

Determination of pore-water dissolved organic carbon fluxes from Mexican margin sediments

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Abstract

Sediment dissolved organic carbon (DOC) fluxes were determined in the oxygen minimum zone along the northwestern Mexican margin using five different methods: in situ benthic chambers, on-deck incubations, slicing, dialysis sampling (peepers), and sipping. For each of the five methods, replicates ($n = 6$ – 12) were made. Directly determined fluxes (whole-core incubations and benthic chambers) and calculated fluxes (sliced and dialysis-sampled cores) agree well (0.41 ± 0.09 , 0.36 ± 0.04 , 0.25 ± 0.05 , and 0.25 ± 0.05 mmol C m⁻² d⁻¹, respectively). On the Mexican margin, the DOC flux was 8% of the sedimentary carbon input, suggesting that it is a significant component to the local carbon budget. Extrapolations of this flux to the total global margin suggest that shelf and slope sediments contribute 96 Tg C yr⁻¹. The residence time of oceanic DOC based on this flux is consistent with measurements of the deep-water DO¹⁴C age. Profiles were also constructed from sip-isolated pore waters and yield consistently lower DOC profile gradients and DOC fluxes (0.06 ± 0.02 mmol C m⁻² d⁻¹). We propose that the consistently observed discrepancy between sip-isolated profiles and other isolation techniques is a result of sampling different reservoirs of pore water present in the heterogeneous sediment matrix.

Oceanic nutrient budgets are influenced by the tight coupling between benthic and overlying water processes. Examples include relationships between benthic biomass growth and production and the resulting oxygen demand (Rowe et al. 1991; Sayles et al. 1994), ammonium excretion (Henrickson et al. 1993), and particle input. The compositions of seawater solutes are, therefore, greatly influenced by sedimentary degradation and dissolution (Martin et al. 1991).

This link between benthic and water column processes can also be extended to the cycling of organic matter. Sediment pore-water DOC (*p_w*DOC) concentrations are elevated with respect to the overlying water, supporting a gradient-driven flux of DOC out of the sediments into the water column (Burdige et al. 1992; Martin and McCorkle 1993). Studies of carbon cycling in sediments have shown that the release of DOC to the water column is potentially large enough to support the entire oceanic DOC pool and may be of equal magnitude to both the preservation of particulate organic carbon (POC) and the sedimentary oxidation of organic matter to dissolved inorganic carbon (DIC) (Burdige et al. 1992).

The large oceanic DOC pool (700×10^{15} g C) cycles through the ocean slowly with a mean ¹⁴C age of 4,000–6,000 yr and has at least four possible sources (Fig. 1). Rivers deliver a significant amount of DOC to the ocean (Meybeck 1982), but the molecular and isotopic composition of river-born DOC is not consistent with the biochemical makeup of the oceanic pool (Hedges et al. 1992). Upper water

column processes are also thought to contribute significantly to the cycling of refractory DOC in the ocean. However, studies that focus on DOC cycling in the upper water column show that most of this DOC cycles on time frames shorter than 1 yr (Carlson et al. 1994), and few studies have examined the production of refractory DOC in the water column (Keil and Kirchman 1992; McCarthy et al. 1997). Degradation of sinking particles is a third contributor of DOC to the water column, but the magnitude of this flux is unknown and likely to be small (Peterson et al. 1993). Finally, once particles reach the sediment they undergo further diagenesis and these sedimentary processes release some DOC back to the water column (Fig. 1). The flux of DOC from sediments to the water column is poorly constrained. Previous estimates of the DOC flux are variable and highly dependent on the method used (e.g., Carignan 1984; Martin and McCorkle 1993). In most studies, DOC flux has been determined from pore-water gradients (Burdige et al. 1992), and there are very few published attempts to directly measure the flux in situ (Alperin et al. 1999; Burdige et al. 1999). One problem in comparisons of these two determinations is the presence of organisms and resulting bioturbation. The objective of this study was to determine the in situ flux of DOC from sediments to the overlying water and to compare this directly measured flux with fluxes calculated from pore-water gradients. The absence of macro- and meiofauna along the Mexican margin eliminated the concern that stressed organisms might release DOC or irrigate the sediments.

Materials and methods

Study site—Samples were collected during a 1999 cruise on the R/V *New Horizon* along the continental margin of northwestern Mexico. Oxygen-deficient waters ($[O_2] < 5$ μM) in the eastern tropical North Pacific impinge upon the sediments between the shelf and slope (100–1,000 m) (Ganeshram and Pedersen 1998). A general description of the

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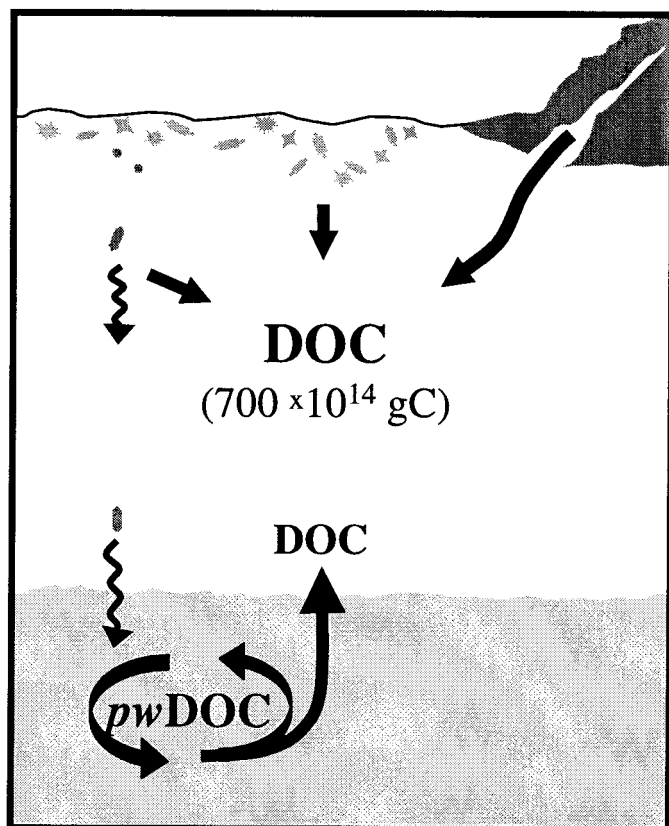


Fig. 1. Schematic representation of sources that may fuel the oceanic DOC pool (700×10^{14} g C). Four potential sources include (1) rivers, (2) primary production, (3) degradation of sinking particles, and (4) flux of DOC from the sediments to the overlying water.

regional oceanography is presented in Roden (1964). Our sampling location is roughly due west of Mazatlan, Mexico ($22^{\circ}42.81'N$; $106^{\circ}8.25'W$) at a water depth of ~ 350 m. Particulate organic carbon content in sediments range from 5–12% (wt) (Hartnett 1998).

Benthic tripod—Two benthic tripods (Devol 1987) were employed to determine the in situ flux of DOC from the sediments to the overlying water (Fig. 2a). Direct measurements of DOC diffusion into the overlying water are sensitive to contamination from instrumentation (Burdige et al. 1999) and to the release of DOC from stressed organisms (e.g., Martin and McCorkle 1993) within an incubation chamber. Each tripod had two chambers, and the chambers were specifically modified to collect very clean DOC samples by removing all plastic and rubber parts that would come into contact with sample water and replacing them with titanium, stainless steel, or Teflon. Prior to deployments, all benthic tripod parts that were to come into contact with the sampled water were cleaned with methanol, allowed to dry, and then rinsed five times with ultrafiltered, ultraviolet (UV)-oxidized water (Milli-Q water). All Teflon tubing was soaked in 6 N HCl then flushed with approximately 1 L of Milli-Q water. Teflon bars inside of the chambers were rotated at 40 rpm in order to maintain realistic benthic

boundary conditions inside the chambers. Tripods were placed on the ocean floor and after 2 h, the chambers were inserted into the sediments. Fifteen minutes later, the chamber lids were closed and 4 ml of 5 M LiCl tracer was injected into the chamber to serve as a volume calibrator (Devol 1987). The water in the chamber was allowed to equilibrate, and after another 15 min, the initial sample of the overlying water was collected. Up to four additional samples were taken over the 4-d deployment. Samples were drawn into, and stored within, Teflon tubing (5 ml) using a spring-loaded 60-ml syringe. After recovery of the tripod, DOC samples were expelled from the Teflon tubing into combusted glass vials and immediately analyzed for the DOC concentration.

DOC profiles/coring details—Sediments were collected using the Model II-XT hydraulically dampened multicorer. Polycarbonate core barrels (9 cm diameter) were mounted on the corer with spring-loaded Teflon stoppers. Only cores with undisturbed interfaces (i.e., clear overlying water) and a penetration depth greater than 30 cm were used. Sediment cores were taken into the cold room ($6^{\circ}C$) immediately and processed shortly after recovery.

Incubation—The DOC flux was directly monitored on deck by incubating sediment cores with sealed Teflon caps. Cores were immediately removed from the multicorer and secured in the cold room, taking care not to disturb the sediment–water interface. Two setscrews were removed from the Teflon cap, gas-tight Teflon tube assemblies were fit to the openings, and the Teflon tubes were then pushed into the overlying water. Nitrogen gas was pumped (1 ml min^{-1}) into the core through one tube, pressurizing the core and forcing some overlying water out through the other tube, thereby never exposing the sediments to oxygen. The excess overlying water was pumped into a polycarbonate 1-L bottle, which was used to monitor the DOC change in the water with time without sedimentary input. Once the water overlying the sediments was reduced to ~ 300 ml, the Teflon tubes were removed from the water, and humidified nitrogen gas was blown over the water (5 ml min^{-1}). Samples (4–8 ml) were taken of the overlying water with a graduated glass syringe at intervals ranging from 6–24 hours. On-deck incubations were kept in a dark cold room for the duration of the experiment. All subsamples from a single incubation core were collected and stored in a refrigerator until the sampling was complete. The time series of samples collected from a single core were then analyzed for DOC on board to reduce between-run variations.

Slicing and centrifugation—Pore waters extracted by sectioning and centrifugation of the sediments were done in a nitrogen-filled glovebag in the cold room to minimize exposure to oxygen. Cores were sectioned at 0.5–2.0-cm intervals, placed in polycarbonate centrifuge tubes, and centrifuged for 10 min at 10,000 rpm ($16,500 \times g$) in a refrigerated centrifuge. Pore water was then removed with a Teflon syringe and passed through a precombusted GF/F filter ($0.5 \mu\text{m}$).

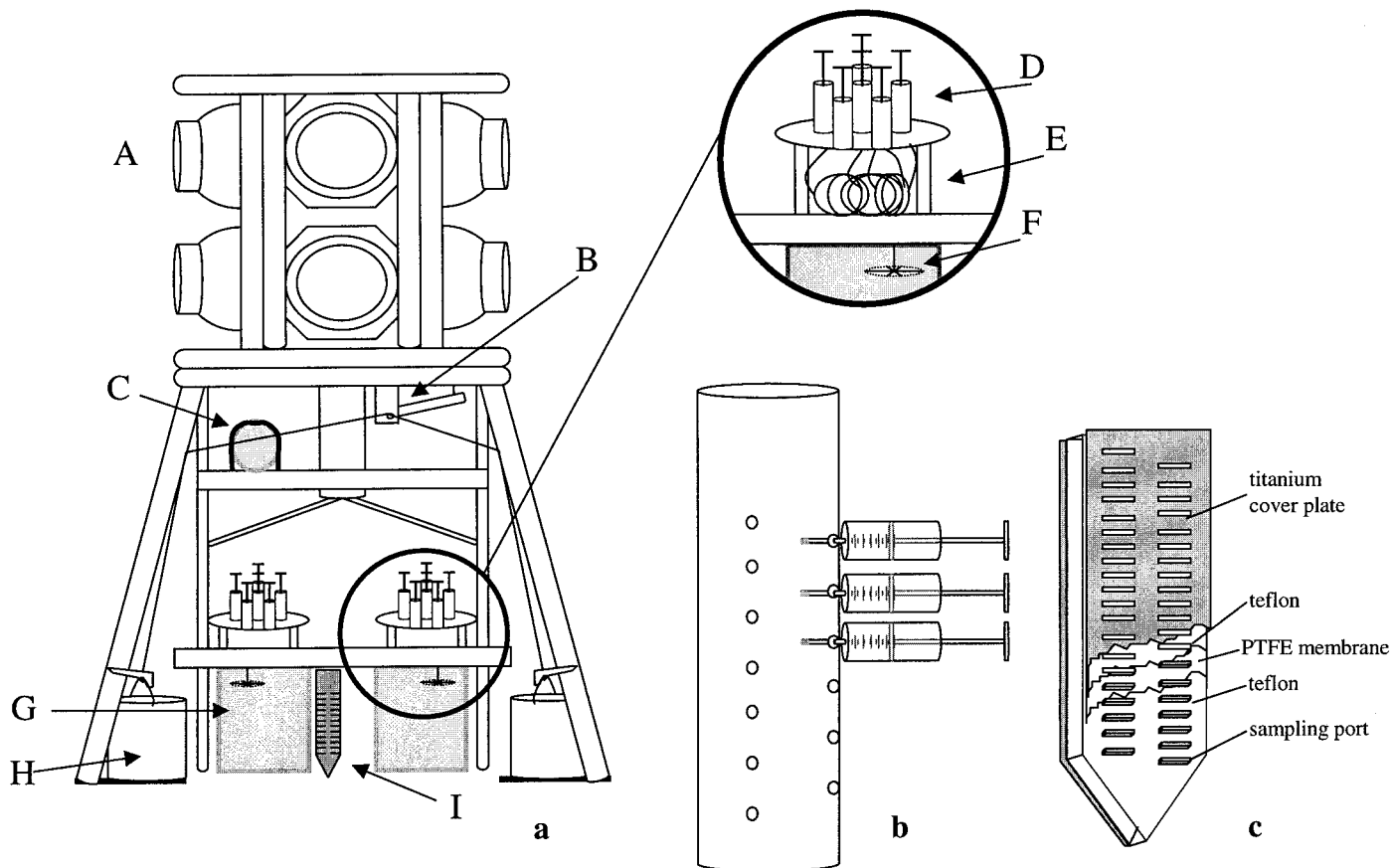


Fig. 2. (a) Schematic representation of benthic tripod used for in situ measurements of the sediment pore-water flux. Tripod stands 3.1 m high and has a base width of 2.0 m. **A**: glass floats; **B**: main ballast release, **C**: battery and electronics pressure case, **D**: sampling syringes, **E**: Teflon sample loops, **F**: chamber stirring mechanism, **G**: flux chamber, **H**: ballast, **I**: peeper. (b) Schematic representation of core and Teflon sampling syringes used for sipping. Cores were polycarbonate ($d = 9$ cm, $h = 70$ cm) with two rows of screw taps (5 mm) drilled down the length of the core (every 2 cm). Teflon syringes were screwed onto swagelock fittings mounted with heat-shrink tubes (3 mm diameter, 2.5 cm long) containing a $0.7\text{-}\mu\text{m}$ frit. Sampling syringe assemblies were threaded into the core. (c) Schematic representation of a peeper. Peepers were 20 cm long, 6 cm wide, and 0.75 cm thick when fully constructed. Sampling ports ($10 \times 2 \times 2$ mm) were in two columns, offset by 0.5 cm down the length of the stake. A $0.5\text{-}\mu\text{m}$ hydrophilic fluoropore (PTFE) membrane covered the ports and was sandwiched between two pieces of Teflon. The filter and Teflon pieces were then secured with two pieces of titanium that were tightened down with 20 screws.

Peepers—Teflon/titanium dialysis samplers, or “peepers,” were also used for collecting pore-water samples (Fig. 2c). Peepers were composed from a Teflon stake ($20 \times 6 \times 0.5$ cm) with sampling ports 1 cm apart ($10 \times 2 \times 2$ mm) in two columns, offset by 0.5 cm down the length of the stake, yielding 0.5-cm resolution. A $0.5\text{-}\mu\text{m}$ hydrophilic fluoropore (PTFE) membrane covered the ports and was sandwiched between two pieces of Teflon. The filter and Teflon pieces were then secured with two pieces of titanium that were tightened down with 20 screws. Peeper ports were initially filled with low-DOC water from the deep Pacific (4,500 m) collected earlier in the cruise. In situ peepers were mounted on the benthic tripods parallel to the flux chambers (Fig. 2a), whereas other peepers were inserted into sediment cores and incubated on deck in the cold room. Peepers remained in the sediments for 66–96 h. Immediately after retrieval, Milli-Q water was used to rinse sediment off the peeper, and samples were extracted by puncturing the membrane with a stainless steel needle and extracting the water into a 1-ml graduated

glass syringe. Because of analytical constraints, samples from adjacent ports were combined ($\sim 1\text{-ml}$ sample volume) resulting in 1-cm resolution. Samples were acidified and frozen for later analysis.

To determine the time required for peepers to equilibrate with surrounding $p_w\text{DOC}$ concentrations, an in-lab experiment was performed. Pore water was extracted from ~ 10 L of Puget Sound sediment by centrifugation. The collected pore water was filtered through a GF/F filter, placed in a 4-L clean glass cylinder with two prepared peepers, and incubated in the cold room (6°C) for 5 d. Typical protocol for the peepers was followed, and bulk surrounding water and individual ports were sampled from each peeper approximately every 12 h. After 30 h, peepers had reached $\sim 85\%$ of their final equilibration concentrations. A single, two-parameter, exponential equation ($y = a(1 - e^{(-bt)})$) was fit to the data and used to calculate percent equilibration to correct DOC data according to incubation time (Brandl and Hanselmann 1991). Most peeper experiments were not in the

sediments long enough for the ports to reach 100% equilibrium with *pw*DOC concentrations; therefore, DOC concentrations were corrected based on the experimentally determined diffusion equilibration times.

Sipping—Pore-water samples were also obtained by “sipping” from the sediment cores (Fig. 2b). Four polycarbonate cores were specifically designed with screw taps down the length of the core in two rows at 2-cm intervals, offset by 1 cm to achieve 1-cm resolution. Core barrels were mounted on the multicorer with stainless steel plug screws flush to the inside walls of the barrel. Teflon sample syringes were screwed onto swagelock fittings mounted with Teflon heat-shrink tubes (3 mm diameter, 2.5 cm length) containing a 0.7- μ M Teflon frit. These syringe assemblies were soaked in 6 N HCl, rinsed, then flushed three times with Milli-Q water. For pore-water extractions, screws were removed from the core and replaced with the syringe assembly that extended into the sediments. Once all syringes were horizontally mounted on the core, syringe plungers were pulled back, creating a vacuum, to collect 3–5 ml of pore water. If the Teflon frits passed particles through to the sample, pore-water samples were filtered through GF/F filters; postextraction filtering (GF/F) showed no change in DOC concentrations.

Gradient calculations—To calculate gradient-driven DOC fluxes, the upper 10 cm of a DOC profile was fit using a second-order polynomial. Fick’s first law was then applied to determine the flux, J .

$$J = -\phi D_{\text{sed}} \left[\frac{\Delta \text{DOC}}{\Delta x} \right] \quad (1)$$

ϕ is the porosity in the first 1-cm interval (0.99 cm³ pore water cm⁻³ sediment), D_{sed} is the sediment diffusion coefficient for DOC, and $\Delta \text{DOC}/\Delta x$ is calculated from the second-order polynomial fit to DOC profiles. Polynomial fits were not forced through the bottom water concentration. In determining D_{sed} , we assumed an average molecular weight of 8,000 Daltons (Da). Using this average molecular weight for DOC, the Stokes–Einstein equation yielded a sediment diffusion coefficient, D_{sed} , of 1.22×10^{-6} cm² s⁻¹ (e.g., Alperin et al. 1994). Burdige and Gardner (1998) suggested that the majority of *pw*DOC in the Chesapeake Bay is <3,000 Da; however, *pw*DOC from continental margin sediments were more evenly distributed in the larger size fractions. Using this continental margin data, we calculated and used a weight-distributed average of 8,000 Da as the representative molecular weight for *pw*DOC.

Experiments with homogenized sediments—On-deck experiments were conducted with homogenized sediments collected from the multicorer. After a core interval was sliced, the sediments were homogenized by stirring with a Teflon spatula in a nitrogen-filled glovebag. To test the effects of centrifugation rate and duration, three sediment intervals were sliced, with average depths of 5, 10, and 20 cm, divided into either two or three portions, placed in polycarbonate centrifuge tubes, and centrifuged at different rates and times.

Table 1. Location and depth information for benthic lander deployments.

Tripod ID	Latitude	Longitude	Depth	Duration of deployment (h)
306-02-a	22°43.34'	106°28.64'	370	77
306-7-a	22°44.00'	106°27.31'	350	72
316-01-c	22°44.08'	106°27.33'	320	90
316-12-c	22°43.51'	106°28.17'	339	95
306D-11-a	22°43.23'	106°28.66'	375	89
306D-11-b	22°43.23'	106°28.66'	375	89

Sediment intervals from a different core were also sliced and homogenized to determine whether perturbations of the natural sediment structure affected the DOC concentration from sip-isolated pore water. After these sediments were stirred, half of the sediment underwent centrifugation and the remaining sediments were placed in a centrifuge tube adapted for sip-extraction of pore water.

Analytical procedures—DOC was measured with the MQ1001 high-temperature combustion system (Qian and Mopper 1996). Samples (75 μ l) were injected a minimum of three times into the analyzer, and a precision better than 3% for repeated injections was achieved. For each DOC sample, the MQ1001 was programmed to rinse all tubing with equal volumes of injected sample prior to each injection. As a result of the low volume (<1 ml) collected from peepers, one rinse of the tubing preceded the set of three analyzed injections (precision >10%). Samples from the deep Sargasso Sea and Pacific Ocean were run in every batch to serve as an external standard. NH₄⁺, PO₄³⁻, and SiO₄ concentrations were measured on board following the methods outlined in Devol and Christensen (1993). Bacterial counts were completed on pore-water samples using the methods of Porter and Feig (1980).

Results

Directly determined fluxes—Six successful lander deployments were completed at Sta. 306 (Table 1). The diffusion rate of DOC from the sediments was determined from linear fits of DOC versus time (Fig. 3). The average in situ flux from six benthic tripod chambers was 0.41 ± 0.09 mmol m⁻² d⁻¹ (complete data are available on the Web appendix http://www.aslo.org/lo/pdf/vol46/issue_2/0298a1.pdf). The average y-intercepts for these linear regressions was 61 μ M \pm 9 and agreed with DOC concentrations of bottom water collected with Niskin bottles mounted on the benthic tripods (60 ± 8 μ M, $n = 19$). The major source of variability in the lander-determined flux was the volume of overlying water used to determine the flux. This value was determined from either the LiCl tracer or the direct measurement of the mud height in the retrieved lander chamber; we estimate this uncertainty to be $\pm 10\%$.

On-deck incubations allowed for longer experiments and an increased sediment area : water volume ratio. Again, lin-

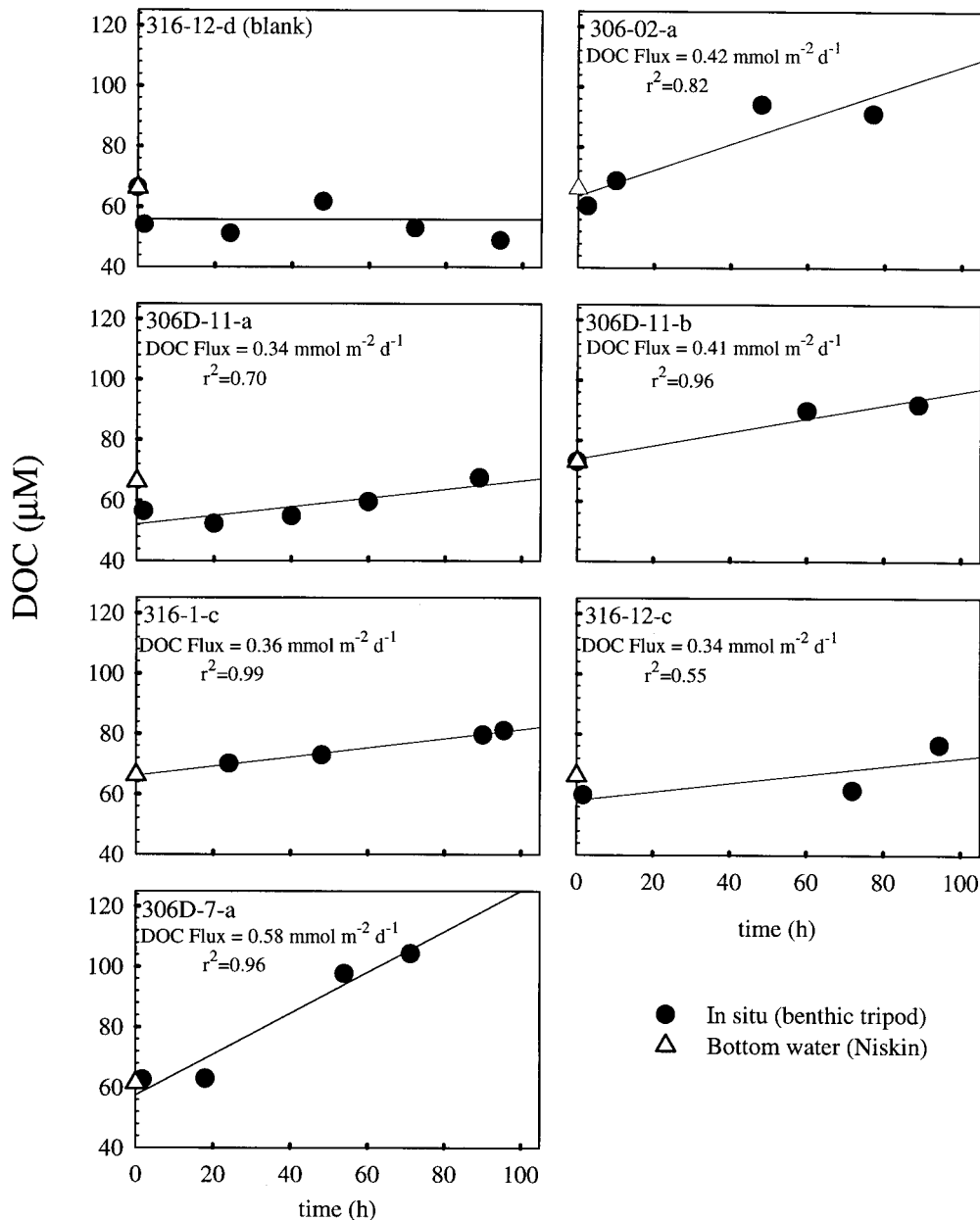


Fig. 3. DOC concentrations as a function of time for in situ flux measurements (solid circles). DOC concentrations of bottom water collected by Niskin bottles mounted on the benthic tripods (open triangles). Missing data points were a result of insufficient sample volume. Flux estimations of DOC were determined using least square linear fits to the data (solid lines), where all points were given equal weight. 316-12-d (blank) did not penetrate into the sediments and demonstrates that sampling-related contamination was negligible. Note that concentrations are absolute and are *not* normalized to the volume of overlying water in the chamber.

ear regressions of the data were made to determine the rate change of DOC in the water overlying the sediments. Note that these rate changes of DOC (μM) were then normalized to the volume of overlying water in the core to determine the DOC flux/sediment area (Fig. 4). Fluxes were calculated in the same manner as for the benthic tripods. The average flux from 12 incubations taken from Sta. 306 cores was $0.36 \pm 0.04 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Table 2) (full data are on the Web appendix <http://www.aslo.org/lo/pdf/vol46/>

[issue_2/0298a2.pdf](http://www.aslo.org/lo/pdf/vol46/issue_2/0298a2.pdf)). To monitor natural consumption and production of DOC in the overlying water, sediment-free water controls were incubated parallel to sediment cores. The average change in DOC in the control experiments was $\leq 10\%$ of the average DOC flux observed in the incubations (Fig. 4). Cores with any evidence of a disturbed sediment-water interface were rejected, and y-intercepts of regression equations for all the cores corresponded to bottom water DOC concentrations.

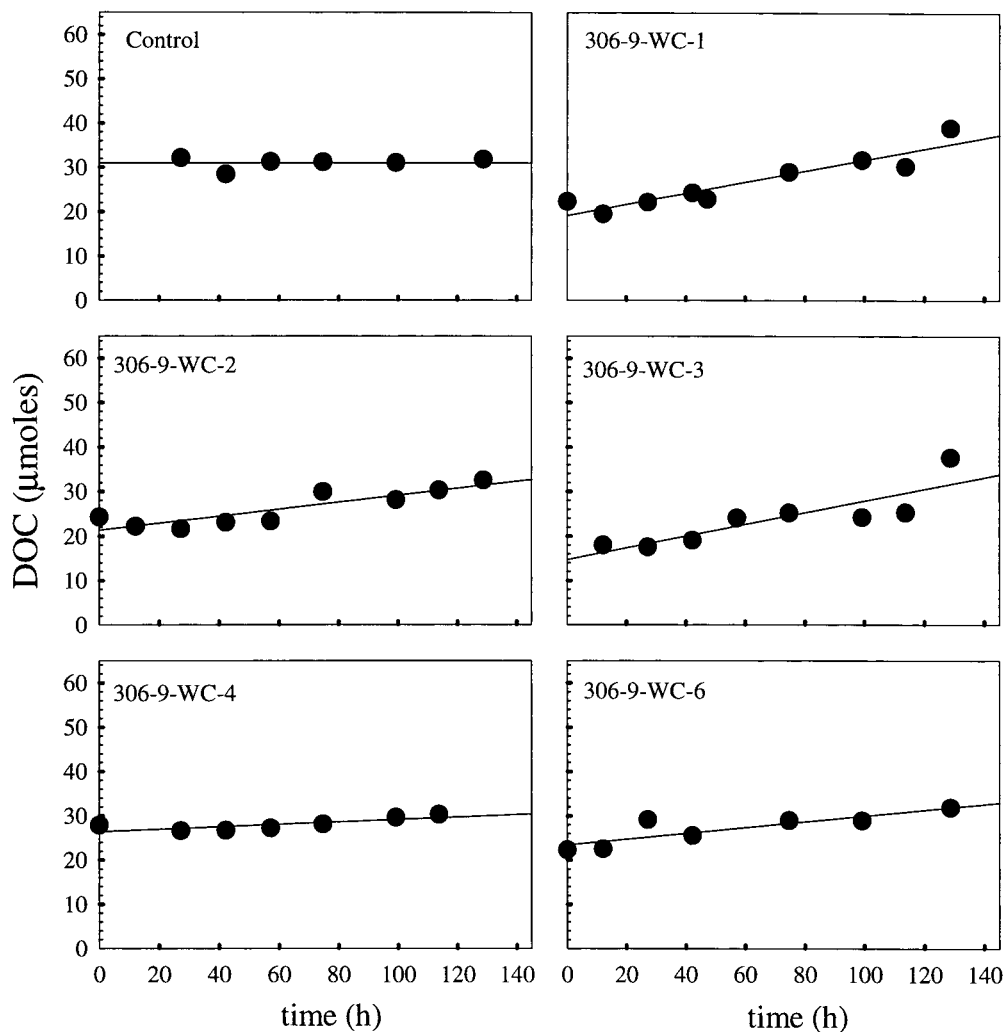


Fig. 4. Moles of DOC as a function of time for a set of five on-deck incubation experiments and one control taken from one multicore event (306-09). Top left panel presents data from a control. Controls were used to monitor consumption and production of DOC without sedimentary sources. Flux estimates of DOC were determined using least square linear fits to the data (solid lines), where all points were given equal weight. Note that concentrations are normalized to the volume of overlying water in the core (different from Fig. 3).

Table 2. Benthic DOC fluxes.

Method	n	Benthic DOC flux (mmol m ⁻² d ⁻¹)		
		Avg	Standard error	Range
Benthic tripods	6	0.41	0.09	0.33–0.64
Whole-core incubations	12	0.36	0.04	0.22–0.52
Slicing	6	0.25	0.05	0.13–0.43
Peeping	9	0.25	0.05	0.07–0.43
Sipping	8	0.06	0.02	0.01–0.08

Avg, mean of n determinations of the flux for each method.

Gradient-determined fluxes—Fluxes were also determined from sediment profiles of *pw*DOC (Fig. 5a). The average calculated diffusive flux from eight anoxic sliced cores was 0.25 ± 0.05 mmol m⁻² d⁻¹ (full data: <http://www.aslo.org/lo/pdf/vol46/issue.2/0298a3.pdf>). Although the average flux was on the lower end of both the tripod- and incubation-determined fluxes, it was not statistically different from them (95% confidence interval) (Table 2).

DOC profiles were also constructed from pore waters collected with peepers (Fig. 5a). The average flux for peepers from nine anoxic cores after the equilibration correction was 0.25 ± 0.05 mmol m⁻² d⁻¹ (full data: <http://www.aslo.org/lo/pdf/vol46/issue.2/0298a4.pdf>). Both on-deck and in situ peeper profiles looked very similar and yielded statistically comparable fluxes. Peeper-determined fluxes also statistically agreed with slice-calculated, in situ, and on-deck determinations of the DOC flux (Table 2).

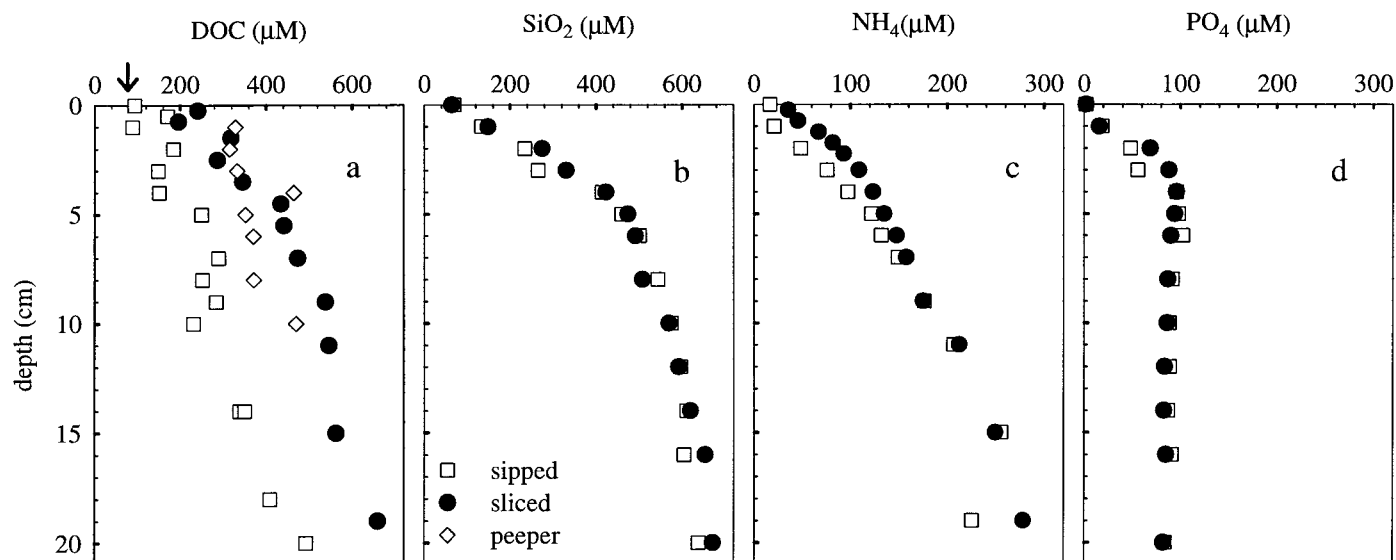


Fig. 5. (a) Comparison of depth distributions of DOC concentrations from pore-water samples isolated by sipping, centrifugation, and peeping. (b,c,d) Nutrient depth distributions from pore water collected by sipping and centrifugation. All solute concentrations for centrifugation and sipping profiles were analyzed from the same core and pore-water aliquot sampled. The peeper profile was collected from a sampler mounted parallel to the benthic lander chamber (95 h deployment), and these pore-water samples were only analyzed for DOC. Arrow denotes the bottom water DOC concentration.

DOC concentrations in pore water collected by sipping were consistently lower than in pore water collected by centrifugation or peeping (Fig. 5a). The average calculated diffusive flux determined with a polynomial fit from eight anoxic sipped cores was $0.06 \pm 0.02 \text{ mmol m}^{-2} \text{ d}^{-1}$ (full data: http://www.aslo.org/lo/pdf/vol_46/issue_2/0298a5.pdf). This gradient-determined flux was approximately 15% of the average DOC flux determined by the four other methods (Table 2).

To examine the discrepancy observed with DOC concentrations between sipping and slicing profiles, complimentary profiles of pore-water nutrients were completed for all sliced

Table 3. Results from centrifugation experiment. Sediments were homogenized and divided into 2 or 3 centrifuge tubes. Rate and duration of centrifugation was varied to monitor effects on *pw*DOC concentrations.

Core ID	Depth (cm)	Speed (rpm)	Time (min)	DOC (μM)
306-5-A	5	1000	15	1059 ± 48
		$164 \times g$		
306-5-B	5	3000	10	1073 ± 42
		$(1479 \times g)$		
306-5-C	5	6000	10	1101 ± 12
		$(5916 \times g)$		
306-11-A	11	3000	10	1247 ± 30
		$(1479 \times g)$		
306-11-B	11	6000	10	1525 ± 105
		$(1596 \times g)$		
306-20-A	20	1000	15	2014 ± 56
		$(164 \times g)$		
306-20-B	20	2000	10	1912 ± 19
		$(657 \times g)$		

and sipped cores (Fig. 5b,c,d). Pore-water profiles for SiO_4 , NH_4 , and PO_4^{3-} agreed between the two methods. Experiments were also performed on the ship to determine if the DOC profile discrepancy was a methodological artifact or a mechanistic response. Pore-water DOC concentration was examined as a function of centrifugation rate (Table 3). Changes in the rate and duration of centrifugation did not significantly change the DOC concentration within sediment intervals. These results are consistent with Martin and McCorkle's (1993) previous study. To test the hypothesis that overlying water might have been channeling down the sipped cores and diluting the DOC concentrations at deeper pore-water intervals, two experiments were conducted (Fig. 6). Pore water from one core (Fig. 6a) was isolated using the typical protocol, while an adjacent core had the overlying water removed. DOC concentration profiles agreed between the two cores, suggesting that the overlying water was not affecting the isolated *pw*DOC concentration in the surface or deep sediment intervals. The second experiment was performed to test if mild disruption of the natural sediment structure using a Teflon spatula affected the sampled DOC concentration from sip-isolated pore water (Fig. 6b). Sediment agitation prior to sipping produced sip DOC profiles that agreed with centrifuge-isolated DOC profiles. Finally, to assess the bacterial contribution to DOC, pore-water samples from the two methods were treated with 4'6'diamidino-2-phenolindole (DAPI) and AO stains and counted. Bacterial counts from pore water collected using these two methods yielded similar numbers.

Discussion

Directly measured fluxes—From previous studies, the magnitude of the sedimentary DOC flux determined from

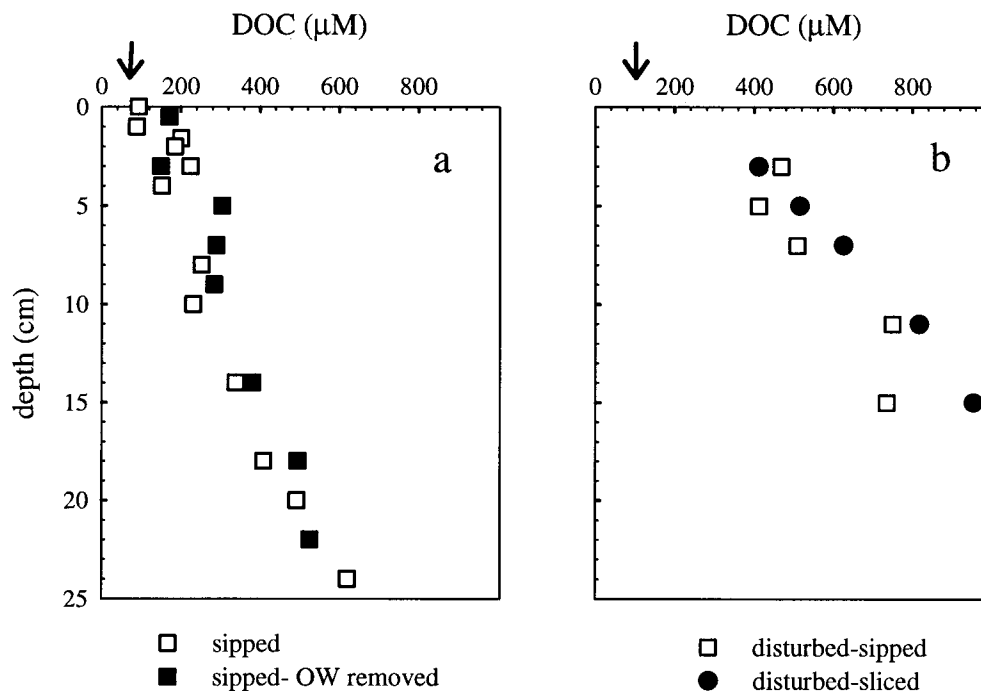


Fig. 6. (a) Results from an experiment to determine if the channeling of overlying water dilutes sip-collected $p_w\text{DOC}$ concentrations. Adjacent cores were examined with and without the overlying water. (b) Pore water from five homogenized sediment intervals from a single core were isolated by sipping and slicing followed by centrifugation. Arrows denote the bottom water DOC concentration.

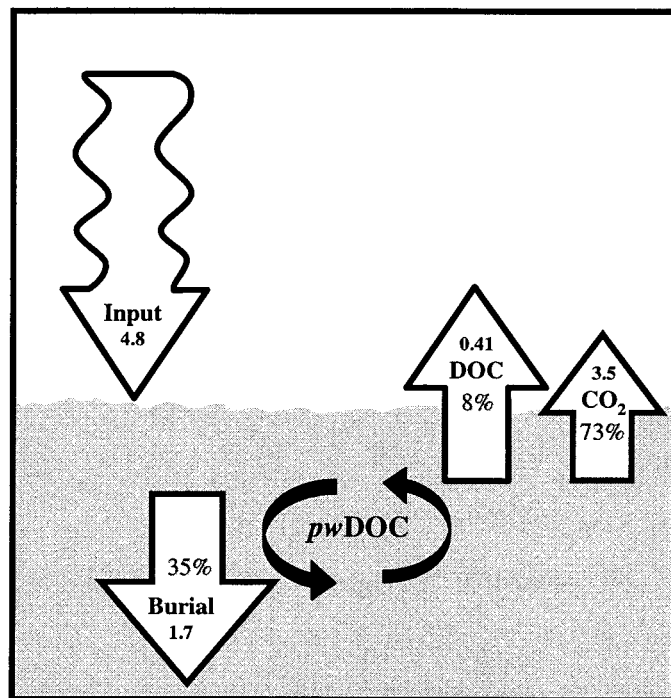


Fig. 7. Schematic representation of the Mexican margin sedimentary carbon budget. Numbers are fluxes ($\text{mmol m}^{-2} \text{d}^{-1}$). Percentages represent the flux relative to total carbon input.

several different methods ranged from 0.05 to 9.59 $\text{mmol m}^{-2} \text{d}^{-1}$ (e.g., Burdige et al. 1992; Otto and Balzer 1998). This high variability observed in published DOC flux data is attributed not only to environmental differences but to the difficult nature of making accurate in situ measurements and to uncertainties in pore-water extraction methods. Our modifications to the in situ benthic tripods enabled us to consistently measure DOC without having to make blank corrections and yielded an average flux of $0.41 \pm 0.09 \text{ mmol m}^{-2} \text{d}^{-1}$ (Fig. 3). The literature-based range for DOC flux as a percentage of the total sedimentary carbon oxidation rate is from 2 to 3% up to 40 to 50% (Martin and McCorkle 1993; Alperin et al. 1999). From our in situ measurements we estimate the DOC flux from the Mexican margin to be equivalent to $\sim 12\%$ of the carbon oxidation rate (determined from tripod-measured NO_3 fluxes and SO_4 reduction rates [Hartnett 1998]). From another perspective, 8% of carbon entering the Mexican margin sediments diffuses out as DOC (Fig. 7). The DOC flux therefore is a significant component to the regional carbon budget. This flux of $p_w\text{DOC}$ represents a “leak” in the carbon system and demonstrates an inefficiency in sedimentary degradation.

Ten studies on sedimentary $p_w\text{DOC}$ profiles and fluxes from anoxic and oxic water studies were compiled to compare with our suboxic DOC profiles. Our first assumption was that $p_w\text{DOC}$ profiles from suboxic waters would yield DOC concentrations greater than anoxic water sediment cores and less than oxic water cores. However, our profiles displayed similar trends and concentration profiles to sediment cores from oxic environments. Therefore, suboxic

DOC profiles resemble those in the majority of the ocean. This provides some backup and confidence for a global extrapolation of this data set.

If our DOC flux determined from in situ measurements is extrapolated to the total global margin sediment area (~16% of the total marine sediment area), shelf and slope sediments could contribute approximately 96 Tg C yr⁻¹ to the ocean. This estimation would represent a lower limit for the sedimentary contribution to the oceanic DOC pool because it neglects possible DOC input from resuspension of margin sediments and neglects ~84% of the total ocean sediment area. Considering the shelf and slope sediments only, this contribution is comparable in magnitude to the globally integrated estimates of carbon burial in marine sediments and is roughly half the magnitude of the riverine DOC or POC input into the ocean (Hedges et al. 1992). This relative size comparison stresses the importance of the inclusion of the sediment contribution to the oceanic carbon cycle (Burdige et al. 1992). If we consider sedimentary DOC to be the only source to the oceanic DOC pool, at steady state, the residence time would be ~7,000 yr. Assuming fresh material diffuses out with an initial age of 500 yr (Bauer et al. 1995), over a period of 7,000 yr the calculated average age of the DOC pool is 4,000 years. This age is comparable to previous estimates for the average apparent ¹⁴C age of deep-water DOC (Bauer et al. 1992). The comparison of the mean residence time and the average apparent ¹⁴C age also implies that the dissolved organic carbon escaping the sediments is not diffusing too rapidly to account for the deep ocean DOC.

Gradient-calculated fluxes—Gradient-determined fluxes have been criticized for their over- or underestimation of the DOC flux relative to in situ measurements (Burdige et al. 1992). Sources of error include (1) evaluating the concentration gradient at the sediment–water interface, (2) assignment of a diffusion coefficient, and (3) the method of pore-water isolation. To decrease the inaccuracies associated with gradient-determined fluxes, DOC profiles were modeled with second-order polynomial fits, and a weighted average of observed molecular weights of *pw*DOC from continental margin sediments was used for the determination of the diffusion coefficient (Burdige and Gardner 1998). This leaves reasonable confidence that the only remaining variable in the gradient calculation is the method of pore-water isolation; this variable controls the change of DOC with depth ($\Delta\text{DOC}/\Delta z$) or profile shape.

Numerous studies have demonstrated that the concentration of DOC is highly dependent on the pore-water isolation method. Pore waters isolated by centrifugation have been reported to have higher, more variable *pw*DOC concentrations relative to peeper-collected (Carignan 1984) and sip-isolated pore water (Chin and Gschwend 1991; Alperin et al. 1999). Martin and McCorkle (1993) noted that the removal of macrofauna from the sediments prior to centrifugation reduced *pw*DOC concentrations and whole-core squeezing elevated *pw*DOC concentrations. It is, therefore, imperative that pore-water isolation methods are closely examined to determine if between-method variability is artificial or if it is a mechanistic response related to some pore-water DOC property.

The previous studies that note profile discrepancies from different pore-water isolation methods were conducted in areas with abundant macrofauna. For this study, we specifically chose the oxygen minimum zone where no macrofauna were present, thus eliminating these complications. However, despite the lack of macroscopic organisms, we still observed differences in *pw*DOC profiles collected by centrifugation and sipping. We examined the possibility of down-core channeling of overlying water in sip-isolated pore waters (Fig. 6a), variations in centrifugation rates and times in slice-isolated pore waters (Table 3), and bacterial carbon contributions to collected pore-water DOC concentrations. Nutrient profile comparisons (Fig. 5b,c,d) and the removal of overlying water during sipping (Fig. 6a) imply that dilution from the overlying water did not contribute significantly to the overall profile discrepancies. Centrifugation test results were consistent with a previous study (Martin and McCorkle 1993), suggesting that varying the rate and duration of centrifugation on sediments does not affect *pw*DOC concentrations sampled. Bacterial enumeration (DAPI) in pore water isolated with the two methods yielded low cell counts that were not significantly different. These experimental results suggest that differences seen in DOC profiles collected by sipping and slicing were not artifacts associated with the methods. Perturbation of the sediments prior to sampling, on the other hand, increased the *pw*DOC concentration isolated by sipping (Fig. 6b), implying that natural sediment structure plays a key role in the physicochemical interactions of DOC.

We do not have a full understanding of the chemical forms and reactions of DOC within sediments and pore water, making it difficult to assign more credibility to any one particular method of pore-water extraction over another. The most logical way to determine which method of extraction results in the most accurate representation of the *pw*DOC gradient is to compare the calculated to the directly measured fluxes. Fluxes calculated from the peep- and slice-isolated pore waters agree with in situ and whole-core incubation measurements (Table 2). However, the flux calculated from sipped cores is a factor of seven less than in situ flux measurements. This calculation assumes an average molecular weight of 8,000 Da for continental margin sediments and a resulting diffusion coefficient, D_{sed} , for DOC of $1.22 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (see *Methods*). Alperin et al. (1999) suggested that along the mid-Atlantic Bight, sip-isolated pore waters provide the best estimate of the diffusive flux. Given our in situ measurements of the DOC flux and our sip-isolated pore-water gradients, we can make a back-of-the-envelope calculation for the diffusion coefficient and average molecular weight of DOC necessary to make the two measurements agree. Using Eq. 1 and the diffusion coefficient–molecular weight relationship provided by Burdige et al. (1992), we calculate that D_{sed} would have to be $8.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and the resulting average molecular weight of the diffusive DOC to be 25 Da. These values are inconsistent with our current understanding of *pw*DOC; the diffusion coefficient is too large and the resulting molecular weight is too small (e.g., Burdige and Gardner 1998). Therefore, we conclude that sip-isolated pore-water gradients do not accurately reflect the diffusive flux of *pw*DOC along the Mexican margin.

The study of Alperin et al. (1999) on pore-water isolation

for DOC analyses and our unpublished Washington coast *pw*DOC data demonstrated similar profile differences between sip and slice-isolated pore water. This difference in *pw*DOC profiles collected using the two methods has been consistently observed in a variety of biological environments, suggesting that the profile discrepancy may not be a biological artifact. Hence, we propose that the differences seen in *pw*DOC profiles collected with the two methods provide mechanistic information on solute distributions. The act of centrifugation disrupts the natural sedimentary structure within a sliced sediment interval, whereas sipping is less rigorous, disrupting only a minor fraction the natural sediment structure. Therefore, these two methods may have collected waters from different pore-water solute reservoirs within the sediment matrix. Physically enclosed reservoirs may be created during the stacking of clay particles, chemically bound reservoirs may develop from the variety of bond strengths and associations between minerals and solutes, or both may occur.

One hypothesis suggests that variable pore sizes, from micro- to macropores, may physically enclose different concentrations of DOC. These different-sized reservoirs could “trap” the DOC, effectively limiting its diffusive interactions with surrounding pores. This implies that when pore water is sampled with centrifugation, the majority of the DOC reservoirs are effectively sampled because pore structure is destroyed and the majority of the water is sampled. On the other hand, sipping only collects a fraction of the pore water and may extract pore water only from unenclosed, diffusively available reservoirs. Based on this illustration, sip-isolated pore waters should produce DOC gradients that yield a flux comparable to the actual diffusive flux measured by the in situ benthic chambers. However, as discussed previously, the sip-based fluxes are too low relative to in situ measured fluxes. Therefore, the presence of physically enclosed DOC reservoirs does not appear to be a viable explanation for the profile discrepancies encountered.

Another hypothesis suggests that organic matter–mineral associations vary in strength, creating different solute reservoirs around the surface of a mineral. Charged chemical species in solution are ionically attracted to oppositely charged mineral surfaces. This can create an adjacent surficial layer of water carrying a charge equal in magnitude and opposite in sign of the particle (Schwarzenbach et al. 1993). At greater distances from the mineral surface, attractive forces are weaker, making charged species more loosely bound and therefore more mobile. Intense perturbation of the natural sediment structure (e.g., centrifugation of sediments) may rapidly dissociate and free weakly bound DOC, allowing the entire pool of DOC present in the pore water to be sampled. Sipping, on the other hand, does not perturb the sediments but, instead, initiates gentle fluid flow through the pore spaces. The horizontal flow of pore water to the syringe may resemble laminar pipe flow and create velocity profiles near zero at the mineral surfaces. Using this model near the surface at a fluid velocity of zero, there would not be sufficient fluid shear to mobilize the organic matter close to the surface. This suggests that sip-isolated pore water does not account for all of the DOC available for diffusion and will not yield the correct gradient-calculated flux. Slicing and

subsequent centrifugation, however, would sufficiently perturb the sediments and sample the majority of the *pw*DOC available for diffusion, yielding a flux comparable to the in situ measurements.

Summary—We have made precise in situ measurements of the DOC flux using benthic tripods. We have also verified that carefully performed whole-core incubations can also be used to determine the sedimentary flux of DOC from suboxic environments to the overlying water. From these measurements, we estimated that 8% of the carbon input to the sediments is escaping as dissolved organic carbon. This DOC flux is a significant leak of energy from the sediments and must be considered in the sedimentary carbon budget in order to more fully understand the global carbon cycle. To better constrain the global importance of the sedimentary contribution to the oceanic DOC pool, seasonal variations in the flux must be examined (Sayles et al. 1994). Novel approaches have been developed to make accurate in situ measurements of solute fluxes in oxic environments (Morse et al. 1999), which can be used to examine dissolved organic carbon in order provide a better understanding of bioirrigational effects on the transport of DOC across the sediment–water interface. Once a firm understanding of the potential global contribution has been established, the age, composition, and reactivity of sedimentary DOC should be investigated.

From this thorough examination of pore-water extraction methods, we suggest a heterogeneous nature for *pw*DOC storage. Observations lead us to a hypothesis suggesting that organic matter interactions with mineral surfaces may control the advective mobility of DOC within sedimentary pore water. This is consistent with studies determining the mechanisms of *pw*DOC–mineral interactions (Arnarson and Keil 2000). A charge or size analysis of *pw*DOC collected from the different methods is necessary to assign more credibility to the hypothesis. However, with the knowledge gained from this study, we can now begin to examine pore-water dynamics in mature systems, rather than continue to try and resolve analytical and methodological intricacies.

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