Abstract

Holmes, Jennifer Cobb. Kerogen in the Eel River system of northern California - Characterization and analytical approaches for its study. (Under the direction of Neal E. Blair and Elana L. Leithold)

Kerogen, ancient organic matter formed over geologic time in sedimentary deposits, is the most abundant form of organic carbon (OC) on Earth. Continental margins are important sites for OC burial and the subsequent sequestering of C out of the atmosphere. Study of dynamics of OC in the global carbon cycle are important to understanding and predicting atmospheric gas levels, especially oxygen and CO$_2$. In the Eel River system in northern California kerogen-laden bedrock is subject to rapid erosion and transport to a marine shelf with high sediment accumulation rates. This area presents an opportunity to study kerogen dynamics in both terrestrial and marine settings. The objective of this study was to characterize changes in kerogen and modern OC associated with fine-grained sediment as particles move from a bedrock source to the seabed in the Eel River system. As a starting point, the organic matter of the kerogen-laden bedrock was characterized using elemental and isotopic analyses, FTIR, solid state NMR and Rock-Eval pyrolysis. The effectiveness of the various analytical tools for tracking the kerogen and studying OC transformations in the Eel River system was investigated.

Characterization of the kerogen found in the clay-rich melange bedrock of the Eel River watershed identified it as a mature Type III kerogen. More then 70% of the OC in the bulk bedrock sediment and ~90% of the OC in the clay-sized fraction of the bedrock was due
to kerogen. Low-density particles in the bedrock included fossilized wood fragments. The FTIR spectrum of the bitumen fraction isolated from the bedrock had a relatively strong aromatic character compared to other published bitumen spectra. The kerogen had low oxygen, nitrogen and sulfur contents and Rock-Eval analysis classified it as highly mature. The FTIR spectrum of the demineralized kerogen had strong aromatic and ether bands and lacked any distinct carbonyl peaks around 1710 cm\(^{-1}\). \(^{13}\)C CP-MAS NMR showed that ~70% of the OC in the kerogen was aromatic. Overall, the kerogen was found to be highly aromatic, un-weathered and with a significant terrestrial source component.

Microbial nitrogen processing complicates the use of C/N ratios for identifying source organic matter in the clay-sized fraction. In soils, C/N ratios reflect the degree of microbial organic matter alteration and are not good OC source indicators. In marine sediments on the Eel shelf, C/N ratios are potentially insensitive to organic matter changes in fine sediment fractions and are better suited for bulk sediment and coarse fraction analysis.

FTIR spectra can provide information about the molecular composition of the organic matter in the clay-sized fraction. Similarity in IR spectra did not consistently correspond to similarity in other characteristics, such as C/N or \(\delta^{13}\)C. Microbial processing may cause organic matter with similar characteristics to be spectrally variable, although microbial alteration is insufficient to explain differences in all the spectra analyzed.

Dual isotope analysis provided the best method for identifying and quantifying kerogen in modern sediments. Fractional kerogen contents were calculated using \(\delta^{13}\)C and \(\Delta^{14}\)C values. Kerogen persists in soils of the watershed and in the sediments of the Eel shelf. The clay-sized particles in all the sediments sampled appear to retain a kerogen OC load.
unaltered from bedrock levels. In the clay-sized fraction of the soils analyzed, generally 50% or more of the total OC was due to kerogen. Similar kerogen contents were also seen in surface sediments and recently buried sediments of the Eel shelf.
KEROGEN IN THE EEL RIVER SYSTEM OF NORTHERN CALIFORNIA -
CHARACTERIZATION AND ANALYTICAL APPROACHES FOR ITS STUDY

by

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APPROVED BY:

__________________________  ____________________________
Co-chair of Advisory Committee  Co-chair of Advisory Committee
Autobiography

While I was born in Louisiana, I grew up from the age of two in Woodruff, SC, a town of three traffic lights and a very active varsity booster club. While I need to mention several excellent teachers from my local schools, Mrs. Lispcomb (1st grade), Mr. Carson (7th grade), Mrs. Blevins (9th grade) and Mr. Thomas and Mrs. Ridings (10th grade), it was my time at the SC Governor’s School for Science and Mathematics that set my feet on this path. My last two years of high school at GSSM revolutionized my education and my life.

I received a B.S. in marine science from Jacksonville University in 1996, and it wasn’t until left I JU that I realized the quality of its program. So, thanks to Quint, Fred, Frank, Leeann and all the rest.

I enrolled at NCSU in 1998. It has taken me a very long time to finish this thesis, but I have learned as much about myself as I have about marine science. For that, I feel lucky.
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    The department is so lucky to have you.

To Dr. Lucinda Sonnenberg - Lucy, you were my boss, mentor and friend. You and the food are the only things I miss from Jax. I probably never would have gone to graduate school if not for you.

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To my parents, William and Elizabeth Cobb - Thank you for marine science camp, GSSM, and all your support. No one could ask for better parents.

To Sean - Thank you and I love you.
# Table of Contents

LIST OF TABLES ............................................................................................................. vi

LIST OF FIGURES .......................................................................................................... vii

1. INTRODUCTION AND BACKGROUND .................................................................1

   1.1 Introduction .............................................................................................................1
   1.2 Objective ...............................................................................................................3
   1.3 Approaches to Kerogen Analysis ..........................................................................4
   1.4 Site Description: The Eel River System ...............................................................8
   1.5 Organic Carbon Dynamics in the Eel River System .............................................12

2. METHODS ..............................................................................................................15

   2.1 Sample Collection ...............................................................................................15
   2.2 Size Separations .................................................................................................16
   2.3 Microscopic Analyses .........................................................................................16
   2.4 Organic Isolates from Shale-Rich Bedrock .........................................................16
   2.5 Elemental and Isotopic Analyses of Bedrock, Sediment and Organic Isolates ....18
   2.6 Surface Area and OC Loading ............................................................................20
   2.7 Rock-Eval ...........................................................................................................20
   2.8 $^{13}$C CP/MAS NMR .......................................................................................21
   2.9 FTIR Spectroscopy ............................................................................................21

3. RESULTS AND DISCUSSION ..................................................................................25

   3.1 Characterization of the Kerogen in an Eel River Bedrock ...................................25
   3.2 Organic Matter Isolates from the Bedrock ...........................................................31
      3.2.1 Low density fraction ....................................................................................31
      3.2.2 Bitumen fraction .........................................................................................37
      3.2.3 Base soluble fraction ...................................................................................39
      3.2.4 Demineralized kerogen .............................................................................42
   3.3 Particle Bound OM in Soils and Sediments .......................................................52
      3.3.1 Mineral composition in the $<4$ µm size class ...........................................52
      3.3.2 OM sources and loading on $<4$ µm particles ............................................57
      3.3.3 C/N ratios and OM sources .......................................................................65
      3.3.4 FTIR analysis: Insights into molecular composition .................................69

4. SUMMARY AND CONCLUSIONS ..........................................................................80

5. REFERENCES ...........................................................................................................82
6. APPENDICES ..................................................................................................................103

6.1 ATR-FTIR spectra of <4 µm sediment samples for mineral identification........104
6.2 ATR-FTIR spectra of <4 µm sediment samples for organic matter analysis .....119
## List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 1.1</td>
<td>Major carbon reservoirs</td>
<td>2</td>
</tr>
<tr>
<td>Table 3.1</td>
<td>Characteristics of Eel River sediments</td>
<td>27</td>
</tr>
<tr>
<td>Table 3.2</td>
<td>Characteristics of the bedrock sample (MV2) used for kerogen isolation</td>
<td>30</td>
</tr>
<tr>
<td>Table 3.3</td>
<td>Key to abbreviations for common band assignments in IR spectra of organic matter</td>
<td>33</td>
</tr>
<tr>
<td>Table 3.4</td>
<td>Brief summary of descriptive kerogen terms used in visual analysis microscopy</td>
<td>33</td>
</tr>
<tr>
<td>Table 3.5</td>
<td>Components suggested by the FTIR spectrum of the bitumen fraction</td>
<td>38</td>
</tr>
<tr>
<td>Table 3.6</td>
<td>Characteristics of the demineralized kerogen isolated from bedrock sample MV2</td>
<td>43</td>
</tr>
<tr>
<td>Table 3.7</td>
<td>Calculation of the fractional kerogen content of terrestrial and marine sediments</td>
<td>63</td>
</tr>
</tbody>
</table>
**List of Figures**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.1</td>
<td>Map of the Eel River system</td>
<td>11</td>
</tr>
<tr>
<td>Figure 2.1</td>
<td>The effect of drying on infrared spectra</td>
<td>24</td>
</tr>
<tr>
<td>Figure 3.1</td>
<td>Organic carbon distribution of the organic matter in the fine-grained melange matrix</td>
<td>29</td>
</tr>
<tr>
<td>Figure 3.2</td>
<td>Testing for inorganic nitrogen</td>
<td>30</td>
</tr>
<tr>
<td>Figure 3.3</td>
<td>ATR-FTIR spectrum of fossil wood fragments isolated from bedrock samples MV1 and MV2 by density fractionation</td>
<td>34</td>
</tr>
<tr>
<td>Figure 3.4</td>
<td>ATR-FTIR spectrum of a wood fragment from the coarse fraction of a soil</td>
<td>35</td>
</tr>
<tr>
<td>Figure 3.5</td>
<td>ATR-FTIR spectrum of the fine-grained particles isolated from bedrock samples MV1 and MV2 by density fractionation</td>
<td>36</td>
</tr>
<tr>
<td>Figure 3.6</td>
<td>ATR-FTIR spectrum of the bitumen extract (from &lt;4 µm fraction of bedrock sample MV2)</td>
<td>40</td>
</tr>
<tr>
<td>Figure 3.7</td>
<td>ATR-FTIR spectrum of the base-soluble fraction isolated from bedrock sample MV2</td>
<td>41</td>
</tr>
<tr>
<td>Figure 3.8</td>
<td>Whole rock/sediment Rock-Eval data in a van Krevelen style diagram</td>
<td>46</td>
</tr>
<tr>
<td>Figure 3.9</td>
<td>ATR-FTIR spectrum of the kerogen isolated by demineralization of bedrock sample MV2</td>
<td>47</td>
</tr>
<tr>
<td>Figure 3.10</td>
<td>CP-MAS solid-state $^{13}$C NMR spectrum of the demineralized kerogen</td>
<td>48</td>
</tr>
<tr>
<td>Figure 3.11</td>
<td>Identifying mineral composition</td>
<td>55</td>
</tr>
<tr>
<td>Figure 3.12</td>
<td>The range of mineral compositions is illustrated by IR spectral characteristics</td>
<td>56</td>
</tr>
<tr>
<td>Figure 3.13</td>
<td>Average values for the &lt;4 µm size class of different sample types</td>
<td>62</td>
</tr>
<tr>
<td>Figure 3.14</td>
<td>Organic carbon loading on &lt;4 µm particles by carbon source</td>
<td>64</td>
</tr>
</tbody>
</table>
Figure 3.15   Applying a δ^{13}C and C/N ratio two end-member mixing model to the Eel River system.................................................................68

Figure 3.16   Interpreting FTIR spectra of particle associated organic matter ..............76

Figure 3.17   Some features of the spectra of organic matter in the clay-sized fraction..77

Figure 3.18   Similar isotopic characteristics do not necessarily correspond to similar IR spectra .................................................................................................78

Figure 3.19   Microbial processing is not sufficient to explain differences in FTIR spectra .................................................................................................79
1. INTRODUCTION AND BACKGROUND

1.1 Introduction

On a billion-year time scale the burial of organic carbon (OC) has contributed to the overall decline of atmospheric CO$_2$ and the accumulation of O$_2$ (Berner, 1982, 1989; Hedges and Keil, 1995). Most carbon (C) on the Earth’s surface exists in large inorganic and organic sedimentary reservoirs with residence times of 10s to 100s of millions of years (Hedges, 1992; Hedges and Keil, 1995) (Table 1.1). The generation of sedimentary C pools occurs primarily on continental margins. OC burial occurs principally along continental shelves and slopes and especially in deltas, where overlying waters supply marine organic matter (OM) and rivers supply terrestrial OM (Hedges and Keil, 1995; Keil et al., 1997). Yearly, 140–160 x 10$^{12}$ g of organic carbon are buried globally, with 43–130 x 10$^{12}$ g C of it having been discharged by rivers (Hedges and Keil, 1995; Schlünz and Schneider, 2000). More than 90% of the sedimentary OM found in marine deposits is associated with mineral particles (Hedges and Keil, 1995). Fine sediments, specifically clay-sized particles, are particularly important because OC content increases with increasing particle surface area (SA) (Mayer, 1994a; Mayer, 1994b). This close association of OM with mineral phases has been postulated to play a role in OM preservation through such mechanisms as physical shielding from bacterial or photolytic attack and chemically stabilization (Keil et al., 1994a; Keil et al., 1994b; Mayer, 1994a; Mayer, 1994b; Skjemstad et al., 1996; Ransom et al., 1998).

About 95% of organic carbon on Earth is stored in the form of kerogen (Hedges, 1992). During kerogen formation, the sedimentary OM evolves toward a more reduced, condensed, and aromatic product by diagenetic (<50 °C) and catagenic processes (50-150 °C).
(Tissot and Welte, 1984). One pathway by which C exits the kerogen pool is the uplift and weathering of sedimentary rock. Rates of kerogen oxidation are poorly constrained, based on either chemical oxidation experiments or the assumption that the oxidation rate must balance the OC burial rates (Berner, 1989; Hedges, 1992). Factors that may complicate the estimation of kerogen turnover rates include microbial oxidation, which is relatively fast compared to chemical processes, and the reburial of uplifted kerogen (Petsch et al., 2001; Blair et al. 2003). Significant rates of reburial appear to occur where rapid uplift and high erosion rates allow kerogen to escape oxidation in soils (Kao and Liu, 1996; Maisello and Druffel, 2001; Perkey, 2003; Blair et al., 2003). As much as a quarter of the total OC delivered fluvially to continental margins may be delivered as kerogen (40-70 x 10$^{12}$ g kerogen C/year) (Blair et al., 2003).

Table 1.1: Major Carbon Reservoirs

<table>
<thead>
<tr>
<th>Carbon Reservoir</th>
<th>Mass x 10$^{18}$ g$^{(1,2)}$</th>
<th>Residence time Years$^{(3)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere (as CO$_2$)</td>
<td>0.66-0.72</td>
<td>10$^1$</td>
</tr>
<tr>
<td>Living Matter (marine, aquatic, terrestrial)</td>
<td>1.6-3.0</td>
<td>10$^1$</td>
</tr>
<tr>
<td>Organic Surface C (dissolved, soil humus, sediment OM)</td>
<td>2.4*</td>
<td>10$^1$ - 10$^3$</td>
</tr>
<tr>
<td>Inorganic Surface C (dissolved, soil carbonates)</td>
<td>39.1-39.5</td>
<td>10$^1$ - 10$^3$</td>
</tr>
<tr>
<td>Kerogen</td>
<td>15,000</td>
<td>10$^8$</td>
</tr>
<tr>
<td>Fossil Fuels</td>
<td>4</td>
<td>10$^9$</td>
</tr>
<tr>
<td>Inorganic Sedimentary C</td>
<td>60,000</td>
<td>10$^7$ - 10$^8$</td>
</tr>
</tbody>
</table>

*$^*$More than half, $\sim$1.6 x 10$^{18}$ g of OC, is found in soils (Lal, 2004).
1.2 Objective

The objective of this study was to characterize changes in the OM associated with fine-grained sediment as particles move from a bedrock source to the seabed in the Eel River system where kerogen is abundant throughout. As a starting point, the organic matter of the kerogen-laden bedrock was characterized. Because of the close association between fine-grained sediments and transported OM, samples of the <4 µm fraction of bedrock, soils, river sediments, and marine sediments were studied. An additional aim was to identify the tools and approaches needed to understand the OM dynamics, while integrating the study of kerogen, terrestrial soils and marine sediments.
1.3 Approaches to Kerogen Analysis

Kerogen is operationally defined as the insoluble (in both aqueous and organic solvents) organic matter found in sedimentary rock (Durand, 1980; Hayes, Kaplan, & Wedeking, 1983; Whelan & Thompson-Rizer, 1993). Mechanistically, it is the major portion of sedimentary OC that survives diagenesis. The insolubility of kerogen in both non-polar organic and aqueous solvents poses an analytical challenge such that a variety of complementary methods must be used to characterize it. Many of the methods useful for kerogen analysis are also employed to study the OM found in soils and sediments. While analysis of the OM found in these surface pools can benefit from additional techniques that rely on physically separable or chemically extractable fractions, the potential complexity of soil and sediment OM suggests the value of analyses of the whole OM. The ability to identify and quantify kerogen in surficial sediments is a first step in improving estimates of kerogen oxidation and survival rates.

The elemental composition of kerogen (C, H, N, O) reflects both its source and its thermal and weathering histories (Tissot et al., 1974; Hayes, Kaplan, & Wedeking, 1983; Tissot and Welte, 1984; Whelan & Thompson-Rizer, 1993; Tyson, 1995). In general, algal (marine or lacustrine) sources tend to produce kerogen with high H/C ratios, whereas vascular plants generate high O/C contents. Kerogen types I-III denote a gradient in sources, where I is primarily algal in origin, III is primarily from vascular plant sources, and II is likely a mixture of algal and continental OC. Early diagenesis tends to decrease the O/C ratio via the loss of H$_2$O and CO$_2$. Late diagenesis and catagenesis reduces the H/C ratio by
the release of H-rich hydrocarbons such as methane. Weathering increases the O/C ratio by oxidation of kerogen side chains.

C/N ratios may reflect the relative importance of vascular plant \((C/N_a > 20)\) and phytoplanktic \((C/N_a 5-9)\) inputs to kerogen source OM (Redfield et al., 1963; Meyers, 1994; Hedges and Oades, 1997). Kerogen C/N contents are highly variable and no doubt reflect diagenetic and catagenetic histories as well as OC sources. Diagenetic microbial processing of OM tends to cause the C/N\(_a\) ratios to converge toward 6-12, while catagenic processing tend to reduce N groups with increasing maturity (Rice and Tenore, 1981; Tissot and Welte, 1984; Tyson, 1995). Metagenetic processes drive kerogens toward a condensed product, removing hydrogen, oxygen, nitrogen and sulfur, leaving predominantly aromatic C=C groups (Tissot and Welte, 1984).

Rock-Eval analysis is a pyrolysis-GC method where kerogen-laden rock is heated, and the volatile products released are monitored (Tissot and Welte 1984; Peters, 1986). As the temperature is increased, CO\(_2\) is first released (designated the S3 component), followed by free hydrocarbons (S1), and finally the pyrolysis of the kerogen generates additional hydrocarbons (S2). The S2 component reflects petroleum production potential. The temperature at which the maximum amount of hydrocarbon is released in the S2 component is called \(T_{\text{max}}\). S1, S2 and S3 are used to determine the hydrogen and oxygen indices (HI, OI), which correlate with H/C and O/C elemental ratios, and \(T_{\text{max}}\) reflects the thermal history of the kerogen.

Visual analysis of polished kerogen-laden rock or organic kerogen isolates by reflected, transmitted light or fluorescence microscopy is used to classify kerogen by
appearance (Tissot and Welte, 1984; Tyson, 1995). Identifiable structures, such as plant cuticle, pollen spores, or algal cells, as well as OM reflectance or opacity provide clues about the origin of the OM and its thermogenic history (Tissot and Welte, 1984; Tyson, 1995).

Vitrinite reflectance, $R_o$, is a measure of the percent of visible light reflected by OM in rock. Within a kerogen type, reflectance increases with increasing OM maturity. $R_o$ values range from <0.5% for immature OM such as woody debris to >2% for metagenic OM such as coal fragments (Tissot and Welte, 1984).

Fourier transform infrared spectroscopy (FTIR) provides information about the chemical structure of molecules. Chemical bonds can absorb infrared radiation; the wavelengths absorbed are characteristic of the different chemical bonds present. In the case of kerogen, FTIR has been used to identify and quantify saturated and unsaturated aliphatic structures, aromatic character, and carbonyl moieties (Robin and Rouxhet, 1978; Rouxhet et al., 1980; Snyder et al., 1983; Tissot and Welte, 1984; Schenk et al., 1986; Ganz and Kalkreuth, 1987; Kister et al., 1990).

$^{13}$C cross-polarization, magic angle spinning (CP/MAS) nuclear magnetic resonance (NMR) analysis also provides information about molecular structure and allows for more rigorous quantification of chemical groups. When a material is subjected to a magnetic field, its atoms experience differing strengths of that field due to the individual environments created by neighboring atoms. Electrons provide varying amounts of shielding to each nucleus, so that different amounts of energy are required to induce a nuclear spin state that resonates with the magnetic field. The energy requirement is expressed as the shift, or difference in energy needed to induce resonance relative to a standard's energy requirement,
typically tetramethylsilane (TMS). Because specific shifts are characteristic of an atom’s molecular environment, the main types of C-containing functional groups can be identified and quantified.

Carbon isotopic ratios can provide information about OM sources. The ratio of stable carbon isotopes, $^{12}$C and $^{13}$C, primarily reflects the photosynthetic source of the OC, i.e. C3 or C4 terrestrial plants, and C3 marine phytoplankton (typical values are illustrated in Figure 3.15). Heterotrophic uptake, diagenesis, and catagenesis may influence the $^{13}$C/$^{12}$C ratio but to a far lesser extent (Tissot and Welte, 1984). Because of its age (typically millions of years), kerogen contains no $^{14}$C ($t_{1/2} = 5730$ yrs) unless it is exposed to the surface environment. Thus, $^{14}$C in kerogen samples reflects inputs of more modern OM. Likewise, $^{14}$C-depleted material in surficial settings such as soils may represent a kerogen contribution or aged soil OC.
1.4 Site Description: The Eel River System

The Eel River watershed of northern California (Figure 1.1) is small, at approximately ~8000 km$^2$, yet it has the highest sediment discharge per drainage area in the contiguous United States at ~14-15 million metric tons per year (Brown and Ritter, 1971; Milliman and Meade, 1983; Milliman and Syvitski, 1992; Sommerfield and Nittrouer, 1999). Heavy precipitation, steep slopes, and highly erodible lithologies all contribute to high sediment mobility throughout the system.

The Eel River system lies along an active margin; the Gorda Plate is subducted under the North American Plate, resulting in rates of uplift exceeding 2 mm/yr near Cape Mendocino (Merritts and Bull, 1989; LaJoie et al., 1991; Clarke, 1992; McCrory, 1996; Orange, 1999; Burger et al., 2001). The southern portion of the watershed overlies a part of the San Andreas transform boundary, while the northern portion lies within the Cascadia Subduction Zone (Kelsey and Carver, 1988). The watershed is underlain by the Jurassic-Tertiary Franciscan Complex, a heterogeneous body of tectonically kneaded rock dominated by highly sheared, shale-rich melange, and additionally containing more coherent sandstone blocks (Kelsey, 1980; Blake et al., 1988; McLaughlin et al., 1994). The fine-grained, shale-rich matrix of the melange bears a type III kerogen with a large humic component and little petroleum potential (Underwood, 1985; Larue, 1991).

The fine-grained, shale-rich melange matrix is thought to be the primary source of fine-grained sediment to the river because of its measured contribution (70% to 94% of total sediment in the years between 1941 to 1975) to the suspended load of the Van Duzen River, a major tributary of the Eel (Kelsey, 1980). Sandstone blocks provided ~17% of the total...
sediment entering the river from 1941–1975, but as relatively coarse material (Kelsey, 1980). One large Van Duzen earth flow has provided, at times, ~10% of the total sediment yield to the Van Duzen River (Kelsey, 1978). A large earth flow along the Van Duzen was extensively sampled because such features were responsible for about 25,000-29,000 metric tons of melange sediment delivered into the Van Duzen river from 1941-1975, and because large erosive gullies and recent roadwork made fresh exposures easily accessible (Kelsey, 1978; Kelsey 1980).

Suspended sediment loads are highly seasonal in the Eel River watershed. Loads are minimal during warm, dry summers. Frequent rainfall and episodic storms deliver 80% of the annual 125-250 cm of rainfall in winter, often with flooding (Kelsey, 1980; Syvitski and Morehead, 1999). Accordingly, more than 90% of the runoff into the river occurs between November and May, which, along with mass wasting events, helps increase the winter-time sediment load (Kelsey, 1980; Sommerfield and Nittrouer, 1999). Approximately 50% of the Eel River’s annual sediment load is discharged during a 1-2 week period of winter storm activity and consequent flooding (Brown and Ritter, 1971).

The Eel River discharges most of its yearly load of sediment to the continental shelf during winter storms when winds from the south and the inshore Davidson Current transport the sediment northward (Geyer et al., 2000; Strub and Corinne, 2002). An estimated 20-25% of the annual riverine discharge is retained on the shelf where clay-rich flood deposits are preserved (Leithold, 1989; Sommerfield and Nittrouer, 1999; Wheatcroft and Borgeld, 2000). High long-term sediment accumulation rates up to 1.8 cm/yr promote flood layer and OM preservation (Alexander and Simoneau, 1999; Sommerfield and Nittrouer, 1999;
Sommerfield et al., 2002; Perkey, 2003; Leithold et al., 2005). The modern Eel Shelf receives both marine and terrestrial organic matter (Leithold, 1989; Leithold and Blair, 2001). Large amounts of woody debris can be deposited and buried, especially during floods (Leithold and Hope, 1999; Sommerfield and Nittroer, 1999; Leithold et al., 2005). Rapid episodic flood deposition, such as the 10-12 cm thick flood deposits from flood events in 1995 and 1999, helps to bury particulate organic carbon below the sediment-water interface and encourage OC survival (Wheatcroft et al., 1997; Leithold and Hope, 1999; Sommerfield and Nittroer, 1999; Perkey, 2003; Blair et al., 2003).
Figure 1.1: Map of the Eel River system. Bedrock, soil, river suspended sediment, and marine sediments were collected at the locations shown here. River collections points at Scotia (S) and Cock Robin Island (CR), marine transects (O and K) and the Van Duzen earth flow (EF) are marked. (Kelsey, 1980; Leithold and Blair, 2001; Blair et al., 2003)
1.5 Organic Carbon Dynamics in the Eel River System

Rapid uplift and erosion in the Eel River system prevent long-term storage of particles in soils and river, creating a “by-pass” system that favors kerogen survival and reburial (Blair et al., 2003; Blair et al., 2004). Kerogen-laden particles can enter the river directly from the bedrock via erosive gullies and mass wasting (landslides, earth flows), possibly with no exposure to bioactive soil zones. Kerogen should be devoid of $^{14}$C because of its age. An average $\delta^{13}$C value of fine-grained, shale-rich bedrock across the watershed was $-24.3 \pm 0.6\%e$ (Leithold and Blair, 2001; Blair et al., 2003). When bedrock sediments are exposed at the surface they are colonized by vegetation, soil microbes, and fauna. Photosynthetically-derived OM, with a carbon isotope signature reflective of its source, enters the developing soil from plant litter at the surface and from roots below the surface. Living plants are expected to have a modern to post-modern $^{14}$C contents. Modern is defined as having 95% of the $^{14}$C activity of the atmosphere in 1950. Since living plants are fixing CO$_2$ from the recent atmosphere, their $^{14}$C activities are elevated from the bomb enrichment of $^{14}$C from nuclear testing in the 1950s and 1960s (Olsson, 1970; Stuiver and Polach, 1977). The measured percent modern carbon, pMC, of a single grass sample collected in 1999 was 108% (Blair et al., 2003). Although woody portions of long-lived trees and of large woody debris can have radiocarbon ages of hundreds to thousands of years, woody debris found in recent sediments had post-modern $^{14}$C contents, 109 ± 1% modern (Blair et al., 2003; Perkey, 2003; Leithold et al., 2005). The average percent modern $^{14}$C content of the OC added to <4 µm particles from river and marine sediments was 110 ± 18% (Blair et al., 2003). Plants collected throughout the watershed (C3 grasses and conifers across 23 species) had an
average δ\(^{13}\)C of -28.0 ± 2.6‰, varying from ~-24 to -32‰ (Blair et al., 2003). No C4 grasses were identified in the Eel watershed (Blair et al., 2003).

Microbial metabolism offers the potential for OM decay and transformation as well as the possible oxidation of kerogen. The OM accumulating in soil, or humus, (2-20 % of the total OC added to soil is sequestered in the soil OC pool; Lal, 2004) reflects the plant source, the microbial activity, and the soil history. Chemically distinct layers, or horizons, form as a soil develops affecting the OM character through processes such as leaching, mineralization, and oxidation (Brady and Weil, 2002). Changes in vegetative cover from such processes as natural succession, land-use, fire, mass wasting, flooding, introduced species and climatic variation could change the terrestrial OM source pool and complicate carbon analysis. Also, situations such as erosive transport of soil from higher elevations and subsequent colluvial mixing could create complex particle histories.

Most particles enter the river after relatively short storage times in the Eel River watershed (Blair et al. 2003; Blair et al., 2004). An estimate of the average δ\(^{13}\)C of terrestrial vegetation-derived OM entering the river was -26.5 ± 1.1‰ (Blair et al., 2003). The river integrates particles from across the watershed, resulting in a <4 μm sediment fraction with a δ\(^{13}\)C of -25‰ and a C/N\(_a\) of ~12. About half its OC load is due to kerogen and half due to modern terrestrial carbon (Leithold and Blair, 2001; Blair et al., 2003). Riverine aquatic plants are thought to be minor sources of OM, especially during the winter season when most sediment loads are highs in the river (Blair et al., 2003). Most sediment reaching the seabed arrives as part of a mass discharged during a flood event. In some cases, thick flood deposits are formed and sediment is quickly buried below the bioturbation zone of 5-10 cm depth.
These particles, loaded with kerogen and terrestrial OM, experience brief exposure to marine OM before burial. Particles that arrive during times of slower accumulation, or that are deposited at the edges of or outside of a flood deposit have a greater chance of OM alteration (Perkey, 2003). Non-flood sediments are more likely to have marine OM additions of marine OC having average estimated isotope signature of 110 ± 18% modern carbon and a $\delta^{13}$C of -21.0 ± 0.7‰ (Blair et al., 2003). Most of the terrestrial OC load and at least half of the kerogen OC load of the <4 µm sediment fraction survives transport through the Eel system and is deposited on the Eel shelf (Blair et al., 2003). Approximately half the OC buried in the <4 µm fraction on the Eel River shelf is from kerogen (Perkey, 2003; Blair et al., 2003; Leithold et al., 2005).
2. METHODS

2.1 Sample Collection

Bedrock, soils, and plants were collected from surface exposures throughout the Eel watershed. Efforts were made to avoid sampling of soils in areas where down-slope transport was suspected and where the connection between the bedrock and overlying soil was unsure. Most soils were collected along failed banks or gullies where a thin oxidized layer, generally <10 cm thick, was observed over visually uniform bedrock. Suspended sediment was collected primarily on the Eel River at Scotia (~33 km from the river mouth) and on Cock Robin Island near the river mouth with a single sample obtained from a gully stream feeding the Van Duzen tributary (Blair et al., 2003). Samples were collected from just below the water surface with a Wildco Beta horizontal water bottle. During high discharge the water column is thought to be reasonably well mixed in terms of the sand-sized material and smaller, which constitutes the bulk of sediment deposited on the adjoining shelf, and thus point sampling is adequate for retrieving representative samples of suspended load (Blair et al., 2003).

Marine sediments were collected on two different sampling trips. Surface sediments were collected in January 1997, several weeks after an 80-yr flood with a box core along the O-transect of the STRATAFORM project (Nittouer, 1999). The box core was subsampled and sectioned in 1 cm intervals. Only samples from the 0-1 cm interval of the O-transect are considered here. Deeper sediments were sampled in 1999 with a box core and piston core at 70 m water depth in the K-transect of the STRATAFORM project, the approximate depocenter of recent Eel shelf sediment accumulation (Perkey, 2003; Leithold et al., 2005).
The box core (~30 cm total) was subsampled and sectioned in 1 cm intervals, while the piston core (~3 m total) was sectioned in 1 cm portions every 10 cm (Perkey, 2003). All samples were stored at -20 ºC before and after processing. A list of all samples and descriptions is given in Table 3.1.

2.2 Size Separations

Portions of bulk samples were suspended in a small volume of deionized water, sonicated for 5 minutes and then washed through a 25 µm stainless steel sieve, to separate samples into >25 µm and <25 µm size fractions. The clay-sized particles were isolated from the <25 µm fractions by standard settling techniques in aqueous solution of sodium metaphosphate (1 g L⁻¹) to prevent flocculation (Blatt et al., 1980; Blair et al., 2003). The clay fraction was collected by centrifugation. All samples were freeze-dried.

2.3 Microscopic Analyses

Various bulk and coarse fractions were examined under low magnification (~ 40-60 X) using a dissecting microscope. The general appearance of the sediments was noted as well as the presence and appearance of recognizable OM. Some large OM fragments, such as wood fragments, were removed from samples for use in other analyses.

2.4 Organic Isolates from Shale-Rich Bedrock

Multiple organic fractions were isolated from both bulk and size fractions of bedrock samples (samples MV1 and MV2 in Table 3.1). These were fine-grained, shale-rich sediments from a large earth flow along the Van Duzen River (Kelsey, 1980) recently exposed due to dramatic erosion and recent roadway repairs. These samples are expected to have experienced minimal weathering and oxidation (Leithold and Blair, 2001).
Low density particles were isolated by density fractionation from >25 µm size fractions. Samples were suspended in a sodium polytungstate (SPT) solution at a density of 1.9 g cm\(^{-3}\) and centrifuged. The lighter organic fraction not bound to clays floated in the high-density fluid and was removed by decanting. No measurable material was isolated in an attempted density fractionation of the <25 µm size class.

Freeze-dried samples of bulk, >25 µm (both of which were ground with mortar and pestle to a fine powder), <25 µm and <4 µm size fractions were sonicated for 3 successive 20 minute intervals in a 1:1 mixture of methanol : toluene to extract the bitumen fraction (Durand and Nicaise, 1980; Tissot and Welte, 1984). This solvent mixture was chosen to extract a wide range of both polar and nonpolar organic components. Similar mixtures are highly effective in extracting the bitumen/lipid fraction from kerogen (Durand and Nicaise, 1980; Tissot and Welte, 1984). Between sonications, samples were centrifuged, and the supernatant removed. The combined supernatant for each sample was concentrated by rotary evaporation then evaporated to dryness under N\(_2\). The extracts were dissolved in a known volume of 1:1 methanol : toluene. Sediment remaining after solvent extraction was vacuum evaporated.

The bitumen-free sediments were shaken with 0.1 N NaOH for 24 hours to extract a humic acid-like, base soluble fraction. Following centrifugation supernatants were decanted, acidified with HCl to pH 4-6, then freeze dried. Only supernatant from the <4 µm portion was analyzed further; the bulk and coarse fractions provided very little material. Sediments were rinsed with DI H\(_2\)O to remove residual NaOH. In the <25 and <4 µm samples, this rinse became a brownish-gray color. Sediments were freeze-dried after rinsing.
The organic matter remaining after the base extraction is considered “non-extractable” and is defined as kerogen (Durand and Nicaise, 1980; Tissot and Welte, 1984). The dried <4 µm sample was demineralized by digestion with 49% HF for 24 hours, then 2 successive 24 hr. digestions with a 5:2 mixture of 49% HF : concentrated HCl, followed by rinsing with deionized water. To remove neo-formed fluorides, samples were shaken three times for 24 hrs in 1.2 M AlCl$_3$. All digestion steps were carried out at room temperature. The demineralized kerogen was rinsed with deionized water and freeze-dried. Although the acid treatment can undoubtedly alter or dissolve some organic components (such as hydrolysis of proteins and carbohydrates), the effects of acid treatment on the elemental ratios of a kerogen are often negligible (Durand, 1980). Generally, potential alterations are minimized in mature samples and by performing the digestion at lower temperatures, without oxidizing chemicals (such as LiAlH$_4$) or under a nitrogen atmosphere (Durand, 1980; Hayes, Kaplan, & Wedeking, 1983; Tissot and Welte, 1984; Whelan & Thompson-Rizer, 1993). Little to no reactivity or solubilization of the kerogen with AlCl$_3$ treatment is expected under aqueous conditions at lower temperatures (Hayes, Kaplan, & Wedeking, 1983).

2.5 Elemental and Isotopic Analyses of Bedrock, Sediment and Organic Isolates

Samples from the <4 µm size class were exposed to vapor phase HCl overnight to remove carbonates then dried under vacuum. Coarser sediments were acidified in a small volume of concentrated HCl overnight then dried. No systematic loss of OC or alteration in $\delta^{13}$C from the isolation or acidification was detected (Blair et al., 2003). The average loss of N with this method on Eel River soils and sediments was 3.9 ± 2.9%, which did not significantly influence reported C/N$_a$ ratios (Leithold and Blair, 2001).
Acidified sediments or solid organic matter samples were weighed into tin boats, combusted, and analyzed for their OC and total nitrogen (TN) concentration (mg C or N/g dry wt sample) with a Carlo Erba 1108 CHNS analyzer (Pella, 1990; Leithold and Blair, 2001). Blanks and standards were analyzed to construct calibration curves. The relative precision was 2% for OC measurements and 4% for TN measurements (Leithold and Blair, 2001). 20-80 µL of the solubilized bitumen samples were dried onto small, flat pieces of weighed aluminum foil under a stream of N₂. The foil pieces containing the samples were then loaded into the elemental analyzer in place of tin boats - tin boats generally leaked sample before the residue could be dried. Foil blanks were run in addition to other procedural blanks.

The CO₂ produced via the oxidation of the OC in elemental analysis was trapped cryogenically for isotopic analysis (Blair and Carter, 1992). The δ¹³C measurements were made on a modified Finnigan MAT Delta E isotope ratio mass spectrometer (Hayes et al., 1977) and are reported relative to the Pee Dee belemnite. Elemental analysis blanks and standards were processed as well to provide blank corrections and quality control of δ¹³C measurements (Blair and Carter, 1992). For replicate analyses, the absolute precision was 0.2‰ (Leithold and Blair, 2001). Duplicate samples were processed to CO₂ in the same manner for ¹⁴C analysis at the WHOI Ocean Sciences AMS facility. CO₂ was converted to graphite for the measurement of ¹⁴C content by accelerator mass spectrometry (Olsson, 1970). Corrections were made for natural fractionations by normalizing the δ¹³C values of each sample to -25‰ and for procedural blank contributions. Blanks were always at least an order of magnitude less than the ¹⁴C-content of the bedrock samples. Results are reported as
percent modern carbon (pMC) relative to the National Bureau of Standards (NBS) Oxalic Acid I standard (Olsson, 1970). Modern is defined as 95% of the radiocarbon concentration (in 1950) of the NBS standard normalized to a $\delta^{13}$C of -19‰ (Olsson, 1970). The relative precision of pMC measured for the NBS-22 hydrocarbon standard (pMC = 0.3%) was 2%.

The percent sulfur of the demineralized kerogen was measured using a Carlo Erba 1108 CHNS analyzer. Precision was 3-10% for sulfur measurements (Aller and Blair, 1996). The percent oxygen of demineralized kerogen was also measured using the same CHNS analyzer, but in oxygen mode (Pella and Colombo, 1972).

2.6 Surface Area and OC Loading

Subsamples of the <4 µm fraction were rinsed to remove the sodium metaphosphate, then freeze-dried. After heating in air for 12 to 14 hours at 350°C to remove organic matter and residual water, samples were degassed at 150°C for 30 minutes, and the surface area was determined by the multi-point method on a Beckman Coulter SA 3600 analyzer (Branauer et al., 1938). Reproducibility of the measurements was 2% (Blair et al., 2003). The organic carbon concentrations of soils and sediments were normalized to the specific surface area of the sample (OC/SA, mg OC/m$^3$) to attenuate artifacts due to grain-size variations (Hedges and Keil, 1995).

2.7 Rock-Eval

Rock-Eval II pyrolysis was performed by DGSI (The Woodlands, TX) on acidified sediment samples and on the demineralized kerogen.
2.8 \textsuperscript{13}C CP/MAS NMR

A cross polarization magic angle spinning (CP/MAS) solid state \textsuperscript{13}C-NMR spectra of the isolated kerogen was taken on a Bruker DMA 300 NMR spectrometer with a \textsuperscript{1}H frequency of 300 MHz and \textsuperscript{13}C frequency of 75.48 MHz by Patrick Hatcher, Department of Chemistry, Ohio State University. Using the method outlined in Dria \textit{et al.}, 2002, approximately 100 mg of sample was packed in a 4-mm rotor and spun at 13 kHz. Contact time was 2 ms, with a recycle delay time of 1 s; 4096 scans were performed.

2.9 FTIR Spectroscopy

FTIR spectra were collected using a Bio-Rad-Digilab FTS-6000 Fourier transform infrared (FT-IR) spectrometer with a cryogenically cooled mercury cadmium telluride (MCT) detector and an attached infrared microscope (model UMA-500). The microscope was fitted with a germanium crystal attenuated total reflection (ATR) objective. The microscope was also enclosed by a glove bag and flushed continually with nitrogen gas, to reduce atmospheric water and CO\textsubscript{2} interference. ATR, an internal reflection technique, produces a spectrum equivalent to absorbance spectroscopy. The infrared waves, instead of passing through the sample, pass through an “IR transparent medium with a high refractive index,” in this case, a germanium crystal (Russell, 1974; Estep-Barnes, 1977; Coates, 1998). Evanescent waves are created from the reflection of the IR within the crystal and penetrate into the sample, which is in intimate contact with the ATR medium (Mirabella, 1993). Samples are typically finely powdered to increase contact with the ATR medium (Estep-Barnes, 1977; Coates, 1998). The evanescent waves, affected by the interaction with the sample, attenuate the IR as if it had passed through the sample, producing a spectrum.
equivalent to a traditional IR transmission spectrum (Mirabella, 1993; Coates, 1998).

Because the IR radiation is not transmitted through the sample, limitations due to particle size, such as high scattering, are avoided (Estep-Barnes, 1977). Since the sample is not suspended in a hygroscopic halide salt, as with more traditional use of KBr pellets, background absorption, especially from water, is reduced and the sample is recoverable.

While IR analysis has been used in both soil and kerogen analysis, soil studies have typically focused on soil profiles with high OM content (such as >20% OC), and kerogen studies have analyzed demineralized kerogen concentrates (Rouxhet, et al., 1980; Schenk et al., 1986; Haberhauer et al., 1998; Haberhauer and Gerzabek, 1999; Haberhauer et al., 2000; Petsch et al., 2000). All of these studies previously cited used the traditional KBr pellet technique. The <4 µm particles of the Eel River system typically contain 1% OC. Because the infrared signal from OM is so diluted among the mineral’s strong absorbancies, high resolution and low interference was essential to adequately examine the sediment bound OM.

Dry samples were important to reduce interference from bands around 1640 cm\(^{-1}\) and 3800-2600 cm\(^{-1}\). The <4 µm size fraction of soil and sediment samples were rinsed of dispersant (from the size fractionation), freeze dried, and stored under a desiccant. These rinsed samples were analyzed to obtain spectra of sample’s mineral content (Fieldes et al., 1972; van der Marel and Beutelspacher, 1976; Russell and Fraser, 1994). Sub-portions of rinsed samples for analysis of sediment-bound organic matter were additionally dried in a vacuum oven by heating at 50 °C for 24 hours and stored under N\(_2\) with a desiccant. By vacuum-drying samples (Figure 2.1), potentially large and broad water bands were reduced, allowing for better resolution of the small organic bands. Extra drying also reduces H-
bonding that can affect absorbance maxima. Effects are also seen in the mineral-dominated parts of the spectra, reducing both –OH stretch and deformation bands.

Solid isolates, such as wood fragments, and other organic matter, such as algae, were freeze-dried. Transmission spectra were obtained from 4000 to 600 cm\(^{-1}\) for 4096 scans for soils and sediments, and 1024 scans for organic samples (wood, bitumen, etc.).

Spectra were converted to absorbance form by ratioing transmission spectra against a daily transmission background spectrum (Gilbert, 1990). Spurious rotational water vapor bands from traces of water vapor in the atmosphere were reduced or eliminated by subtracting a water-vapor/atmosphere background spectrum. The resulting data were exported to Origin (version 6) graphing software (OriginLab Corp.) for further processing. Each spectrum was plotted, and a baseline was drawn across the pertinent region, then subtracted to correct for baseline drift (Coates, 1990; Gilbert, 1990). Baseline corrected spectra were normalized to the maximum absorbance, always the large Si-O peak ~975 cm\(^{-1}\) in sediment samples, to allow quantitative comparisons of ATR-FTIR spectra (Coates, 1990; Mirabella, 1993).
Figure 2.1: The effect of drying on infrared spectra. By drying the <4 μm sediments, adsorbed and possibly intercalated water was removed. Absorbancies due to water at 3800-2600 cm$^{-1}$, ~1640 cm$^{-1}$, and 900 - 700 cm$^{-1}$ decreased. Removing water also reduces hydrogen bonding and causes some band shifts. These spectra are of river suspended sediment sample RC1.
3. RESULTS AND DISCUSSION

3.1 Characterization of Kerogen in an Eel River Bedrock

The melange of the Central Belt of the Franciscan Complex contains sandstone, siltstones, shales, chert, schists, as well as other rock types (Kelsey, 1980; Blake et al., 1988; Cashman et al., 1995). Particles up to pebble size (1-2 cm) with unweathered appearances (sharp edges, etc.) are often seen in the > 25 µm fraction when examined with no or low magnification. Organic fragments, both woody and fibrous, can also be seen in the coarse fraction.

Samples of the fine-grained, shale-rich melange matrix from the Van Duzen earth flow (samples MV1 and MV2, described in Table 3.1) were used in a detailed study of the kerogen found in this system. These samples provided the least exposed material identified in the study and should reflect the unaltered bedrock OM. While <4 µm particles make up less than 1/3 of the total weight of the sample, they account for the largest percentage of the total carbon budget at 44% of OC by weight (Table 3.2). This enrichment of OM in finer, higher surface area particles has been reported in many soils and sediments (Mayer, 1994a; Mayer, 1994b; Bergamaschi et al., 1997; Ransom et al., 1998). The $\delta^{13}$C of the OM was constant at -23.8‰ throughout all size classes, suggesting that the OM in this bedrock is homogenous across size classes. This value is similar to the average $\delta^{13}$C value of -24.3 ± 0.6‰ for the <4 µm size fraction of fine-grained bedrock matrix sampled across the watershed (Leithold and Blair, 2001; Table 3.1). It is also identical to the $\delta^{13}$C of the demineralized kerogen. The percent modern carbon (pMC) of 1.5 ± 0.8% calculated from the $^{14}$C content shows that essentially all the OC in the sample is ancient. Accordingly, the
stepwise extraction and demineralization of the fine-grained, shale-rich bedrock sample showed that 70-90% of the OM was non-extractable (Figure 3.1).

In the demineralization of <4 µm particles of the kerogen-containing bedrock, 103% of OC was accounted for in the base-soluble, bitumen and insoluble fractions. Only 27% of N was recovered, the loss coming at acid dissolution of the mineral phase. One possibility considered for this loss is that inorganic N, such as fixed NH$_4^+$, may be contributing to total nitrogen (TN). Fixed ammonium occurs in most soils and being bound into the lattice structures of fine clay minerals, it is largely dictated by the clay minerals present and is not readily exchanged or leached out (Stevenson, 1982; Brady and Weil, 2002).

To estimate inorganic N content, weight percent OC can be plotted versus weight percent TN. As the percent of organic matter changes due to varying dilution with the mineral material, the %OC and %TN should respond linearly, if the nitrogen is largely organic (Hedges et al., 1986; Hedges et al., 1988; Bergamaschi et al., 1997). A plot of the %OC vs. %TN for the bedrock sample MV2 shows a good linear fit for both the coarse and fine fractions (Figure 3.2). The line extrapolates to a negative %TN where organic carbon is zero, suggesting that there is essentially no inorganic N (Hedges et al., 1986; Hedges et al., 1988). Since essentially all nitrogen in this bedrock sample appears to be organic, the poor recovery of N in the demineralization of the kerogen suggests a substantial loss of N-rich organic matter. Because of the large difference in nitrogen and carbon concentrations, small losses of organic matter, due to acid solubility or handling, could measurably affect the percent TN while changes in the percent OC remained undetectable.
<table>
<thead>
<tr>
<th>ID</th>
<th>Area</th>
<th>Location</th>
<th>Description</th>
<th>&gt;25 μm %</th>
<th>4-25 μm %</th>
<th>&lt;4 μm %</th>
<th>OC %</th>
<th>TN %</th>
<th>C/Na</th>
<th>δ13C PDB</th>
<th>pMC</th>
<th>SA (m²)</th>
<th>OC:SA (mg C/m²)</th>
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<td></td>
<td><strong>Bedrock</strong></td>
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<td></td>
<td></td>
<td><strong>Grassland, exposed rock/gully, base of soil horizon</strong></td>
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</tr>
<tr>
<td>MA1</td>
<td>Main Fork</td>
<td></td>
<td>Dark gray brown</td>
<td>59.9</td>
<td>25.7</td>
<td>14.5</td>
<td>0.685</td>
<td>0.033</td>
<td>24</td>
<td>-23.6</td>
<td>37.9</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>MM1</td>
<td>Middle Fork</td>
<td></td>
<td>Light gray with white, crumbly portions, flaky texture, rootlets/fungi present</td>
<td>69.8</td>
<td>12.9</td>
<td>17.3</td>
<td>0.496</td>
<td>0.018</td>
<td>32</td>
<td>-24.5</td>
<td>18.3</td>
<td>0.27</td>
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</tr>
<tr>
<td>MN1</td>
<td>South Fork</td>
<td><strong>Wall of marginal gully failure</strong></td>
<td>Crumbly, grey</td>
<td></td>
<td>1.29</td>
<td></td>
<td>0.10</td>
<td>15</td>
<td>-24.1</td>
<td>29.0</td>
<td>0.11</td>
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</tr>
<tr>
<td>MN2</td>
<td>South Fork</td>
<td><strong>Wall of marginal gully failure</strong></td>
<td>Crumbly, grey</td>
<td>64.8</td>
<td>17.6</td>
<td>17.6</td>
<td>1.27</td>
<td>0.071</td>
<td>21</td>
<td>-23.7</td>
<td>27.8</td>
<td>0.46</td>
<td></td>
</tr>
<tr>
<td>MV1</td>
<td>Van Duzen</td>
<td><strong>Earthflow</strong></td>
<td>Freshly exposed at a road cut, near surface</td>
<td>43.1</td>
<td>21.6</td>
<td>35.3</td>
<td>0.812</td>
<td>0.042</td>
<td>23</td>
<td>-24.3</td>
<td>41.3</td>
<td>0.20</td>
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<td></td>
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<td></td>
<td>Thick, moist, dark grey with white, orange-brown and griny green-white inclusions. Fine black particles</td>
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<tr>
<td>MV2</td>
<td>Van Duzen</td>
<td><strong>Earthflow</strong></td>
<td>Gully wall, ~1 ft in, unexposed</td>
<td>44.3</td>
<td>24.4</td>
<td>31.3</td>
<td>1.24</td>
<td>0.098</td>
<td>15</td>
<td>-23.9</td>
<td>41.9</td>
<td>0.28</td>
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<td></td>
<td></td>
<td></td>
<td>Thick, moist, grey, white inclusions</td>
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<tr>
<td>MV3</td>
<td>Van Duzen</td>
<td><strong>Earthflow</strong></td>
<td>Gully wall, exposed surface</td>
<td>57.3</td>
<td>22.1</td>
<td>20.6</td>
<td>1.31</td>
<td>0.077</td>
<td>20</td>
<td>-23.7</td>
<td>44.7</td>
<td>0.24</td>
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<tr>
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<td>Thick, moist, grey</td>
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<tr>
<td>MV4</td>
<td>Van Duzen</td>
<td><strong>Earthflow</strong></td>
<td>Base of gully wall, loose colluvium/aluvium</td>
<td>47.8</td>
<td>30.0</td>
<td>22.1</td>
<td>1.28</td>
<td>0.10</td>
<td>15</td>
<td>-24.0</td>
<td>35.4</td>
<td>0.36</td>
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</tr>
<tr>
<td>MV5</td>
<td>Van Duzen</td>
<td><strong>Earthflow</strong></td>
<td>Colluvial mix of bedrock and soil at toe of flow. Some loose vegetation</td>
<td>68.8</td>
<td>17.6</td>
<td>13.6</td>
<td>1.26</td>
<td>0.086</td>
<td>17</td>
<td>-24.0</td>
<td>33.2</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Grey, flaky</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SE1</td>
<td>Main Fork</td>
<td><strong>Sandstone, failing bank</strong></td>
<td>Red/orange color, sandy, coarse</td>
<td>0.516</td>
<td>0.042</td>
<td></td>
<td>12</td>
<td>-25.8</td>
<td>35.6</td>
<td>0.15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>Soils</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>Topsoil at large sandstone slide</strong></td>
<td>Sandy, coarse, light reddish-brown,</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SA1</td>
<td>Main Fork</td>
<td></td>
<td>Dark gray brown</td>
<td>0.465</td>
<td>0.025</td>
<td>10</td>
<td>-25.7</td>
<td>54.9</td>
<td>0.085</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TA1</td>
<td>Main Fork</td>
<td></td>
<td>Dark gray brown</td>
<td>50.7</td>
<td>23.4</td>
<td>25.9</td>
<td>1.17</td>
<td>.11</td>
<td>12</td>
<td>-24.8</td>
<td>37.1</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>TB1</td>
<td>Middle Fork</td>
<td><strong>Grass covered road failure</strong></td>
<td>Light brown, loose rootlets</td>
<td>57.3</td>
<td>19.6</td>
<td>23.1</td>
<td>0.461</td>
<td>0.11</td>
<td>5.1</td>
<td>-24.1</td>
<td>35.7</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>TM1</td>
<td>Middle Fork</td>
<td><strong>Gully</strong></td>
<td>Light brown</td>
<td>68.0</td>
<td>10.5</td>
<td>21.5</td>
<td>0.886</td>
<td>0.10</td>
<td>10</td>
<td>-24.8</td>
<td>24.0</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>TM2</td>
<td>Middle Fork</td>
<td><strong>Forest</strong></td>
<td>Very dark brown, humus rich with conifer needles, rootlets and woody debris. Loose texture</td>
<td>85.9</td>
<td>10.9</td>
<td>3.17</td>
<td>9.42</td>
<td>0.51</td>
<td>22</td>
<td>-25.0</td>
<td>22.0</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>TN1</td>
<td>South Fork</td>
<td><strong>Marginal gully failure, top 2-3 cm of vegetated gully wall (above MN1)</strong></td>
<td>Light brown, sandy texture, conifer needles, rootlets</td>
<td>78.2</td>
<td>12.5</td>
<td>9.20</td>
<td>1.01</td>
<td>0.15</td>
<td>7.9</td>
<td>-25.0</td>
<td>34.5</td>
<td>0.29</td>
<td></td>
</tr>
</tbody>
</table>
### Table 3.1: Characteristics of Eel River Sediments, continued

<table>
<thead>
<tr>
<th>ID</th>
<th>Area</th>
<th>Location</th>
<th>Description</th>
<th>&gt;25 μm %</th>
<th>4-25 μm %</th>
<th>&lt;4 μm %</th>
<th>OC %</th>
<th>TN %</th>
<th>C/Na</th>
<th>δ¹³C, PDB</th>
<th>pMC</th>
<th>SA (m²)</th>
<th>OC/SA (mg C/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TV1</td>
<td>Van Duzen Earthflow</td>
<td>Thin topsoil only 2-3 cm thick at top of gully wall (above MV2, MV3). Grassy</td>
<td>Grey, with coarse, black, magnetic grains</td>
<td>58.4</td>
<td>26.5</td>
<td>15.1</td>
<td>1.47</td>
<td>0.082</td>
<td>21</td>
<td>-25.6</td>
<td></td>
<td>29.6</td>
<td>0.48</td>
</tr>
<tr>
<td>TV2</td>
<td>Van Duzen Earthflow</td>
<td>Thick topsoil exposed at fresh road cut, below surface in brown oxidized horizon (above MV1)</td>
<td>Very moist, dark grey-brown, crumbly, sandy texture</td>
<td>86.6</td>
<td>8.37</td>
<td>5.07</td>
<td>1.14</td>
<td>0.12</td>
<td>11</td>
<td>-24.6</td>
<td>50</td>
<td>30.2</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Suspended Sediment</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MV6</td>
<td>Van Duzen Earthflow Coastal</td>
<td>Suspended sediment in gully during rain event Eel River at Cock Robin Bridge during high discharge event</td>
<td>Grey, Light grey, coarse</td>
<td>42.5</td>
<td>36.6</td>
<td>20.9</td>
<td>1.45</td>
<td>0.12</td>
<td>14</td>
<td>-24.8</td>
<td></td>
<td>27.8</td>
<td>0.52</td>
</tr>
<tr>
<td>RC1</td>
<td>Van Duzen Earthflow Coastal</td>
<td>Eel River at Cock Robin Bridge during high discharge event</td>
<td>Light grey, coarse</td>
<td>39.4</td>
<td>40.6</td>
<td>20.0</td>
<td>1.08</td>
<td>0.075</td>
<td>12.1</td>
<td>-25.0</td>
<td>47</td>
<td>26.0</td>
<td>0.41</td>
</tr>
<tr>
<td>RS1</td>
<td>Main Fork Eel River at Scotia Bridge during high discharge event</td>
<td>Light grey, coarse</td>
<td>46.0</td>
<td>38.0</td>
<td>16.0</td>
<td>1.00</td>
<td>0.075</td>
<td>13.3</td>
<td>-25.1</td>
<td>45</td>
<td>28.4</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>RS2</td>
<td>Main Fork Eel River at Scotia Bridge during high discharge event</td>
<td>Light grey, coarse</td>
<td>37.0</td>
<td>39.6</td>
<td>23.4</td>
<td>1.06</td>
<td>0.076</td>
<td>11.4</td>
<td>-25.0</td>
<td>46</td>
<td>26.0</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Marine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O70</td>
<td>Eel Shelf</td>
<td>1997 O transect, 70m depth, 0-1 cm in fresh flood deposit</td>
<td>Light brown</td>
<td>1.98</td>
<td>70.5</td>
<td>27.5</td>
<td>1.01</td>
<td>0.13</td>
<td>9.3</td>
<td>-25.0</td>
<td>44</td>
<td>26.7</td>
<td>0.38</td>
</tr>
<tr>
<td>O150</td>
<td>Eel Shelf</td>
<td>1997 O transect, 150m depth, 0-1 cm at edge of fresh flood deposit, near shelf/slope break</td>
<td>Light brown</td>
<td>31.9</td>
<td>42.3</td>
<td>25.8</td>
<td>1.16</td>
<td>0.11</td>
<td>9.3</td>
<td>-24.2</td>
<td>42</td>
<td>22.2</td>
<td>0.52</td>
</tr>
<tr>
<td>O250</td>
<td>Eel Slope</td>
<td>1997 O transect, 250m depth, 0-1 cm</td>
<td>Light brown</td>
<td>4.0</td>
<td>33.0</td>
<td>25.0</td>
<td>1.31</td>
<td>0.15</td>
<td>10</td>
<td>-23.8</td>
<td>76</td>
<td>33.9</td>
<td>0.55</td>
</tr>
<tr>
<td>O550</td>
<td>Eel Slope</td>
<td>1997 O transect, 550m depth, 0-1 cm</td>
<td>Light brown</td>
<td>21.4</td>
<td>50.0</td>
<td>28.6</td>
<td>1.87</td>
<td>0.20</td>
<td>8.5</td>
<td>-22.9</td>
<td>76</td>
<td>33.9</td>
<td>0.55</td>
</tr>
<tr>
<td>K8</td>
<td>Eel Shelf</td>
<td>1999 K transect, 70m depth, box core, 8-9 cm, non-flood layer from 1990*</td>
<td>Dark brown</td>
<td>59.2</td>
<td>27.9</td>
<td>13.0</td>
<td>1.32</td>
<td>0.12</td>
<td>10</td>
<td>-23.8</td>
<td>64</td>
<td>23.0</td>
<td>0.57</td>
</tr>
<tr>
<td>K27</td>
<td>Eel Shelf</td>
<td>1999 K transect, 70m depth, box core, 27-28 cm, flood layer from 1990*</td>
<td>Dark brown</td>
<td>14.5</td>
<td>56.7</td>
<td>28.9</td>
<td>1.03</td>
<td>0.11</td>
<td>11</td>
<td>-24.3</td>
<td>49</td>
<td>25.8</td>
<td>0.40</td>
</tr>
<tr>
<td>K46</td>
<td>Eel Shelf</td>
<td>1999 K transect, 70m depth, piston core, 46 cm, circa 1950*</td>
<td>Dark brown</td>
<td>50.0</td>
<td>41.1</td>
<td>8.90</td>
<td>0.997</td>
<td>10</td>
<td>-23.9</td>
<td>26.5</td>
<td>0.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K325</td>
<td>Eel Shelf</td>
<td>1999 K transect, 70m depth, piston core, 325 cm, circa 500 A.D*</td>
<td>Dark brown</td>
<td>79.7</td>
<td>14.5</td>
<td>5.80</td>
<td>1.31</td>
<td>10</td>
<td>-23.8</td>
<td>19.5</td>
<td>.67</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Perkey, 2003; Leithold *et al.*, 2005
Figure 3.1: Organic carbon distribution of the organic matter in the fine-grained melange matrix (sample MV2, an exposed sediment from an earthflow). In all size classes non-extractable organic matter, or kerogen, accounted for the majority of the organic carbon.
Table 3.2: Characteristics of the bedrock sample (MV2) used for kerogen isolation

<table>
<thead>
<tr>
<th></th>
<th>Bulk</th>
<th>&gt;25 µm</th>
<th>4-25 µm</th>
<th>&lt;4 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size distribution, by wt.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% of total C, by wt.</td>
<td>45%</td>
<td>24%</td>
<td>31%</td>
<td></td>
</tr>
<tr>
<td>% OC</td>
<td>0.85%</td>
<td>0.63%</td>
<td>0.91%</td>
<td>44%</td>
</tr>
<tr>
<td>% TN</td>
<td>0.052%</td>
<td>0.029%</td>
<td>0.046%</td>
<td>0.098%</td>
</tr>
<tr>
<td>C/Na</td>
<td>19</td>
<td>26</td>
<td>23</td>
<td>15</td>
</tr>
<tr>
<td>δ¹³C_PDB</td>
<td>-23.8‰</td>
<td>-23.9‰</td>
<td>-23.8‰</td>
<td>-23.9‰</td>
</tr>
<tr>
<td>% modern carbon from Δ¹⁴C</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>1.5 ± 0.8 pMC *</td>
</tr>
</tbody>
</table>

* average of separate samples from the Van Duzen earthflow (n=3)

Figure 3.2: Testing for inorganic nitrogen. If nitrogen is essentially all organic, changes in OC content should respond linearly to changes in nitrogen content. Data here are from elemental analyses of different size separates (bulk, >25 µm, <25 µm, and <4 µm) of the bedrock sample (MV2) used to isolate kerogen. The relationship between OC and N is linear and intercepts the y-axis at a positive value, suggesting there is little to no inorganic nitrogen present.
3.2 Organic Matter Isolates from the Bedrock

3.2.1 Low density fraction

Visual examination of the low density fraction, material which floated in an SPT solution of 1.8 g cm$^{-3}$, showed discrete fossilized wood fragments (as large as several mm in size) and fine black particles, some with a coal-like appearance, having no visible structure at 60X magnification. Such a combination is consistent with a Type III kerogen and confirms the presence of terrestrial OM (Tissot and Welte, 1984). It is also consistent with the findings by Underwood (1985), where a detailed optical microscopic analysis of samples from the vicinity found 54-100% of the visually identifiable kerogen content was due to herbaceous and humic material with the remaining material being amorphous and/or inertinite (Table 3.4). The light material, which is >30% OC by weight, accounts for approximately 6.5% of the total carbon in the fine-grained, shale-rich melange matrix sample and exists almost exclusively in the coarse size fractions. The rest of the organic carbon has a higher density, suggesting that it is inseparable from denser (~2.6 g/cm$^3$) mineral particles.

The fossilized wood fragments in the light density fraction are on the order of 100 million years old, based on the age of the Central Belt of the Franciscan Complex (Blake et al., 1988; Terabayashi and Maruyama, 1998). Bands from C-O stretching in residual carbohydrate subunits of cellulose dominate the FTIR spectrum of the fossil wood (Figure 3.3). Table 3.3 contains explanations for abbreviations used to label IR spectra. Phenolic groups are also present, which may be the remains of lignin. Compared to a spectrum of fresh cellulose (Zhbankov, 1966) and a soil wood fragment (Figure 3.4), the fossil wood shows a reduction in carbonyl character, an enrichment in aromatic groups, and the removal
of some -CH₂ and -CH₃ groups. The fossil wood is expected to have a similar composition to fresh wood, but with decreased cellulose and side groups (methyl, methoxy, etc.) on aromatic rings and increased C-O groups and ring substitution from carbohydrate and phenolic rings oxidation (Bates and Hatcher, 1989). The low nitrogen content, increased aromatization, and loss of C=O, methyl, and methoxy groups are expected indicators of wood decay and thermal maturation (Tissot and Welte, 1984; Bates and Hatcher, 1989).

The spectrum of the fine particles in the low density fractions is shown in Figure 3.5. Although some mineral content obscures a portion of the FTIR spectrum, these particles have a nearly identical spectrum to the fossil wood fragments. These particles are likely very fine fragments of woody debris.
Table 3.3: Key to abbreviations for common band assignments in IR spectra of organic matter (Coulthup et al., 1975; Nakanshi and Solomon, 1977; D’Acqui, 1999)

<table>
<thead>
<tr>
<th>Wavenumber, cm(^{-1})</th>
<th>Functional groups</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>~ 3030</td>
<td>Aromatic –CH stretch</td>
<td>Aro CH</td>
</tr>
<tr>
<td>~ 2950-2850</td>
<td>Aliphatic -CH(_2) &amp; -CH(_3) stretching</td>
<td>Ali CH</td>
</tr>
<tr>
<td>~ 1710</td>
<td>Carbonyl C=O stretch</td>
<td>C=O</td>
</tr>
<tr>
<td>~ 1700-1630</td>
<td>Conjugated carbonyl C=O stretch</td>
<td>Conj C=O</td>
</tr>
<tr>
<td>~ 1650-1680</td>
<td>Amide C=O stretch</td>
<td>Amide I</td>
</tr>
<tr>
<td>~ 1600</td>
<td>Aromatic ring C=C stretching</td>
<td>Aro C=C</td>
</tr>
<tr>
<td>~ 1542</td>
<td>Amide NH bending</td>
<td>Amide II</td>
</tr>
<tr>
<td>~ 1440-1375</td>
<td>Linear &amp; cyclic -CH(_2) &amp; -CH(_3) bending</td>
<td>-CH(_2&amp;3)</td>
</tr>
<tr>
<td>~ 1300-1380</td>
<td>Amide C-N stretch (gen. weak)</td>
<td>Amide III</td>
</tr>
<tr>
<td>~ 1310-1200</td>
<td>Aromatic &amp; vinyl ethers, C-O-C stretch</td>
<td>Aro&amp;Vi E</td>
</tr>
<tr>
<td>~ 1250-1180</td>
<td>Phenolic C-OH stretch</td>
<td>Phen</td>
</tr>
<tr>
<td>~ 1140-1080</td>
<td>Aliphatic ethers, Carbohydrate C-O-C stretch</td>
<td>Ali E, Carbo</td>
</tr>
<tr>
<td>~ 1050-1000</td>
<td>Aromatic ethers, Carbohydrate C-O-C stretch</td>
<td>Aro E, Carbo</td>
</tr>
</tbody>
</table>

Table 3.4: Brief summary of descriptive kerogen terms used in visual analysis microscopy (Tissot and Welte, 1984)

<table>
<thead>
<tr>
<th>Kerogen</th>
<th>Description</th>
<th>Type</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algal</td>
<td>The remains of algae/plankton, identifiable by remaining structure and morphology, major component of Type I kerogen, also found in Type II</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amorphous</td>
<td>Organic matter without identifiable or distinct structure, often having algal source, typically abundant in Type II and to a lesser degree Type I kerogens</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Herbaceous</td>
<td>Fibrous plant material, generally of a terrestrial origin, seen on Types II and III</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Humic</td>
<td>Terrestrial organic matter retaining its woody structure, Type III, can be a minor component of Type II</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inertinite</td>
<td>Coal-like particles, generally having dark, angular appearance, probably result of weathering and/or redeposition of humic type organic matter</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.3: ATR-FTIR spectrum of fossil wood fragments isolated from bedrock samples MV1 and MV2 by density fractionation. A key to abbreviations for band assignments is found in Table 3.3.
45% C
C/N$_a$ = 68
$\delta^{13}$C$_{PDB} = -24.7\%$o

Figure 3.4: ATR-FTIR spectrum of a wood fragment from the coarse fraction of a soil (TM2).
37% C
C/N<sup>a</sup> = 95
δ<sup>13</sup>C<sub>PDB</sub> = -25.0‰

Figure 3.5: ATR-FTIR spectrum of the fine-grained particles isolated from bedrock samples MV1 and MV2 by density fractionation.
3.2.2 Bitumen fraction

Bitumen was extracted with a mixture of both polar and non-polar solvents and should contain a mixture of hydrocarbons (lower molecular weight, aromatic or aliphatic, nonpolar compounds), asphaltenes (high molecular weight, aromatic, relatively polar compounds), and resins (intermediate in composition between asphaltenes and hydrocarbons) (Tissot and Welte, 1984). Asphaltenes are more similar to the kerogen in composition than other extractable material (Rouxhet et al., 1980; Tissot and Welte, 1984; Christy et al., 1989). The bitumen FTIR spectrum shows (Figure 3.6) both large aliphatic bands from hydrocarbons and less intense bands that mirror the kerogen (i.e. aromatic, see Figure 3.9). Carbonyl (1710 cm$^{-1}$) content is clear, but is small compared to other published Type III resin/asphaltene spectra, suggesting greater maturity (Rouxhet et al., 1980; Christy et al., 1989). Some components suggested by the spectrum, grouped by type, are listed below in Table 3.5 (Nakanishi and Solomon, 1971; Czarnecka and Gillott, 1980; Tissot and Welte, 1984; Rose et al., 1999):
Table 3.5: Components suggested by the FTIR spectrum of the bitumen fraction.

<table>
<thead>
<tr>
<th>Bands</th>
<th>Band Assignments</th>
<th>Compounds Suggested</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) <strong>Strong bands at 2950-2850 cm(^{-1}) and 1450-1375 cm(^{-1})</strong></td>
<td>CH(_2) &amp; CH(_3) groups of the hydrocarbon backbones</td>
<td>Saturated hydrocarbons (straight, branching and cyclic)</td>
</tr>
<tr>
<td>weak bands below 1375 cm(^{-1}) and ~1300-1200 cm(^{-1}).</td>
<td>CH(_2) &amp; CH(_3) groups</td>
<td>n-alkanes and branching alkanes</td>
</tr>
<tr>
<td>~1100 cm(^{-1})</td>
<td>C-OH stretches</td>
<td>alkanols</td>
</tr>
<tr>
<td>diffuse bands at ~3600 cm(^{-1})</td>
<td>-OH</td>
<td>alkanols</td>
</tr>
<tr>
<td>~1710 cm(^{-1})</td>
<td>C=O stretches</td>
<td>alkanones</td>
</tr>
<tr>
<td>2950-3080 cm(^{-1})</td>
<td>CH(_2) stretching</td>
<td>polycyclic compounds</td>
</tr>
<tr>
<td><strong>Examples include pristine, decane, octanol, and hopanes.</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bands</th>
<th>Band Assignments</th>
<th>Compounds Suggested</th>
</tr>
</thead>
<tbody>
<tr>
<td>2) <strong>Small bands at 3020-3065 cm(^{-1})</strong></td>
<td>CH of aromatic and alkene groups</td>
<td>Unsaturated hydrocarbons</td>
</tr>
<tr>
<td>1600 and 1700 cm(^{-1}).</td>
<td>C=C stretch and cyclic ring C=C</td>
<td>alkenes and cycloalkenes</td>
</tr>
<tr>
<td>1600 cm(^{-1}) and possibly 1585 cm(^{-1})</td>
<td>C=C stretching</td>
<td>aromatic hydrocarbons</td>
</tr>
<tr>
<td>below 900 cm(^{-1})</td>
<td>aromatic ring bending/puckering</td>
<td>aromatic hydrocarbons</td>
</tr>
<tr>
<td><strong>Examples include pyrene, 1-octene, terpenes, and alkyl-phenols</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bands</th>
<th>Band Assignments</th>
<th>Compounds Suggested</th>
</tr>
</thead>
<tbody>
<tr>
<td>3) <strong>1500 and 1600 cm(^{-1})</strong></td>
<td>ring C=C stretch</td>
<td>Heterocyclic rings</td>
</tr>
<tr>
<td>below 900 cm(^{-1})</td>
<td>ring bending</td>
<td></td>
</tr>
<tr>
<td><strong>S and O rings are most likely given the low N content. An example is thiophene</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Maturity can be determined and related to vitrinite reflectance of the rock/sediment from which the bitumen was extracted from by the intensity of the 1710 cm\(^{-1}\) band (C=O) relative to the intensity of the band at ~1600 cm\(^{-1}\) (aromatic ring C=C stretch) (Rouxhet et al., 1980; Christy et al., 1989; Karstang, et al., 1991). The ratio for this bitumen is 0.5, a value similar to bitumen fractions associated with other Type III kerogens and suggests a R\(_o\).
value of ~0.5 for the associated kerogen, which is consistent the values reported by Underwood (1985) (Christy et al., 1989; Karstang, et al., 1991).

3.2.3 Base soluble fraction

The base soluble fraction (Figure 3.7) is expected to be similar to humic substances with prominent carboxylic and phenolic content. This fraction was rich in N, as humic substances often are, but had a more negative $\delta^{13}$C than expected. Humic substances generally have a more positive $\delta^{13}$C than their corresponding kerogens or insoluble OM fractions (Stevenson, 1982; Tissot and Welte, 1984). Inorganic species, such as silica, dissolved from the mineral in the basic extraction, obscure much of the FTIR spectrum and prevent further analysis.
Figure 3.6: ATR-FTIR spectrum of the bitumen extract (from <4 µm fraction of bedrock sample MV2). Peak intensities used in the maturity index calculation are marked (*) (Christy et al., 1989; Karstang et al., 1991).
Figure 3.7: ATR-FTIR spectrum of the base-soluble fraction isolated from bedrock sample MV2. Mineral impurities obscure absorbancies from the organic matter.
3.2.4 Demineralized kerogen

Elemental analysis of the demineralized kerogen demonstrates low N, S, and O content and indicates maturity (Table 3.5; Tissot and Welte, 1984). Rock-Eval whole rock pyrolysis, pyrolysis of the demineralized kerogen, and vitrinite reflectance ($R_o$) indicate a moderately mature to very mature Type III kerogen (Tissot and Welte, 1984; Underwood, 1985). The $T_{\text{max}}$ value places the kerogen in the thermally mature oil window and plots on a HI vs. $T_{\text{max}}$ diagram in a median position along the Type III maturation line (Tissot and Welte, 1984; Tyson, 1995). On a HI vs. OI diagram (Figure 3.8), various melange samples plot along the Type III evolution line. Samples with the highest OI values also contained talc and are from the Franciscan Eastern Belt, possibly the Yolla Bolly terrane (Blake et al., 1988). Talc is formed by the weathering of metamorphic rock, such as schists and amphibole suggesting the samples may have experienced a higher grade metamorphism and possibly more subaerial weathering than other samples examined here (Klein, 2002). While whole rock pyrolysis is routinely used to characterize the kerogen in bedrock, it can be subject to artifacts associated with low %C, the type of OM, high clay content, and the presence of bitumen (Katz, 1983; Crossey et al., 1986; Peters, 1986; Hartman-Stroup, 1987; Wilhelms et al., 1991). Here, the fine-grained melange matrix is ~1% OC and clay rich, both conditions that could cause spuriously low HI values. When analyzed via Rock-Eval the demineralized kerogen has an HI indistinguishable from most of the whole rock melange samples, validating that parameter for the whole rock analyses (Peters, 1986). In addition, the low carbon content of the sediment samples makes them susceptible to anomalously high OI values. Residual carbonate minerals, CO$_2$ and oxygen gas adsorbed to clay surfaces and
difficulties from poor signal to noise ratios probably contribute to high OI values in sediment samples (Katz, 1983; Peters, 1986).

Table 3.6: Characteristics of the demineralized kerogen isolated from bedrock sample MV2

<table>
<thead>
<tr>
<th>%OC</th>
<th>66%</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ¹³C_{PDB}</td>
<td>-23.7‰</td>
</tr>
<tr>
<td>C/N_a</td>
<td>63</td>
</tr>
<tr>
<td>C/S_a</td>
<td>293</td>
</tr>
<tr>
<td>O/C_a</td>
<td>0.11</td>
</tr>
<tr>
<td>R_o</td>
<td>~ 0.6–1%</td>
</tr>
</tbody>
</table>

Note: A maximum value as oxygen from mineral residues may contribute to the measured %O

<table>
<thead>
<tr>
<th>Rock-Eval</th>
<th>Analysis by DGSI, The Woodlands, TX</th>
</tr>
</thead>
<tbody>
<tr>
<td>HI</td>
<td>76 mg HC/g OC</td>
</tr>
<tr>
<td>OI</td>
<td>7 mg CO₂/g OC</td>
</tr>
<tr>
<td>T_{max}</td>
<td>438 °C</td>
</tr>
</tbody>
</table>

The FTIR spectrum of the demineralized kerogen is consistent with that of a Type III kerogen (Figure 3.9). Aliphatic bands are modest, while aromatic C=C and -CH bands at 1600 and 3030 cm⁻¹ are prominent. Additional aromatic ring bands (930-700 cm⁻¹) that are expected to appear as a result of catagenesis are strong, and the spectrum resembles some spectra from metagenic samples (Rouxhet et al., 1980; Tissot and Welte, 1984). The usually distinctive bands from C=O are inconspicuous and possibly shifted down in frequency,
which indicates maturity, a lack of weathering and their presence in conjugated aromatic units (Colthup et al., 1975; Nakanishi and Solomon, 1977; Rouxhet et al., 1980; Tissot and Welte, 1984; Petsch, 2000). There are strong bands in the C-O region ~1200-1000 cm$^{-1}$. While the C-O stretching vibration typically gives rise to strong bands, several other bands probably contribute to the response here, such as mineral Si-O and alkyl groups (Colthup et al., 1975; Nakanishi and Solomon, 1977). Various ether and aromatic oxygen functional groups are indicated. Given other maturity indicators, this spectrum suggests that much of the oxygen present is in aromatic (phenyl, heterocyclic, etc) or ether units with lesser amounts in hydroxyl, and carbonyl groups; carboxyl and ester groups are largely absent. This suite of oxygen functionalities is consistent with a Type III and/or mature kerogen, where significant terrestrial OM contributes to aromatic functionality. Ether and ester groups characteristic of algal OM are absent, while oxygen groups reflecting their cellulose and lignin precursors dominate. Thermal processes have reduced overall oxygen content while increasing aromatization (Tissot and Welte, 1984).

The CP/MAS $^{13}$C NMR spectrum of the demineralized kerogen also indicates a highly aromatic, mature, and unweathered material. The peak due to aromatic carbons dominates the spectrum (Figure 3.10). The position of the peak, centered at 127 ppm, is very similar to the peak that arises in fossilized wood from the carbon-substitution of a ring carbon in lignin subunits (Bates and Hatcher, 1989). The large aromatic carbon content, 71% of all carbons, relative to a much smaller aliphatic content, 19 %, suggests both a terrestrial source OM and very high maturity (Vucelic et al., 1979; Tissot and Welte, 1984; White et al., 1987; Mann et al., 1991). Oxygen containing groups are minimal (1.6% O-alkyl and
4.1% total C=O) and indicate that the kerogen has experienced little to no weathering (Tissot and Welte, 1984; Petsch et al., 2000). The O/C₄ ratio was estimated from the peak areas of the NMR spectrum and is consistent with the Rock-Eval and elemental analysis data (Tissot and Welte, 1984). A minimum value, 0.05, was derived by assuming that the signal from ~160-220 ppm was due solely to carbonyl groups. A maximum value, 0.1, was derived by assuming that the signal around 180 ppm was due to COOH groups.
Figure 3.8: Whole rock/sediment Rock-Eval data in a van Krevelen type diagram. HI and OI indices are proportional to H/C and O/C ratios, respectively, and are often used instead of elemental ratios to determine kerogen type. Data for bedrock samples from the Van Duzen and Middle Fork areas are shown (●). The position of the demineralized kerogen is marked for reference (☆) (after Tissot and Welte, 1984; Peters, 1986).
Figure 3.9: ATR-FTIR spectrum of the kerogen isolated by demineralization of bedrock sample MV2.
Figure 3.10: CP-MAS solid-state $^{13}$C NMR spectrum of the demineralized kerogen. Shift assignments by functional group (carbonyl, aromatic, etc.) and the relative percent of each type of carbon are shown. An estimate of 0.5-1 for the O/C elemental ratio was calculated from these percentages. The minimum value was derived by assuming that the signal from $\sim$160-220 ppm was due solely to $C=O$ groups. The maximum value was derived by assuming that the signal around 180 ppm was due to COOH groups and that a portion of the O-alkyl signal was due to O-C-O groups. Spinning sidebands, $\sim$3.5% of the total signal, are marked (*).
The carbon isotope signature can provide information about the sources of organic matter to a kerogen and possibly its geothermal history. The δ¹³C of low maturity kerogens, like recently deposited OM, reflects the C signature of the OM sources (Deines, 1980; Whelan & Thompson-Rizer, 1993). As a kerogen matures, its δ¹³C is still dominated by its original source OM, allowing some inference about the kerogen’s depositional environment (Schidlowski, 1986; Whelan & Thompson-Rizer, 1993). Isotopic shifts from the elimination of relatively ¹³C enriched groups, such as carboxylic acids, or from relatively ¹³C depleted groups, such as aliphatic compounds, can occur but are generally small, often <1‰ (Galimov, 1980; Peters et al., 1981a; Peters et al., 1981b; Tissot and Welte, 1984; Clayton, 1991). Sufficient thermogenic methane production can cause larger isotopic shifts, but all shifts tend to be minimized in more aromatic or humic type kerogens, as they generally do not produce substantial quantities of gas or oil (Peters et al., 1981a; Peters et al., 1981b; Tissot and Welte, 1984). Overall, isotopic shifts in a developing kerogen are primarily due to the loss of isotopically light hydrocarbons, but until enough hydrocarbon is lost to reduce the H/C ratio to 0.2 or less, a kerogen is considered "well-preserved," and its isotope signature is a reliable predictor of the original source OM (Schidlowski et al., 1983; Strauss et al., 1992). The kerogen analyzed here, while mature, has shown little evidence of and limited potential for hydrocarbon production and has a H/C ratio > 0.2, suggesting that post-burial isotopic shifts are minimal (Underwood, 1985; Larue, 1991). Therefore, the isotope signature of this kerogen likely reflects the original OM immobilized in the accumulating sediment. The Franciscan complex originated as a sedimentary accumulation that was incorporated into an accretionary wedge on the continental margin along a subduction zone (Underwood, 1985;
Blake et al., 1988). While deposition occurred in a marine setting, sediment was probably largely terrigenous and the presence of terrestrial OM in the kerogen is easily confirmed by visual analyses. The $\delta^{13}C$ signature of -23.7‰ of the demineralized kerogen suggests a mixture of marine (-19 to -22‰) and terrestrial C3 plant (-25 to -30‰) organic matter based on modern values (Meyers, 1994; Tyson, 1995. However, the $\delta^{13}C$ of marine organic matter has not always remained constant over geologic time, complicating any estimation of terrestrial and marine OM sources to the kerogen-laden bedrock.

During the Mesozoic and early Cenozoic eras, the $\delta^{13}C$ of marine primary productivity is thought to have shifted as much as 5-7‰ more negative with changing concentrations of dissolved CO$_2$ in seawater (Dean et al., 1986; Rau et al., 1989; Rau et al., 1991; Laws et al., 1995; Popp et al. 1997). Marine OM generated during periods of CO$_2$ enrichment could have a $\delta^{13}C$ indistinguishable from terrestrial OM, which has remained fairly consistent. Evidence from isotope signatures of geoporphyrins suggests that the $\delta^{13}C$ of marine OM varied to a value as negative as -28‰ during this period (Popp et al., 1989).

The age of the Central Belt of the Franciscan assemblage, of which the Van Duzen bedrock examined here is part, is about 110 Ma, with blocks ranging from ~90–170 Ma in age - a time period well within the window for a more negative marine $\delta^{13}C$ value (Blake et al., 1988; Terabayashi and Maruyama, 1998). Accordingly, contributions from terrestrial versus marine OM sources calculated from the $\delta^{13}C$ will be ambiguous because of the poor constraint on the marine end-member. A purely marine OM source could be postulated if based solely on the kerogen’s isotope signature, but is refuted by other data. Knowing that there is a significant terrestrial OM component and given the kerogen’s $\delta^{13}C$ of -23.7‰, the
marine $\delta^{13}C$ must have been at least as positive as -23‰, a value within the range suggested by Popp et al. (1989). The low density fraction isolated from the bedrock is largely, if not entirely, terrestrial. It accounts for 6.5% of the total carbon in the fine-grained matrix of the bedrock sampled, and suggests a minimum terrestrial OC content of around 7% in the bedrock OM. Assuming the terrestrial end-member to be -25‰ (the $\delta^{13}C$ ratio of the light density material isolated from the bedrock) and the marine end-member to be -23‰, the ratio of OC in the kerogen is predicted to be about 2:1. If the actual marine $\delta^{13}C$ at the time of deposition was more similar to modern values, such as -19‰, the estimated marine:terrestrial ratio is about 1:3.
3.3 Particle Bound OM in Soils and Sediments

3.3.1 Mineral composition in the <4 µm size fraction

In order to understand the dynamics of particle-bound OC, some information about the particles themselves is necessary. Do the particles that reach the seabed have characteristics consistent with those of the particles found in the watershed? Most samples analyzed from the system, both terrestrial and marine, have a similar clay mineral composition. Figure 3.11 shows two mineral spectra that represent the compositional range of samples. Most samples are mainly a mixture of illite and chlorite with lesser quantities of kaolinite and quartz, and in a few cases, talc (van der Marel and Beutelspacher, 1976; Estep-Barnes, 1977; Russell and Fraser, 1994). These minerals are consistent with the fine-grained melange matrix (rich in shales and schists) and sandstone block composition of the watershed and with sedimentary rock of a detrital marine origin (Grim 1968; Buol et al., 1973; Velde 1985; Klein 2002). The sandstone (SE1) and the fine-grained matrix (MM1) samples are examples illustrating the variety of bedrock and soils seen in this study. The sandstone is a more highly weathered unit composed of largely kaolinite and quartz, whereas the fine-grained matrix sample is relatively chlorite-rich (a common mineral in schists and shales) and contains talc, suggesting a low grade metamorphic ultramafic origin (Grim, 1968; Velde, 1985; Klein, 2002). All other samples fell between the two compositional extremes (see all mineral spectra in Appendix 6.1). The range of mineral composition is demonstrated by a graph of the absorbance at 3552 cm⁻¹ versus the position of the maximum absorbance due to Si-O stretching in the silicate tetrahedral layers of the clays (Figure 3.12). Here, where chlorite is the only mineral assignable to that peak, $\text{ABS}_{3552}$ can be used as a proxy for
chlorite content. These spectra lack peaks that suggest the presence of other minerals that may have spectra with an absorbance at 3552 cm\(^{-1}\) (glauconite, for example, which has very sharp peaks at \(\sim3600, 3533\), strong bands at 1098, 976, 682 and a doublet at 838/798 cm\(^{-1}\), Russell and Fraser, 1994). The position of the most intense Si-O band reflects the varying composition between a more kaolinite/illite-rich sample and a more chlorite-rich sample. Bedrock samples (fine-grained matrix and sandstone) are spread across the range, as are soils. River sediments (collected during high discharge events) fall in a median position, perhaps reflecting the mixing of various bedrock and soil sources. All marine samples fall within the same range.

In a study of marine sediments on the Eel Shelf, Perkey (2003) analyzed the clay mineralogy of samples using X-ray diffraction (XRD) throughout a 2-m long core, which recorded deposition to approximately 1500 years before present. Mineralogy was consistent throughout the core; chlorite and illite were major constituents with quartz and smectite also present, probably as more minor constituents (Perkey, 2003). Vermiculite was considered another possible minor component, but could not be verified (Perkey, 2003). The mineral composition found by XRD is consistent with that found here by FTIR. Kaolinite, which was easily identified by FTIR, was not detected by XRD and may be a minor component for many samples. Kaolinite has a high absorption coefficient because of its highly ordered mineral lattice, so infrared analysis is especially sensitive to its presence (Estep-Barnes, 1977). The composition of soils and sediments identified here agrees with previous mineralogical studies of the area except in the detection of smectite/montmorillonite (Schlocker 1974; Griggs and Hein, 1980; Karlin, 1980; Ransom et al., 1998). While other
mineralogical studies using XRD have found various percentages of smectite (as much as >20%) in river and marine sediment samples, the presence of smectite could not be positively identified by IR analysis. Unfortunately, absorbance peaks characteristic of smectites around 1000 cm\(^{-1}\) could be obscured by kaolinite, while the smectite \(-\text{OH}\) stretching region might be similar to illite or chlorite or be fairly indistinct (van der Marel and Beutelspacher, 1976; Estep-Barnes, 1977; Russell and Fraser, 1994).
Figure 3.11: Identifying mineral composition. FTIR spectra of the \(<4 \mu m\) size fraction of two samples, a sandstone (-----) and a fine-grained melange matrix sediment (-----) are shown. Absorbances indicating specific mineral components, Chlorite (C), Illite (I), Kaolinite (K), Quartz (Q), and Talc (T) are marked. Note that peaks can often be due to multiple components. Where more than one mineral may contribute, components are listed in order of decreasing importance.
Figure 3.12: The range of mineral compositions is illustrated by IR spectral characteristics. River sediments are from large discharge events (i.e. floods). Marine samples are from both surface and subsurface flood and non-flood deposits.
3.3.2 OM sources and loading on <4 µm particles

Most soil and sediment samples contained ~1% OC (Table 3.1 and Figure 3.13). C/N\textsubscript{a} ratios were highest in bedrock and lowest in marine samples. pMC values generally increased from bedrock to soil, to river, to marine samples suggesting the progressive addition of modern OM as particles spend more time in contact with the photosynthetic environment. Soils were the most variable group in all analyses.

Kerogen, modern terrestrial and modern marine OC fractional percentages of total OC were calculated using $\delta^{13}$C and and $\Delta^{14}$C data (Table 3.7). The absolute concentration, or loading, of each fraction was then calculated using the fractional percentages, %OC and SA (Figure 3.14). Organic carbon contributions to a sediment sample were resolved using a mixing model for three OC pools: kerogen, terrestrial, and marine. This mixing model is described by equations 1-3 below where $\delta$ is the $\delta^{13}$C, $f$ is the fraction of total OC due to an OM source, and $\Delta$ is the $\Delta^{14}$C value. The subscripts denote that each variable attributable to the total sediment OM (s), or to the kerogen OM (k), modern terrestrial OM (t), or modern marine OM (m) fractions.

\begin{align*}
1 & \quad \delta_s = f_k \delta_k + f_t \delta_t + f_m \delta_m \\
2 & \quad \Delta_s = f_k \Delta_k + f_t \Delta_t + f_m \Delta_m \\
3 & \quad 1 = f_k + f_t + f_m
\end{align*}

In bedrock, soil and river sediments there is no marine component ($f_m = 0$) and $f_k$ and $f_t$ can be calculated by simplifying equations 1 and 3.

\begin{align*}
4 & \quad f_k = (\delta_s - \delta_t)/(\delta_k - \delta_t) \\
5 & \quad f_t = 1 - f_k
\end{align*}
δ^{13}C end-member values used in this calculation were chosen with consideration of location and the potential history of each sample (Table 3.7). When possible, the δ^{13}C value of the bedrock underlying each soil sampled was used as the kerogen end-member; otherwise the average δ^{13}C value for melange across the watershed was used. The δ^{13}C value from plants growing in the sampled soil or from OM fragments isolated from the coarse fraction were used as terrestrial end-members for soils when possible. In two cases the average δ^{13}C value of plants of the type observed at the sampling site, such as grasses, were used (subsets of the plant samples described in Blair et al., 2003, which had a average δ^{13}C of -27.9 ± 2.4‰). The integrated terrestrial δ^{13}C value calculated from river sediment coarse fractions, -26.5 ± 1.1‰, was used for riverine suspended sediments (Blair et al., 2003). The potential movement of a developing soil, such as down slope with a landslide, creates some uncertainty that a soil overlays its parent material. OM leaching into parent material from the overlying developing soil could affect the isotope signature of the bedrock OM, leading to underestimates of the terrestrial fraction. While coarse OM fragments in a soil provide direct evidence of the OC entering the soil, they do not necessarily represent the multiple species of plants that might have contributed to the OM in the soil. Seasonal as well as longer-term shifts in vegetative cover and differences in debris size, since only larger fragments could be visually identified, may bias the value.

All soil samples were taken near the surface from profiles showing little evidence of soil development, except the thick soil sample, TV2. Here the soil sample was taken from a freshly exposed 12-18 ft thick oxidized soil layer. Given the potential for aged OM in this sample, caution in the interpretation of the ^{14}C analysis is necessary. This sample has a ^{14}C
content equivalent to ~5000 years in age or to 50% modern carbon and 50% $^{14}$C depleted carbon. The kerogen content of the <4 µm particles accounts for, at most, half the OC to at minimum, none of the OC. While soil OM can be thousands of years old (Brady and Weil, 2002), the high rates of erosion in the Eel watershed in general, and recovery of this sample from an area underlain by a large earth flow, suggest the soil is unlikely to be that old. Also, for the soil OM to be totally composed of aged terrestrial OM, the kerogen load from the parent material must have been completely oxidized, unlikely considering its recalcitrance. Assuming that the OC is 50% modern, the calculated kerogen concentration is 0.19 mg OC/m$^3$, the same as the underlying bedrock (0.20 mg OC/m$^3$). Here, this sample was therefore considered to have an OC load of 50% kerogen carbon and 50% essentially un-aged (<500 years) terrestrial carbon.

For marine sediments, the measured $\Delta^{14}$C and $\delta^{13}$C were used to resolve contributions from kerogen, terrestrial and marine OM. Here, both terrestrial and marine OM can contribute to the $^{14}$C-containing pool and together are responsible for the modern fraction. Combining equations 2 and 3 and using $+100‰$ for the terrestrial and marine values and $-1000‰$ for the kerogen value reduces $f_k$ to $(100\Delta)_1/1100$ (Blair et al., 2003). Substituting this term, $-21‰$ for $\delta_m$ and $-26.4‰$ for $\delta_k$ (the calculated values for marine and terrestrial OC added to particles in Blair et al., 2003), equations 1 and 3 can be combined and solved for $f_t$. Finally, $f_m$ is found using equation 3. Since the marine end-member value was calculated from analysis of surface sediments (Blair et al., 2003), it may only represent marine OM deposited recently and not that added to the sediments found deeper in the seabed.
The $\Delta^{14}C$ end-member for marine organic matter can be lowered by aged carbon from upwelling of deeper water reservoirs, an occurrence reported off the California coast (Berger et al., 1966; Stuiver and Braziunas, 1993; Goodfriend and Flessa, 1997). The dual isotope calculation is fairly insensitive to lowered $\Delta^{14}C$ in the marine fraction. For instance, a $\Delta^{14}C$ of 0‰ instead of 100‰ yields a $f_k$ of 0.27 instead of 0.32 for sample O550, the sample with the highest marine load in this study. The effect is less in samples with a lower marine content; using 0‰ as the marine $\Delta^{14}C$ end-member yields a change of 0.02 for a $f_k$ in sample O150.

Bedrock, even disturbed and exposed samples, contain very little modern/terrestrial OC (Figure 3.14). Soils can have large kerogen components. While plant-derived OC is obviously added as soil develops from kerogen-laden bedrock, kerogen loads remain within the range seen in bedrock samples. Short residence times due to rapid erosion, chemical stability and physical protection within stable soil micro-aggregates are all factors that promote kerogen survival in the pedosphere and help create a exportable load of sediment-borne ancient carbon (Oades, 1993; Golchin et al., 1994; Keil et al., 1994a; Keil et al., 1994b; Mayer 1994a; Skjemstad, et al., 1996; Ransom et al., 1998; Bock and Mayer, 2000; Blair et al., 2004). Kerogen accounts for up to nearly 60% of OC in the river and marine clay-sized sediments analyzed. There is a general trend for increasing modern content and % marine OC going offshore and away from Eel River flood deposits (Leithold and Blair, 2001; Blair et al., 2003). Sediments deposited in slower accumulation regimes (i.e. non-flood periods, sample K8) generally have more marine OC than those deposited during periods of more rapid accumulation (i.e. flood deposits, sample K27) (Perkey, 2003; Blair et al., 2003;
Leithold et al., 2005). While additions of marine OC increase the $^{14}C$ content, kerogen or terrestrial OC loads on the marine particles appear largely unchanged from OC loads delivered by river to the shelf.
Figure 3.13: Average values for the < 4 μm size class of different sample types. Error bars show the standard deviation. Sample sizes are n=9, n=2, n=6 and n=8 for fine-grained bedrock, sandstone, soil, suspended sediment, and marine samples respectively. Sample sizes for pMC measurements are n=4, n=1, n=3, and n=5 for fine-grained bedrock, soil, suspended sediment and marine samples respectively.
Table 3.7: Calculation of the fractional kerogen content of terrestrial and marine sediments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Kerogen $\delta^{13}$C end-member, %</th>
<th>Terrestrial plant $\delta^{13}$C end-member, %</th>
<th>$f_i$ by equations 4 and 5</th>
<th>$f_i$ by simultaneous solution of equations 1, 2 and 3</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>MV4</td>
<td>Van Duzen disturbed bedrock</td>
<td>-24.0 ± 0.25</td>
<td>-28.7 ± 0.17</td>
<td>1.0 ± 0.0076</td>
<td>0.95 ± 0.01</td>
<td>1, 2</td>
</tr>
<tr>
<td>MV5</td>
<td>Van Duzen disturbed bedrock</td>
<td>-24.0 ± 0.25</td>
<td>-28.7 ± 0.17</td>
<td>1.0 ± 0.0076</td>
<td>0.95 ± 0.01</td>
<td>1, 2</td>
</tr>
<tr>
<td>TV1</td>
<td>Van Duzen soil</td>
<td>-24.0 ± 0.25</td>
<td>-28.7 ± 0.17</td>
<td>0.67 ± 0.0050</td>
<td></td>
<td>1, 2</td>
</tr>
<tr>
<td>TV2</td>
<td>Van Duzen soil</td>
<td>-24.0 ± 0.25</td>
<td>-26.2</td>
<td>0.72 ± 0.0061</td>
<td>0.55 ± 0.08</td>
<td>1, 3 (n=1)</td>
</tr>
<tr>
<td>TN1</td>
<td>Soil, grassy and conifer vegetation</td>
<td>-24.1</td>
<td>-28.3 ± 2.4</td>
<td>0.80 ± 0.051</td>
<td></td>
<td>4, 5</td>
</tr>
<tr>
<td>TA1</td>
<td>Soil, grassy vegetation</td>
<td>-23.6</td>
<td>-27.6 ± 1.9</td>
<td>0.70 ± 0.037</td>
<td></td>
<td>4, 5</td>
</tr>
<tr>
<td>TM1</td>
<td>Soil</td>
<td>-24.5</td>
<td>-27.0 ± 0.41</td>
<td>0.90 ± 0.0060</td>
<td></td>
<td>4, 3 (n=3)</td>
</tr>
<tr>
<td>TM2</td>
<td>Forested soil</td>
<td>-24.5</td>
<td>-25.6 ± 1.1</td>
<td>0.58 ± 0.018</td>
<td></td>
<td>4, 3 (n=4)</td>
</tr>
<tr>
<td>MV6</td>
<td>Van Duzen suspended sediment</td>
<td>-24.0 ± 0.25</td>
<td>-28.7 ± 0.17</td>
<td>0.83 ± 0.0063</td>
<td></td>
<td>1, 2</td>
</tr>
<tr>
<td>RC1</td>
<td>River suspended sediment</td>
<td>-24.3 ± 0.6</td>
<td>-26.5 ± 1.1</td>
<td>0.67 ± 0.022</td>
<td>0.57 ± 0.19</td>
<td>6, 7, 8, 9</td>
</tr>
<tr>
<td>RS1</td>
<td>River suspended sediment</td>
<td>-24.3 ± 0.6</td>
<td>-26.5 ± 1.1</td>
<td>0.63 ± 0.021</td>
<td>0.59 ± 0.20</td>
<td>6, 7, 8, 9</td>
</tr>
<tr>
<td>RS2</td>
<td>River suspended sediment</td>
<td>-24.3 ± 0.6</td>
<td>-26.5 ± 1.1</td>
<td>0.67 ± 0.022</td>
<td>0.58 ± 0.19</td>
<td>6, 7, 8, 9</td>
</tr>
<tr>
<td>O70</td>
<td>Surficial flood deposit</td>
<td>-24.3 ± 0.6</td>
<td>-26.5 ± 1.1</td>
<td>0.61 ± 0.20</td>
<td></td>
<td>6, 7, 8, 9</td>
</tr>
<tr>
<td>O150</td>
<td>Surficial sediment</td>
<td>-24.3 ± 0.6</td>
<td>-26.5 ± 1.1</td>
<td>0.58 ± 0.19</td>
<td></td>
<td>6, 7, 8, 9</td>
</tr>
<tr>
<td>O550</td>
<td>Surficial sediment</td>
<td>-24.3 ± 0.6</td>
<td>-26.5 ± 1.1</td>
<td>0.32 ± 0.12</td>
<td></td>
<td>6, 7, 8, 9</td>
</tr>
<tr>
<td>K8</td>
<td>Non-flood layer, 1990s</td>
<td>-24.3 ± 0.6</td>
<td>-26.5 ± 1.1</td>
<td>0.42 ± 0.14</td>
<td></td>
<td>6, 7, 8, 9</td>
</tr>
<tr>
<td>K27</td>
<td>Flood layer, 1980s</td>
<td>-24.3 ± 0.6</td>
<td>-26.5 ± 1.1</td>
<td>0.55 ± 0.19</td>
<td></td>
<td>6, 7, 8, 9</td>
</tr>
</tbody>
</table>

1. Kerogen value from average $\delta^{13}$C of Van Duzen bedrock samples MV1-4
2. Plant value from average $\delta^{13}$C of grasses collected onsite (n=3)
3. Plant value from $\delta^{13}$C of OM in >25 μm fraction of that sample
4. Kerogen value from $\delta^{13}$C of melange directly underlying soil sample
5. Plant value from average $\delta^{13}$C of grasses or grasses and conifers collected across watershed (Blair et al., 2003)
6. Kerogen value is from the average $\delta^{13}$C of melange sampled across the watershed (Blair et al., 2003)
7. Plant value is the calculated $\delta^{13}$C of OC added to <4 μm particles that accounts for added OC load in river sediments (Blair et al., 2003)
8. Marine value is the calculated $\delta^{13}$C of OC added to <4 μm particles that accounts for added OC load in shelf and slope sediments, -21.0 ± 0.7 (Blair et al., 2003)
9. Error by method given in Blair et al., 2003
Figure 3.14: Organic carbon loading on < 4 μm particles by carbon source. Surface area normalized OC concentrations for the kerogen, modern terrigenous OC, and modern marine OC fractions on the clay-sized particles is calculated. Terrigenous inputs are minimal for the bedrock samples. River suspended sediments are similar to the soils in terrigenous content. Samples from flood deposits (K27, O70, and O150) resemble river sediments, while non-flood sediments (K8 and O550) have increased marine OC fractions.
3.3.3 C/N ratios and OM sources

Carbon to nitrogen ratios have been used as OM source indicators in marine sediments (Meyers, 1994; Hedges and Oades, 1997). Often on continental margins where both terrestrial and marine OM can contribute to sedimentary OM, the system is treated with a two end-member mixing model (see Figure 3.15), where the sources are resolved by the use of C/N ratios and $\delta^{13}$C values. Applying that concept to soils developing from kerogen-laden bedrock with plant OM additions, we see that the mean C/N$_a$ ratio of fine-grained matrix samples, 20.2 ± 5.6 (n=9), is much lower than that of most plant OM (25->300), but the C/N$_a$ ratios of the soils are not intermediate, as expected for a simple mixture, but lower than the bedrock (11.3 ± 5.4, n=6) (Meyers, 1994; Tyson, 1995; White et al., 2000). Generally, C/N decreases with depth in soils due to nitrogen immobilization (Stevenson, 1982; Gregorich et al., 1996; Hedges and Oades, 1997; Schulten and Schnitzer, 1998). Because of differences in microbial cycling of C and N, C/N values of a soil do not simply mimic the overlying vegetation.

As bacteria decompose plant OM of high C/N ratio, generally 2/3 of carbon is lost as CO$_2$ by respiration, while nitrogenous wastes are scavenged by bacteria and fungi to maintain their biomass at a C/N$_a$ ratio of 5 - 15 (Oades, 1984; Hedges and Oades, 1997; Brady and Weil, 2002). The type of vegetation growing in a soil affects nutrient and C cycles and influences the resultant C/N. Fast growing, non-woody plants with relatively low C/N ratios are rapidly decomposed by a bacteria-dominated microbial community and the soil has high nutrient recycling and bioturbation rates, so little OC is sequestered (Brady and Weil, 2002; Wardle et al., 2004). Slower growing woody plants with high C/N ratios provide more
recalcitrant OM that is slower to decompose. Fungi dominate the soil's microbial community where nutrient recycling and bioturbation rates are low and much of the added OC is sequestered (Brady and Weil, 2002; Wardle et al., 2004). Generally, microbes require 1 part nitrogen for every 28 parts carbon to maintain growth; 19 parts C are respired while 9 parts C and essentially all of the 1 part N are incorporated into biomass (Brady and Weil, 2002). When the C/N ratio of the OM entering the soil is >28, nitrogen is highly scavenged. Once the C/N ratio of the soil OM nears the value of microbial biomass, N is no longer highly scavenged and excess N is mineralized.

Microbial processing also results in proteinaceous aromatic polysaccharide metabolites, readily sorbed to fine aluminosilicate clay minerals found in the <4 µm size fraction (Hedges, 1978; Rice and Tenore, 1981; Bladock et al., 1992; Hedges and Oades, 1997). Accordingly, these byproducts tend to accumulate in the clay-sized fraction and its C/N ratio tends to shift toward that of microbial biomass (Oades, 1984; Amato and Ladd, 1992; Hassink et al., 1993; Keil et al., 1994a; Keil et al., 1994b; Hedges and Oades, 1997). Chemical sorption can also help enrich organic nitrogen on the aluminosilicate clay minerals of the fine fraction (Aufdenkampe et al., 2001). So, while a soil's decrease in its C/N ratio is partially due to nitrogen accumulation in microbial biomass, it is more probably due to extracellular microbial excretions, like mucopolysaccharides, that make up the proteinaceous and heterocyclic organic pools that account for most nitrogen in soil (Rice and Tenore, 1981; Schulten and Schnitzer, 1998). As suggested by Natelhoffer and Fry (1988) C/N ratios may provide sensitive indicators of bacterial alteration of OM. While δ^{13}C ratios are generally conserved with OM degradation, C/N ratios decrease with degradation (Natelhoffer and Fry,
Because of the ease of elemental analysis, C/N ratios may be useful as a screening technique to identify samples for more expensive and involved analysis for microbial activity such as amino acid, \(\delta^{15}\)N or fatty acid analysis (Natelhoffer and Fry, 1988; Dauwe and Middleburge, 1998; Petsch, 2000).

When considering possible organic matter sources to marine sediments, plant debris can be distinguished from marine OM by C/N ratios, but sediment-bound terrestrial OM may have a C/N indistinguishable from marine OM. The overlapping ranges of Eel River soil and marine OM ratios are demonstrated in Figure 3.15. Since terrestrial sediment is delivered to the marine shelf via the river's suspended sediment load it provides the best terrestrial end-member for inputs to the marine sediment (Leithold and Blair, 2001; Blair et al., 2003). River sediments (<4 \(\mu\)m) had C/N\(\_a\) ~12, a value near the upper limit of typical marine C/N\(\_a\) ratios, rendering C/N analyses functionally insensitive to additions of marine OM. C/N ratios have greater utility in analyzing coarse fractions and whole sediments for resolving OM sources. Larger, more intact OM fragments retain their source chemical signature better than OM in the <4 \(\mu\)m fraction, where microbial processing tends to alter its C/N signature.
Figure 3.15: Applying a $\delta^{13}C$ and C/N ratio two end-member mixing model to the Eel River system.
3.3.4 FTIR analysis: Insights into molecular composition

FTIR spectra were taken to more closely examine the sediment bound OM in the <4 µm size fraction. While FTIR has been often used to analyze soil OM, studies have generally focused on organic matter extracts (such as humic acids), bulk soils, or organic-rich soils (Fieldes et al., 1972; Schnitzer, 1982; Schnitzer et al., 1988; Haberhauer et al., 1998; Haberhauer and Gerzabek, 1999). In the <4 µm sediments studied here, samples are commonly ~1% OC by weight. Accordingly, the OM infrared absorbance signal is small and obscured by the spectra of inorganic components at some wavelengths (Figure 3.17). The prominent features are due to the mineral absorbencies, specifically –OH stretching (3800-3000 cm\(^{-1}\)) and deformation (800-600 cm\(^{-1}\)) and Si-O-Si/Si-O-Al bonds (1250-800 cm\(^{-1}\)). Useful regions not obscured by mineral peaks, ~2000–1200 cm\(^{-1}\) and 3100–2600 cm\(^{-1}\), are illustrated.

Mineral content can also have other affects in the OM spectra. Some peak broadening is possibly due to the close association of the organic material with the minerals of clay-sized particles. For example, the N-H stretching band of OM absorbed by clays can vary as follows: 3311 cm\(^{-1}\) with H-montmorillonite, 3333 cm\(^{-1}\) with Ca-montmorillonite, 3280 cm\(^{-1}\) with Na-montmorillonite and 3250 cm\(^{-1}\) with hectorite (Yariv, 2002). Different mineral compositions and varying cationic substitutions create sorption sites of differing electronegativity, hydrogen bonding potential, and abilities to act as Lewis acids or bases, etc., and thereby affect the position and intensity of the peaks in IR spectra of absorbed organic matter (Billingham et al., 1996; Yariv, 2002). Heterogeneity in the mineral matrix and the resultant possible band shifts could broaden the peaks in the spectra of absorbed OM.
Infrared absorbance of carbon to oxygen bonds can be especially sensitive to differences between clay minerals, and their reactions with metals (such as iron) can reduce or shift C=O bands found at 1700-1730 cm\(^{-1}\) (Klaus and Zech, 1997; Kubicki \textit{et al.}, 1999; Yariv, 2002). Carbonyl bands, although having typically very strong absorbancies, were often indistinct in spectra of the OM in the <4 \(\mu\)m fraction, even when a spectrum shows other bands attributable to amide C-N bands (proteinaceous material should contain both). These bands may be truly absent (along with the absence of amide bands) or reduced and/or shifted by mineral interaction so that they are lost amongst the broad band at \(\sim\)1650 cm\(^{-1}\).

These analyses are further handicapped by the difficulties in obtaining consistent, high-quality spectra. Mineral absorbancies obscure potentially informative areas of the spectra. In addition, the clay-minerals that are abundant in this fraction are hydroscopic. The minerals present, like chlorite, and any trace water in the sample rendered the region from 3100 to 2600 cm\(^{-1}\) useless in most samples. Any variations in dryness, or water vapor contamination of samples while scanning could reduce spectra quality. Poor sample contact with the ATR element is also a potential problem. If micro-aggregates are present in the sample, the ATR technique might only "see" OM on aggregate exteriors, not necessarily the same as OM inside the aggregate.

Examples of spectra of bedrock, soil and marine samples are shown in Figure 3.17. Some spectra show distinct bands from OM, while many are relatively simple, with only a couple broad absorbance bands. The bedrock spectrum shown is typical of all the fine-grained melange matrix spectra, possessing a broad aromatic band with some contribution from carbonyl bands, and bands from methyl groups and phenolic/ether C-O bonds.
Although obscured by mineral peaks, this pattern reflects the kerogen in the bedrock (see demineralized kerogen spectra, Figure 3.9), with its strong bands from aromatic and ether bonds. Figure 3.17 illustrates some to the bands identified in the OM spectra (see all organic matter spectra in Appendix 6.2).

Spectral features were examined for correlations with other sample characteristics and several questions were posed.

1. Do spectral features correlate with other analyses?

Similar C/N ratios, $\delta^{13}\text{C}$, pMC or OC loads do not indicate similar FTIR spectra, nor do they necessarily predict the presence or intensity of particular bands.

2. Are there changes indicative of kerogen oxidation, possibly increasing with bedrock exposure and particle transport through the system, such as increased C=O bands and decreased aromatic bands (Rouxhet et al., 1980; Tissot and Welte, 1984; Petsch, 2000)?

No distinct C=O bands were seen in any bedrock sample. The height of the broad band from C=O and C=C bonds varied. Clear C=O bands were only seen when other distinct bands were present, suggesting their presence was due to modern OM additions, not kerogen oxidation.

3. Do spectra become more complex and show increasing band intensities with additions of modern OM or OC loads?

Some modern sediment samples had spectra indistinguishable from bedrock samples, lacking distinct features. Other modern sediments did have sharper, distinct peaks easily attributed to modern OM contributions, such as aromatic C=C and amide groups.
4. Are there bands indicative of woody, terrestrial OM that increase with increasing terrestrial OC loads, such as C=C bands at 1600 and 1500 cm\(^{-1}\)?

While some terrestrial sediments did have IR spectra with distinct woody-type bands, others did not. A greater \(f_t\) did not consistently predict the presence of such bands.

5. Are there bands indicative of marine OM that increase with increasing marine OC loads, such as C=O and amide bonds?

While some marine samples did have a protein-like signal, others did not. A greater \(f_m\) did not necessarily coincide with the presence of these bands.

6. Does the presence of amide bands correspond with lower C/N ratios?

For all sample types, a lower C/N ratio did not consistently predict the presence or absence of amide bands.

As with C/N ratios, the source molecular composition of OM as detected by IR spectra is not necessarily conserved. Microbial processes may alter the molecular form of the OM. IR spectra of decomposing plant matter become less characteristic as distinct bands decrease and background increases from multiple by-products; overall, spectra begin to resemble those of humic acid (Flaig, 1964). In deeper horizons and older soils, microbial decomposition helps immobilize N, largely in a degraded, humified, processed form in the clay-sized fraction (Flaig, 1964; Suberkropp et al., 1976; Hedges, 1978; Rice and Tenore, 1981; Hopkins and Shiel, 1991; Bladock et al., 1992; Gregorich et al., 1996; Hedges and Oades, 1997). Even though the OM is nitrogen enriched, the nitrogen is bound up by the humification process and becomes less readily available through condensation reactions of amino acids/proteins with carbohydrate and phenolic groups, which may obscure protein
absorbance bands (C=O and amide) (Suberkropp et al., 1976; Hedges, 1978; Rice, 1982; Yamamoto and Ishiwarari, 1989). Concurrent with the decrease in C/N ratios, the particle-bound OM of the clay-sized fraction can lack visually identifiable plant OM as well as the phenolic subunits of the unbound OM in the soil (Golchin et al., 1994). Gregorich et al. (1996) also reported that as OM is incorporated into the clay-sized fraction it can lose the distinct carbohydrate and phenolic character seen in the woody OM of the surface soil. This process is especially evident in the clay-sized fraction where microbial by-products accumulate, possibly aided by the formation of stable micro-aggregates (Oades, 1984; Hopkins and Shiel, 1991; Amato and Ladd, 1992; Hassink et al., 1993; Golchin et al., 1994; Keil et al., 1994a; Keil et al., 1994b; Skjemstad et al., 1996; Hedges and Oades, 1997).

Similar to soil, the mineral-associated OM in the clay-sized fraction of marine sediments is more degraded than the coarser, lower density fraction (OM fragments) (Arnarson and Keil, 2001).

The IR spectrum of the OM in the <4 µm fraction reflects not only the source OM but also the microbial processes that can degrade it and probably have some role in the flux of OM into that fine faction. Accordingly, characteristics that are good source OM markers, like δ¹³C or fractional loadings from dual carbon isotope analysis, are not always consistent with IR spectra. For example, intuitively, one would expect soil OM, being a mixture of kerogen and plant residues, to have a spectral signal intermediate between the kerogen and plant, becoming more plant-like as modern terrestrial OC increased. While soil spectra generally had larger band intensities, only some had clear plant-like components to their spectra, such as soil sample TV1 (Figure 3.18A). However, a soil sample, TN1, (Figure
3.18B) has a spectrum more similar to bedrock samples (Figure 3.18C). Here, similar $\delta^{13}$C and terrestrial OC contents of samples TV1 and TN1, do not correspond to similar spectra. The high C/N value of 21 for sample TV1 suggests the presence of un-decomposed plant fragments, reflected in the carbonyl, aromatic and amide bands of the spectrum. A lower C/N of 12 suggests the OM in sample TN1 is microbially processed which may have erased the molecular signal from the plant OM.

Microbial degradation of OM cannot always explain the presence of absence of bands in the IR spectra of the <4 µm fraction. A comparison of marine sediments, where C/N ratios generally reflect the presence of marine OM and are insensitive to bacterial degradation, illustrates the difficulty of interpreting these spectra. In Figure 3.19, the spectrum of a flood deposit (K27) sample is fairly indistinct but has a some woody-type components with aromatic peaks at 1600 cm$^{-1}$ and 1500 cm$^{-1}$ and phenolic bands below 1300 cm$^{-1}$. This suggests that discrete OM fragments are present, agreeing with the finding that flood layers tend to be enriched in light density OM relative to non-flood layers (Leithold and Blair, 2001). A non-flood layer, K8, from the same core has reduced aromatic and phenolic bands and increased carbonyl and amide bands. Non-flood deposits are expected to have longer exposure times in the bio-active surface zone, which could allow the terrestrial OM to be degraded. This exposure also allows for additions of marine carbon, seen in the fractional carbon budget, K27 has 0.06 mg marine OC/m$^2$ while K8 has 0.18 mg marine OC/m$^2$. One explanation of the two spectra is that the terrestrial OM of the non-flood sediment has been microbially processed, so that the woody signature is no longer evident and that added marine OM accounts for the increased carbonyl and amide content. However, a sediment
sample from the same location, but much deeper in the sediment bed (K325) has distinct aromatic and phenolic bands that indicate woody OM. This sample has been on the Eel shelf for an estimated 1500 years, meaning it has had a much longer time for the OM to degrade. Microbial processing is not sufficient to explain the differences between this spectrum compared to the more recent sediments. The difficulty in interpreting the FTIR spectra of the OM in the <4 µm fraction highlights the lack of understanding about the processes that control OM in the size class.
Figure 3.16: Interpreting FTIR spectra of particle associated organic matter. Spectral regions correspond to different bond types. Because most soil and sediment samples from the Eel River system have low OM contents, bands from organic bonds are obscured in some portions of the spectrum. The region from ~2000 cm⁻¹ to ~1200 cm⁻¹ is most useful for providing information about the particle bound OM. The spectrum shown is the of bedrock sample MV1.
Figure 3.17: Some features of the spectra of organic in the clay-sized fraction. Bedrock (MV2), soil (TM1) and marine (O150) sediments are shown.
Figure 3.18: Similar isotopic characteristics do not necessarily correspond to similar IR spectra. A) The spectrum of a soil sample, TV1, has distinct bands attributable to woody OM. B) Soil sample, TN1, has a similar terrestrial content but a spectrum more similar to that of a C) bedrock sample, MV1.
Figure 3.19: Microbial processing is not sufficient to explain differences in FTIR spectra. C/N ratios and $\delta^{13}$C values suggest these three samples have similar compositions. The flood layer, K27, has a woody character with high phenolic content and the two aromatic C=C bands at 1600 and 1500 cm$^{-1}$. The non-flood layer, K8, has proteinaceous signal from carbonyl and amide bands. A deep sediment has strong aromatic and phenolic bands, yet has had the longest time for terrestrial OM to be degraded.
4. SUMMARY AND CONCLUSIONS

The ancient sedimentary organic matter found in the Central Belt of the Franciscan Complex is a mature Type III kerogen. It was deposited in an accretionary wedge environment along a continental margin that received substantial amounts of terrestrial organic matter. The terrestrial character and the fossilized wood found in the bedrock OM suggests that the ancient Eel shelf has some similarities to the modern shelf, where periodic flooding brings much particle-bound terrestrial matter as well as discrete organic fragments (i.e. woody debris). The kerogen shows little to no evidence of weathering and appears to pass through the watershed without significant oxidation or carbon loss. Rapid uplift and erosion likely prevent significant subariel weathering, while the highly aromatic character and its chemical stability predict that the kerogen will be resistant to both chemical weathering and microbial attack.

Mineralogical analysis of the clay-sized fraction of the sediments revealed a mixture of illite and chlorite, with lesser quantities of other minerals, like kaolinite and quartz. The mineral composition of the clay-sized particles in the Eel River and on the Eel shelf are consistent with a mixture of sediment sources from across the watershed.

Kerogen is a substantial component of the total OM bound to clay-sized sediments in the Eel River system. In both soils and marine deposits, typically half of the OC load on a clay-sized particle is due to kerogen. Both kerogen and terrestrial OC appear to survive in many recent sediments at concentrations indistinguishable from those found on particles being discharged from the river. Blair et al., 2003 showed that nearly half the OC reaching the Eel shelf in the clay-sized particle fraction is kerogen C. Like other small, mountainous
rivers, rapid erosion and high sediment discharge act to deliver kerogen to marine
depositional areas, an important by-pass of kerogen oxidation and potential modulator of
atmospheric CO$_2$ (Kao and Liu, 1996; Maisello and Druffel, 2001; Perkey, 2003; Blair et al.,
2003).

The difficulties in interpreting IR spectra and C/N ratios illustrate some of the power
and problems of integrating soil and marine geochemical investigations. Some of the
common chemical analyses used in these fields cannot fully describe the changes in OM seen
in the clay-sized fraction. Identifying the weaknesses of such analyses is an important step to
better understanding of OC in the global carbon cycle. For soils, C/N ratios may reflect the
degree of microbial OM alteration more strongly than they do OM source. In marine
sediments, C/N ratios may be most valuable for bulk sediment and coarse fraction analyses,
where changes in C/N respond to variations in larger OM fragments, like woody debris.
FTIR spectra demonstrate that the molecular composition of OM in the clay-sized fraction is
a result of poorly understood processes that can alter source OM. Microbial processing may
explain some OM alterations that are masked by C/N and isotope ratios, but it is insufficient
to explain all spectral characteristics.
5. REFERENCES


Geomorphic Processes and Aquatic Habitat in the Redwood Creek Basin, Northwestern California, USGS Professional Paper 1454.


Dependence of phytoplankton carbon isotopic composition on growth rate and [CO$_2$]$_{aq}$:


6. APPENDICES
Appendix 6.1  ATR-FTIR spectra of <4 µm sediment samples for mineral identification.

Spectra are in order according to Table 3.1 and are labeled alphabetically A-AB.
Figure 6.1 A: ATR-FTIR spectrum for mineral identification, sample MA1

Figure 6.1 B: ATR-FTIR spectrum for mineral identification, sample MM1
Figure 6.1 C: ATR-FTIR spectrum for mineral identification, sample MN1

Figure 6.1 D: ATR-FTIR spectrum for mineral identification, sample MN2
Figure 6.1 E: ATR-FTIR spectrum for mineral identification, sample MV1

Figure 6.1 F: ATR-FTIR spectrum for mineral identification, sample MV2
Figure 6.1 G: ATR-FTIR spectrum for mineral identification, sample MV3

Figure 6.1 H: ATR-FTIR spectrum for mineral identification, sample MV4
Figure 6.1 I: ATR-FTIR spectrum for mineral identification, sample MV5

Figure 6.1 J: ATR-FTIR spectrum for mineral identification, sample MV6
Figure 6.1 K: ATR-FTIR spectrum for mineral identification, sample SE1

Figure 6.1 L: ATR-FTIR spectrum for mineral identification, sample TA1
Figure 6.1 M: ATR-FTIR spectrum for mineral identification, sample TM1

Figure 6.1 N: ATR-FTIR spectrum for mineral identification, sample TM2
Figure 6.1 O: ATR-FTIR spectrum for mineral identification, sample TN1

Figure 6.1 P: ATR-FTIR spectrum for mineral identification, sample TV1
Figure 6.1 Q: ATR-FTIR spectrum for mineral identification, sample TV2

Figure 6.1 R: ATR-FTIR spectrum for mineral identification, sample RC1
Figure 6.1 S: ATR-FTIR spectrum for mineral identification, sample RS1

Figure 6.1 T: ATR-FTIR spectrum for mineral identification, sample RS2
Figure 6.1 U: ATR-FTIR spectrum for mineral identification, sample O70

Figure 6.1 V: ATR-FTIR spectrum for mineral identification, sample O150
Figure 6.1 W: ATR-FTIR spectrum for mineral identification, sample O250

Figure 6.1 X: ATR-FTIR spectrum for mineral identification, sample O550
Figure 6.1 Y: ATR-FTIR spectrum for mineral identification, sample K8

Figure 6.1 Z: ATR-FTIR spectrum for mineral identification, sample K27
Figure 6.1 AA: ATR-FTIR spectrum for mineral identification, sample K46

Figure 6.1 AB: ATR-FTIR spectrum for mineral identification, sample K325
Appendix 6.2  ATR-FTIR spectra of <4 µm sediment samples for organic matter analysis

Spectra are in order according to Table 3.1 and are labeled alphabetically A-AA.
Figure 6.2 A: ATR-FTIR spectrum for organic matter analysis, sample MM1

Figure 6.2 B: ATR-FTIR spectrum for organic matter analysis, sample MN1
Figure 6.2 C: ATR-FTIR spectrum for organic matter analysis, sample MV1

Figure 6.2 D: ATR-FTIR spectrum for organic matter analysis, sample MV2
Figure 6.2 E: ATR-FTIR spectrum for organic matter analysis, sample MV3

Figure 6.2 F: ATR-FTIR spectrum for organic matter analysis, sample MV4
Figure 6.2 G: ATR-FTIR spectrum for organic matter analysis, sample MV5

Figure 6.2 H: ATR-FTIR spectrum for organic matter analysis, sample MV6
Figure 6.2 I: ATR-FTIR spectrum for organic matter analysis, sample SE1

Figure 6.2 J: ATR-FTIR spectrum for organic matter analysis, sample SA1
Figure 6.2 K: ATR-FTIR spectrum for organic matter analysis, sample TB1

Figure 6.2 L: ATR-FTIR spectrum for organic matter analysis, sample TM1
Figure 6.2 M: ATR-FTIR spectrum for organic matter analysis, sample TM2

Figure 6.2 N: ATR-FTIR spectrum for organic matter analysis, sample TN1
Figure 6.2 O: ATR-FTIR spectrum for organic matter analysis, sample TV1

Figure 6.2 P: ATR-FTIR spectrum for organic matter analysis, sample TV2
Figure 6.2 Q: ATR-FTIR spectrum for organic matter analysis, sample RC1

Figure 6.2 R: ATR-FTIR spectrum for organic matter analysis, sample RS1
Figure 6.2 S: ATR-FTIR spectrum for organic matter analysis, sample RS2

Figure 6.2 T: ATR-FTIR spectrum for organic matter analysis, sample O70
Figure 6.2 U: ATR-FTIR spectrum for organic matter analysis, sample O150

Figure 6.2 V: ATR-FTIR spectrum for organic matter analysis, sample O250
Figure 6.2 W: ATR-FTIR spectrum for organic matter analysis, sample O550

Figure 6.2 X: ATR-FTIR spectrum for organic matter analysis, sample K8
Figure 6.2 Y: ATR-FTIR spectrum for organic matter analysis, sample K27

Figure 6.2 Z: ATR-FTIR spectrum for organic matter analysis, sample K46
Figure 6.2 AA: ATR-FTIR spectrum for organic matter analysis, sample K325