matter.

A different perspective emerges, however, from the DOC concentration profiles. DOC is a key intermediate in carbon remineralization pathways, and DOC concentrations reflect

the outcome of production *via* hydrolysis/solubilization of POC and accumulation of fermentation products, and consumption of DOC by terminal members of the food chain. The different profiles among S4, S6, and S9 show that the balance of DOC production and removal must differ among the three stations (Fig. 3).

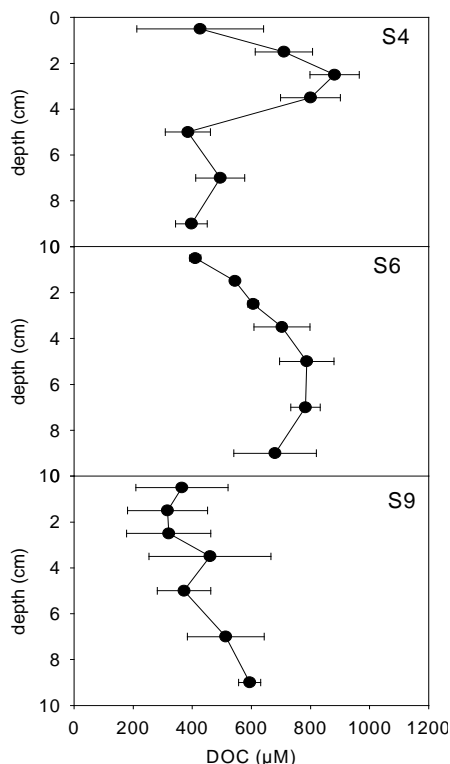


Fig. 3. Depth-dependent concentration of dissolved organic carbon (DOC) at three stations in the Skagerak.

Rates of extracellular enzymatic hydrolysis, the initial step in carbon remineralization, also showed depth- and site-related variations (Fig. 4).

Different terminal remineralization processes also dominated the three stations. Both sulfate and iron reduction were important at S4 and S6, whereas manganese reduction dominated S9 (Fig. 5).

Measurements of total carbon remineralization rates in intact cores showed that overall carbon oxidation rates at the three stations were quite high:  $14.5 \pm 4.1$ ,  $12.9 \pm 7$  and  $7.96 \pm 0.6$   $\text{mmol m}^{-2} \text{d}^{-1}$ , at S4, S6, and S9, respectively. These rates are especially high in comparison to other continental margin sediments from similar depths with comparable bulk POC characteristics. Rates measured in sediments from the mid-Atlantic shelf/slope break (BURDIGE *et al.*, 2000), the continental margin off Nova Scotia (GRANT *et al.*, 1998), and off the Pacific coast of Washington (KRISTENSEN *et al.*, 1999) ranged from  $1.92\text{-}4.66$   $\text{mmol m}^{-2} \text{d}^{-1}$ ,  $1\text{-}10$   $\text{mmol m}^{-2} \text{d}^{-1}$ , and  $2.33\text{-}6.07$   $\text{mmol m}^{-2} \text{d}^{-1}$ , respectively.

The rate measurements therefore suggest that carbon was being cycled relatively rapidly at these stations, despite their apparently unpromising bulk POC characteristics. Carbon flow through the DOC pool can be estimated by comparing DOC inventories (Fig. 3), extracellular enzyme activities (Fig. 4), and terminal remineralization rates (Fig. 5). Extracellular enzyme activities, as measured *via* polysaccharide hydrolysis, is particularly relevant to DOC remineralization, since carbohydrates appear to make a disproportionately large contribution to porewater DOC (e. g. ARNOSTI & HOLMER 1999; BURDIGE *et al.*, 2000).

Beginning with the simplifying assumption that DOC consists solely of carbohydrates, DOC concentrations can be recalculated as concentrations of hexose ( $\text{C}_6$  sugar) in polysaccharides. By comparing the potential hydrolysis rates (Fig. 4) with these DOC concentrations, the rates at which com-

bined carbohydrates in porewaters could theoretically be hydrolyzed to monomers (and therefore made available to a greater proportion of the sedimentary microbial community) can be estimated. This rate can be expressed as theoretical fractional turnover ( $\text{d}^{-1}$ ) of DOC.

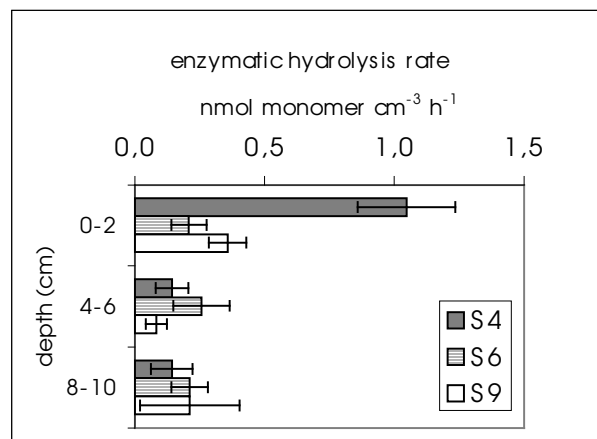


Fig. 4. Extracellular enzymatic hydrolysis rates as a function of depth for three stations in the Skagerak.

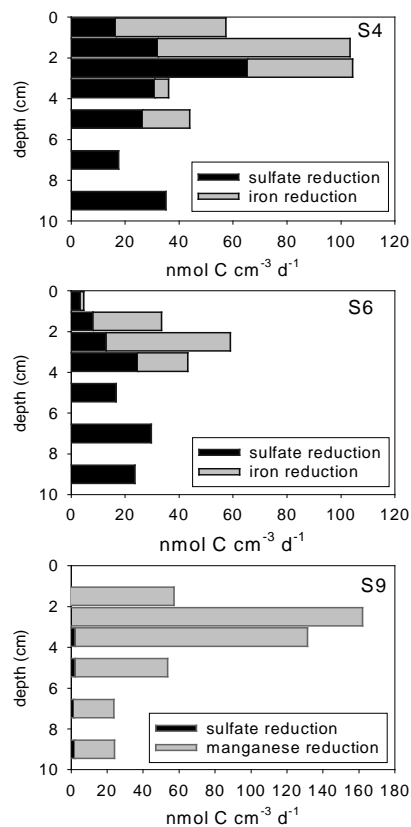


Fig. 5. Depth-related sulfate, iron and manganese remineralization rates at three stations in the Skagerak.

DOC turnover can be constrained by measurements of terminal remineralization processes (Fig. 5), which are fueled by low-molecular-weight substrates and therefore responsible for DOC consumption. Assuming 2, 0.25, and 0.5 moles of organic carbon oxidized for every mole of sulfate, iron, and manganese reduced, respectively (CANFIELD *et al.*, 1993), a carbon-equivalent fractional turnover can be calculated for the sum of the terminal remineralization processes (Fig. 6).

The fractional turnover rates demonstrate that a large proportion of the sedimentary DOC pool must, in fact, be turned over on a daily basis in order to support measured rates of carbon oxidation. For example, at S4, activities of

pullulanase enzymes could in theory hydrolyze 7-90% (average 36%) of the entire DOC pool to monomers over the course of a day. Turnover calculations based on terminal re-

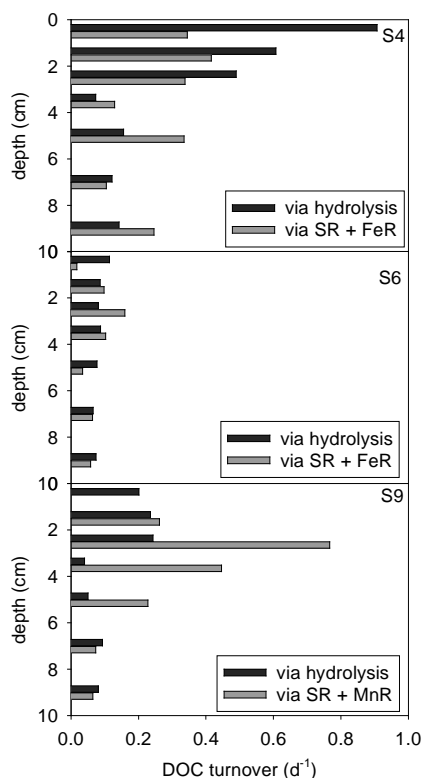


Fig. 6. DOC turnover rates for three stations in the Skagerrak.

mineralization rates at S4 show that the equivalent of 11-42% (average 28%) is cycled on a daily basis. These calculations show that in theory, activity of just one type of extracellular enzyme, pullulanase, is sufficient to provide much or all of the carbon ultimately remineralized in these sediments. These potential hydrolysis rates provide no information on the quantity of substrate actually available in sediments, however. Even if highly active enzymes are present, the quantity of carbon provided to the sedimentary microbial community may be limited by the availability of suitable starting substrate. The differences in depth-profiles of theoretical and 'real' fractional turnover shown in Fig. 6 may in part arise from this comparison between a specific enzyme potential and a net measure of carbon oxidation. Irrespective of the exact relationship between pullulanase enzyme activity and DOC consumption, however, some fraction of the DOC inventory must be rapidly cycled to fuel measured rates of carbon oxidation. Conversion of some fraction of POC to DOC must also be sufficiently rapid to provide this DOC for microbial consumption.

The contrast between bulk POC composition and rates of carbon oxidation demonstrate that bulk organic matter characteristics are not reliable indicators of the nature and quality of substrates available to sedimentary microbial communities in the Skagerrak. Rapid cycling of a small, microbially-available fraction of POC could account for high carbon flow through the DOC pool. This perspective becomes apparent, however, only when comparing rates of specific steps in the carbon remineralization pathway with sedimentary DOC inventories. Standard methods of assessing POC 'quality' are clearly insufficient in this case to reveal variability in organic matter reactivity that is important on a microbial scale.

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