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Use of a high-resolution pore-water gel profiler to measure groundwater fluxes at an underwater saline seepage site in Lake Kinneret, Israel

**Abstract**—We have used new gel pore-water profilers and conventional seepage meters to determine the advective flux of water from an underwater saline seep into Lake Kinneret. The gel probes sampled pore waters from medium to coarse sands that could not be sampled by conventional coring methods. The anions Cl, Br, and SO₄ were constant at levels just above those for the lake for 3–5 cm into the sediment due to wave action or other turbulent mixing processes. There was then a sharp increase in concentration to values of approximately 8,000 mg Cl liter⁻¹, 370 mg SO₄ liter⁻¹, and 120 mg Br liter⁻¹ at a depth of ~8.5 cm. Using an advection–diffusion model, the linear interstitial advection velocity (LIV) of the groundwater into the lake was calculated to vary between 140 and 275 cm yr⁻¹. The LIV values from conventional seepage flux meters at the same site were 30 and 164 cm yr⁻¹. Differences between the LIV measurements of these two methods may be due to a number of possible factors, including groundwater flux heterogeneity.

Groundwater seepage directly into lakes can be an important process both as it affects the overall water budget and in many situations the water quality of the lake (see Boyle [1994] and references therein). The flux of saline water from seepage into a lake can be estimated from detailed pore-water chemical profiles using an advection–diffusion model (Munk 1966; Berner 1972; Lee et al. 1980; Cornett et al. 1989). A requirement of such studies is that it is possible to determine a pore-water profile of sufficient resolution to resolve different solutions of the model. In this study, we have used a recently developed technique employing gel sampler probes (Krom et al. 1994; Mortimer et al. 1998). Previous attempts to sample pore waters at these sublittoral sites have not been successful because conventional sediment corers, whether deployed from a boat or by a diver, tend to bounce off the sandy substrate or the corers do not hold the sediment. We have measured high-resolution pore-water profiles of chloride, bromide, and sulfate at three locations in the area of the saline seeps offshore from the Tiberias hot springs and then modeled the resulting profiles to estimate the flux of saline water into Lake Kinneret.

The seepage rate of groundwater into a lake can also be measured directly using seepage meters. Several designs have been proposed (e.g., Lee 1977; Cherkauer and McBride 1988; Boyle 1994). It has been shown that the most reliable and cost-effective seepage meter design employs an inverted container with a seepage bag mounted on its top to measure water displacement over a specified area of the lake bottom (Lee 1977; Lee and Cherry 1978; Boyle 1994). In the Kinneret study we have used a modified seepage meter designed by Boyle (1994) to measure the groundwater seepage rate directly. The seepage rates measured by the seepage meter were compared with flux rates estimated from modeling the pore-water profiles measured using the gel probes.

The primary purpose of this research was to make an initial assessment of the compatibility, reproducibility, and installation logistics of these two methods with the aim of providing better estimates of littoral groundwater discharge into lakes.

Lake Kinneret serves as a major source (~30%) of drinking and irrigation water to Israel. The principal source of freshwater into Lake Kinneret is the inflowing Jordan River with a chlorinity of 17 mg Cl liter⁻¹. There are a number of onshore saline springs that discharged into the lake and were diverted in 1964 into a channel. As a result, the salinity of the lake decreased from 365 mg Cl liter⁻¹ in 1964 to its present level of 225 ± 30 mg Cl liter⁻¹ (Nishri et al. 1999). The present salinity balance indicates that there are substantial internal salinity sources to the lake estimated to be 90,000 tons of chloride per year (Smith et al. 1989). A number of point sources of saline groundwater have been identified on the lake bottom (e.g., Tabgha and Fulya areas). However, there have been no studies that quantify the flux of saline water from these subaqueous springs. Recently, an area of saline seeps has been located offshore of the Tiberias Hot Springs (THS) (Manwaring 1996); springs that have been used for therapeutic and recreational purposes since at least Roman times. It was an aim of this study to determine the flux of saline water from these potentially important seepage areas into the lake.

**Protocol**—Pore waters at three sites were sampled using gel probes. The sites were situated at 30 m (Sta. 30), 35 m (Sta. 35), and 37 m (Sta. 37) offshore from the THS in water depths of 4.5, 5.0, and 5.5 m, respectively. The sampling was carried out on 20–21 November 1996. Seepage flux meters were deployed at the first two of these sites, 30 m and 35 m from the 23rd of October 1996 for 1 week. In addition, a sample of water from the THS was collected for chemical comparisons with the pore-water samples.

Gel sampling of the pore waters was performed using the procedure described by Krom et al. (1994). Probe lengths used in this investigation were 40 cm; but it was only possible to insert the probes ~20 cm into the sand because a hard layer was encountered at this depth. The polyacrylamide gels were prepared in Leeds, UK, transported to Israel in watertight plastic containers with Milli-Q water, and assembled a few days before use. The probes were placed directly into the sediment by divers, left to equilibrate overnight, and recovered the next day. The gel was divided immediately after recovery into narrow sections (~0.5 cm), put into tightly closed microcentrifuge tubes, and weighed. Analysis was performed within 1 week using a Dionex ion chromatograph with an autosampler attached.

Replicate analysis of known standards was 1.3% (Cl⁻), 2.9% (Br⁻), and 4.6% (SO₄²⁻); relative standard deviation,
Table 1. Parameters used in Eq. 1 to calculate best-fit curves to the measured pore-water profile.

<table>
<thead>
<tr>
<th>Station</th>
<th>Anion</th>
<th>Linear interstitial velocity</th>
<th>Surface layer concentration: depth of constant concentration from surface*</th>
<th>Constant concentration at depth (C in mg L⁻¹)</th>
<th>Depth to top of high constant concentration (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>Cl⁻</td>
<td>275</td>
<td>250:4.5</td>
<td>9,400</td>
<td>9.0</td>
</tr>
<tr>
<td>30</td>
<td>Br⁻</td>
<td>275</td>
<td>2:4.5</td>
<td>135</td>
<td>9.0</td>
</tr>
<tr>
<td>30</td>
<td>SO₄²⁻</td>
<td>275</td>
<td>50:4.5</td>
<td>380</td>
<td>9.0</td>
</tr>
<tr>
<td>35</td>
<td>Cl⁻</td>
<td>140</td>
<td>370:3</td>
<td>7,950</td>
<td>8.5</td>
</tr>
<tr>
<td>35</td>
<td>Br⁻</td>
<td>140</td>
<td>5:3</td>
<td>109</td>
<td>8.5</td>
</tr>
<tr>
<td>35</td>
<td>SO₄²⁻</td>
<td>140</td>
<td>55:3</td>
<td>370</td>
<td>8.5</td>
</tr>
<tr>
<td>37</td>
<td>Cl⁻</td>
<td>200</td>
<td>450:3.5</td>
<td>8,400</td>
<td>10.0</td>
</tr>
<tr>
<td>37</td>
<td>Br⁻</td>
<td>200</td>
<td>5:3.5</td>
<td>115</td>
<td>10.0</td>
</tr>
<tr>
<td>37</td>
<td>SO₄²⁻</td>
<td>200</td>
<td>75:3.5</td>
<td>350</td>
<td>10.0</td>
</tr>
</tbody>
</table>

* Surface layer concentration refers to C, in mg L⁻¹; depth of constant concentration from surface measured in centimeters.

1s, n = 12). Total precision (1s), determined by analyzing five replicate samples of anion gel taken from several centimeters above the benthic boundary, was 2.5% (Cl⁻) and 3.8% (SO₄²⁻; Krom et al. 1994). At the same time the sample of water from THS was determined after dilution by a factor of 40 to bring the sample within analytical range.

Seepage flux meters were constructed following the design given in Boyle (1994). The seepage collector component of the meter is a large inverted, round plastic container with a cross-sectional area of 0.322 m². It is gently worked into the lake sediment by a diver until it is well seated (generally 5–10 cm) and then stabilized on the lake floor by a surrounding perforated tubular collar filled with sand. After the diver has placed the collector component on the sediment surface it is allowed to stabilize for several days. A 7-liter seepage sampling bag was filled with exactly 1 liter of water colored with red food dye to aid visual observation during sampling and seepage volume measurement. The sampling bag and a protective pail used to protect it from wave action (artificial pumping) and nibbling fish were then lowered into the water and connected to the seepage collector as described in Boyle (1994). At the end of the collection period (7 d), the seepage bag was closed off and disconnected from the collector and the volume of water in it was measured (after subtracting the initial bag volume of 1 liter). The seepage flux from the sediment into the lake (liters m⁻² d⁻¹) was calculated by dividing the net volume collected (liters) by the seepage collector area (0.322 m²) and the period of collection (7 d). The macroscopic seepage flux (MSF, cm yr⁻¹) at the sediment–water interface can be calculated by multiplying the measured seepage flux (liters m⁻² d⁻¹) by 36.5 (1,000 cm² × 365 d/10⁴ cm²). The linear advection velocity within the sediment (LIV) is then calculated by dividing the MSF by the sediment porosity.

Lee (1977), Erickson (1981), and Cherkauer and McBride (1988) have all noted a drop in the ability of their meters to measure true seepage fluxes when tested using laboratory tank studies. This drop in efficiency that can be between 15 and 40% is largely a factor of design features of the meter that cause resistance to fluid flow and the lack of proper equilibration time of the meter in the lake sediments before arming with a seepage bag. Lee (1977) has also noted that silt sedimentation, after disturbance during installation of the meter, may also cause reductions in efficiency. The use of an equilibration time before arming with a seepage bag and a premeasured amount of water in the bag, shown by Erickson (1981) to increase efficiency, suggest that the efficiency for the present system is on the order of 80%. In the absence of a measured efficiency factor for the meter system, the measured seepage fluxes obtained should be considered minimum values.

**Pore-water profiles and seepage flux data obtained**—The chloride concentration at Sta. 35 was almost constant at a value of 370 mg Cl liter⁻¹ from 1.5 cm above the sediment–water interface to a depth of 3 cm into the sediment (Fig. 1; Table 1). Below 3 cm there was a sharp increase in pore-water chloride concentration reaching a value of 7,950 mg Cl liter⁻¹ at 8.5 cm and then remaining constant to the bottom of the sediment profile (12.5 cm). The pore-water profiles of sulfate and bromide were similar in shape to that of chloride with constant values of ~5 mg Br liter⁻¹ and ~55 mg SO₄²⁻ liter⁻¹ to a depth of 2.5 cm, a sharp increase to values of 109 mg Br liter⁻¹, and 370 mg SO₄²⁻ liter⁻¹ at a depth of 8.5 cm, and constant concentrations below 8.5 cm.

The anion profiles at Sta. 37 (Fig. 1) were similar in shape to those at Sta. 35 with overlying values of approximately 450 mg Cl liter⁻¹, 5 mg Br liter⁻¹, and 75 mg SO₄²⁻ liter⁻¹ to a depth of 3.5 cm followed by sharp increases in concentrations to a depth of 8.5 cm where the concentrations are 8,400 mg Cl liter⁻¹, 115 mg Br liter⁻¹, and 350 mg SO₄²⁻ liter⁻¹. However, beneath that depth the concentrations of all the anions continued to increase to the bottom of the depth sampled (19.0 cm). The anion profiles at Sta. 30 (Fig. 1) were also similar in shape to those at Sta. 37, but the increase in concentrations began deeper at 5 cm with a sharp change in slope commencing at 8.5 cm.

Figure 2 shows the Cl/Br weight ratio with depth for the three profiles. The results from Stas. 35 and 37 showed constant Cl/Br ratios of 72 and 73 from 3.0 cm and 5.0 cm downward, respectively. Above these depths the Cl/Br ratio increased to values of ~80 at and somewhat above the sediment–water interface. At Sta. 30 the constant Cl/Br ratio beneath 8 cm was 69, somewhat lower than at the other two stations. The ratio above this depth increased more sharply, reaching values of >100 immediately at and above
the sediment–water interface. The measured composition of the THS was 17,340 mg Cl liter⁻¹, 237 mg Br liter⁻¹, and 727 mg SO₄ liter⁻¹ with a Cl/Br weight ratio of 73.1.

A seepage flux meter deployed off the THS in the approximate area of gel profile Sta. 35 measured an MSF of 97 cm yr⁻¹ for a porosity of 0.59 that gives a LIV of 164 cm yr⁻¹ (Table 2). A flux meter located near gel profile Sta. 30 measured an MSF of 18 cm yr⁻¹ and an LIV of 30 cm yr⁻¹ during the same time interval.

The pore-water profiles and seepage meter measurements
Table 2. Seepage rate measurements made at the Tiberias Hot Springs site, Lake Kinneret, Israel.

<table>
<thead>
<tr>
<th>Seepage meter no.</th>
<th>Seepage rate (cm yr⁻¹)</th>
<th>Seepage velocity (µm yr⁻¹)</th>
<th>Linear interstitial velocity (µm yr⁻¹)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>TH35</td>
<td>2.66</td>
<td>97.0</td>
<td>164</td>
<td>Station 35 of the gel probe measurements</td>
</tr>
<tr>
<td>TH30</td>
<td>0.49</td>
<td>17.8</td>
<td>30</td>
<td>This meter was lost during a storm shortly after these measurements were taken</td>
</tr>
</tbody>
</table>

This suggests that the mixing energy at the shallower station (Sta. 30, 4.5 m depth) is greater than that at Stas. 35 (5.0 m) and 37 (5.5 m).

Modeling of pore-water profiles—The profiles of chloride, bromide, and sulfate were compared with calculated profiles produced by an advection–diffusion model. It was assumed for the model that the anion profiles were at steady state. The calculation was carried out using an analytical solution of Fick’s 2nd law as proposed by Munk (1966).

\[
C_z = \frac{(e^{Ud/d} - 1)}{(e^{Ud/d} - 1)} \cdot (C_d - C_o) + C_o
\]

where \(C_z\) is the concentration of the ion at depth \(z\) (mg cm⁻³), \(U\) is the LIV—negative measured from the sediment–water interface downward (cm s⁻¹) and positive from the sediment, upward into the lake, \(z\) is depth from the sediment–water interface downward (cm), \(D_z\) is the sediment diffusion coefficient (cm² s⁻¹), \(d\) is the depth in the sediment at which the ion concentration is constant (cm), \(C_d\) is the constant ionic concentration in the sediment at depth \(d\) (mg cm⁻³), and \(C_o\) is the pore-water concentration at the sediment surface (mg cm⁻³).

In order to use the analytical solution of the advection–diffusion model (Eq. 1), it was necessary to define appropriate boundary conditions as follows: (1) there was a fixed concentration of anions (\(C_o\)) close to the sediment–water interface. It appears that lake water is moving into the coarse sediment down to a few centimeters depth. The upper boundary was thus taken as the deepest point in the sediment where the concentration of ions is the same as that in the overlying lake water (Table 1). This occurred at 3 cm depth in the sediments at Sta. 35, 3.5 cm at Sta. 37, and 4.8 cm at Sta. 30. (2) The depth \(d\) and the concentration at that depth, \(C_o\), was taken from the pore-water profiles and was the depth where the change in concentration with depth decreased to almost zero (8.5–10 cm; Table 1). (3) To use Eq. 1, it is necessary to have a suitable value for \(D_z\), the sediment diffusion coefficient, because self diffusion of ions in pore waters is hindered by the sediment. The in-situ temperature of the lake in late November when the sampling was carried out was 18°C. Subsequent measurements made at the seep site have shown that although the saline water that is up-
welling originates from or is associated with the THS, the
temperature in the upper 10–20 cm of the sediment is similar
to that of the overlying water (A. Nishi unpubl. data). Thus,
we have used values from Li and Gregory (1974) for the
anionic diffusion coefficients at infinite dilution and 18°C.

In order to convert the diffusion coefficient at infinite di-
lution to a sediment diffusion coefficient, the following
equation was used from Krom and Berner (1980).

\[ \frac{D_s}{D_i} = \phi \cdot F \]  

(2)

where \( D_s \) is the sediment diffusion coefficient, \( D_i \) is the dif-
fusion coefficient at infinite dilution, \( F \) is the formation fac-
tor, and \( \phi \) is the porosity.

A measured value of 0.59 (water content = 34%) was
used for sediment porosity. Archie’s factor (Manheim 1970)
was then used to estimate the formation factor \( F = \phi^{2.5} \).
Substituting into Eq. 2 and simplifying results in:

\[ D_s = \phi \cdot D_i \]  

(3)

A spreadsheet program was created that included the mea-
sured pore-water depth profile and the calculated values of
anion and concentration \( C_r \) at depth \( z \) for a given value of
advection \( U \). The initial values of \( C_r, C_{r0}, \) and \( d \) (Eq. 1)
taken from Fig. 1. The value of \( U \) was then altered by
\pm 10\% until the best fit to the measured profile of chloride
was obtained using a least-squares fit procedure. It was
found, however, that with minor adjustments to the values
of \( C_r, C_{r0}, \) and \( d \) those given in Table 1, a modified value of
\( U \) resulted in the lowest value for the least-squares fit.
For each value of this best-fit value of \( U \), values for \( U2 \) and
\( U/2 \) were calculated at the same time to show the sensitivity
of the procedure (Fig. 3). The final best-fit values obtained
involved using data with the maximum concentration gra-
dient. This suggested that there had been a minor relaxation
of the concentration of chloride (and other ions) at the upper
and lower boundaries (\~{}1 cm) between the time the probe
was removed from the sediment and the time it was sec-
tioned. The best-fit values of \( U \) and \( z \) calculated in this man-
ner for chloride were then used to generate modeled profiles
for bromide and sulfate. In all cases, it was found that
the best fit obtained for chloride was also the best fit for bromide
and close to the best fit for sulfate.

Figure 3 shows the modeled pore-water profiles of chloro-
ride, bromide, and sulfate with depth together with the mea-
sured interstitial profiles for all three stations. In order to
give some feel for sensitivity of the best fit to different val-
ues of the linear advection velocity \( U \), the curves obtained
for \( U/2 \) and \( U \) are plotted also in Fig. 3. Based on
this procedure, the value for \( U \) (and hence LIV) for each station
could be discriminated to \pm 25\% or better. The linear inter-
stitial velocity (cm yr^{-1}), initial concentration \( C_r, \) mg liter^{-1},
concentration at depth \( C_{r0}, \) mg liter^{-1}, and the depths
where the sharp concentration gradient started and ceased are
given in Table 1.

Between 3.0 and 8.5 cm in the sediments there were steep
chemical gradients in all three locations of approximately
1,250 ppm Cl cm^{-1}, 15.4 ppm Br cm^{-1}, and 50 ppm SO_4
cm^{-1}. The quality of the fits of the modeled curves of chloro-
ride and bromide to the measured data shows that the as-
sumptions involved in the advection–diffusion model are
valid. Although the effective diffusion coefficient of sulfate
is approximately half that of chloride and bromide, the mod-
eled curve using the same value of advection rate and bound-
ary conditions also fits well to the measured sulfate data.
There was, however, evidence for some minor nonconser-

vative behavior in the sulfate profiles. In the normal muddy
sediments of the lake, sulfate is often entirely removed in the
upper few centimeters as a result of microbial sulfate reduc-
tion (Hadas and Pinkas 1995). In the sandy littoral area of
the Tiberias underwater seeps some biological remediation
of sulfate can be expected.

An assumption of the simple analytical solution to Fick’s 2nd
law used in this study is that the porosity remains con-
stant with depth over the depth interval where the concen-
tration changes. It was not possible to obtain a sediment core
at this location to determine directly the porosity profile with
depth. However, a core was obtained from a location close
to the 30-m site but in somewhat shallower water. This core
showed no systematic change in porosity with depth with a
variability of less than \pm 0.1 porosity units. Figure 4 shows
that differences in modeled profiles obtained for a change in
porosity of \pm 0.1 units have little effect on the calculated
LIV. Furthermore in locations where porosity has been
shown to vary systematically with depth, by far the largest
changes occur over the upper 1–2 cm (Andrews and Bennett
1981). In this system the major anion gradient and the mod-
eling depth was from 3 to 8 cm in the core.

Andrews and Bennett (1981) have suggested that in cer-
tain types of sediment, \( \phi^{-3} \) is a better representation of Ar-
chie’s factor than the \( \phi^{-2} \). Their data suggest that a value of
\( \phi^{-2.1} \) is appropriate for sandy sediments increasing to \( \phi^{-3} \)
in fine muds. Thus, although it is most appropriate to use \( \phi^{-2} \)
in this study, we have also calculated our \( D_s \) values using an
Archie’s factor of \( \phi^{-3} \) as a measure of sensitivity. This
resulted in a decrease of \~{}35–40\% in the LIV, with the values being
160, 90, and 120 cm yr^{-1} for Stas. 30, 35, and 37,
respectively.

The linear advection velocities measured by the seepage
meters at Stas. 30 and 35 were 30 and 164 cm yr^{-1}, re-
spectively. These values represent 12\% and 109\% of the modeled
gel profile values for these stations. There are a number of
good reasons as to why these two methods agree within
error for Sta. 35 but not for Sta. 30. Generally, for littoral
seepage work, seepage meters have efficiency factors of 60–
80\%. For Sta. 30 the results are so far apart that this effi-
ciency factor cannot be the only reason causing discrepan-
cies in the two methods. A number of workers (Lee 1977;
Shaw and Prepas 1990; and references therein) have shown
that seepage in the littoral zones of lakes can be quite het-
erogeneous, both spatially and temporally. Furthermore
the flux meter measures an area of 0.322 m², whereas the gel
profiler occupies an area less than 0.002 m². Thus seepage
heterogeneity is probably the main factor causing the large
discrepancy in flux rates at Sta. 30. Seepage measurement
at an adjacent site was \~{}25 cm yr^{-1} (Dror and Stiller unpubl.
data). At this time, neither of these methods can be consid-
ered to measure absolute seepage fluxes; to do so would
require extensive simultaneous calibration of both systems
under standardized known flow conditions.
Fig. 3. Best-fit modeled pore-water profile at Stas. 30, 35, and 37 for the values of $U$ given in Table 1, together with the profile obtained by using $U/2$ and $U/2$, compared with the measured profiles for chloride, bromide, and sulfate.
Fig. 4. Sensitivity of the advection-diffusion model to changes in porosity of ±0.1 porosity units from the measured value.

Smith et al. (1989) have calculated that the total influx of chloride to the lake from internal sources is 90,000 tones. Stiller (1994) estimated that approximately 10% of this input is derived from chloride that diffuses into the lake via the muddy sediment found at water depths greater than 23 m throughout the lake. In order to estimate the importance of the THS seepage (and other similar seeps) to the overall chloride budget of the lake, a simple flux calculation was carried out. The average measured advective flux of 250 cm yr⁻¹ corresponds to a water flux of 6.8 liters m⁻² d⁻¹ or 2,500 liters m⁻² yr⁻¹. Each liter of this saline seep contains 8 g Cl liter⁻¹ (~8,000 mg liter⁻¹). Therefore, the input of chloride to the lake is 20 kg Cl m⁻² yr⁻¹. At present we do not know the area affected by this particular seep. A conservative estimate might be 40 m x 30 m (1,200 m²), which corresponds to a total input of 24 tons of chloride per year. Alternatively, the area of seepage required to contribute 81,000 tones of chloride per year at the flux rate determined in this study would be 4 km². It seems unlikely that there is such a large area of saline seeps in the bottom of the lake. This suggests that saline springs that input water directly into the lake are probably the major point source of salt to the lake.

Both the gel profiling and seepage flux meter systems were used to estimate groundwater seepage fluxes in the littoral environment of the THS site. The gel profiler system, which was used for the first time in this study, displays excellent potential as a littoral groundwater seepage measurement system, especially in sandy lake sediments that cannot be sampled easily using conventional methods. Provided there is sufficient contrast between the chemical composition of lake column and sediment pore waters, the gel profiler has good application also in the non-littoral portions of lakes. The present research demonstrates some of the advantages, disadvantages, and discrepancies in using physical (flux meters) and chemical modeling (gel profile) methods of measuring littoral lake seepage fluxes.

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Linking diagenetic alteration of amino acids and bulk organic matter reactivity

Abstract—Examination of amino acids in particulate samples from a variety of marine environments (fresh phytoplankton to deep-sea sediments) revealed systematic compositional changes upon progressive degradation. These consistent trends have been used to derive a quantitative degradation index (DI) that is directly related to the reactivity of the organic material, as indicated by its lability to enzymatic decay and its first-order degradation rate constant. This direct link between molecular composition and degradation rate allows us to quantify the quality of organic matter based solely on its chemical composition.

Decomposition of particulate organic matter (POM) is responsible for oxygen consumption in the ocean and its sediments, for the recycling of essential nutrients, and for most early diagenetic processes. The heterogeneous composition of POM leads to selective preservation of more stable (or less available) molecular compounds and to the loss of labile compounds, resulting in a continuously altered biochemical composition of the material during diagenesis (Tegelaar et al. 1989; Cowie and Hedges 1994; Wakeham et al. 1997). These compositional changes in POM are probably the reason for a decreasing first-order degradation rate (Middelburg 1989) and a reduced nutritional value toward heterotrophic consumers (Tenore et al. 1984) as degradation proceeds. Although intrinsic differences in molecular structure (de Leeuw and Largeau 1993) and differences in physiochemical association with the sediment matrix (Keil et al. 1994; Mayer 1994) are documented factors acting on early diagenesis of POM, there are few studies that directly link the resulting shifts in biochemical composition to the degradation state (Cowie and Hedges 1994; Wakeham et al. 1997; Dauwe and Middelburg 1998). Moreover, compositional characteristics of organic matter have not yet been linked to its biological availability or its degradation dynamics.

A series of molecular diagenetic maturity indicators have been used to estimate the relative degradation state of the organic matter (Cowie and Hedges 1994; Wakeham et al. 1997), varying from short-term (e.g., chlorophyll) to longer term (e.g., nonprotein amino acids) indicators. Broadly applicable degradation state indicators should be based on major components that are widely distributed geographically and that are omnipresent in organisms so that variability in sources of organic matter is minimized. Moreover, they should ideally be sensitive to all stages of alteration. Proteins are ubiquitous components of all source organisms and degradation mixtures (Cowie and Hedges 1992). Although there is some dissimilarity in amino acid composition of the ultimate source organisms (e.g., diatoms, cocolithophorids, and bacteria) (Cowie and Hedges 1992), these differences are minor compared to the alteration of the spectra upon degradation (Dauwe and Middelburg 1998).