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A carbon budget for a eutrophic marine ecosystem and the role of sulfur metabolism in sedimentary carbon, oxygen and energy dynamics

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ABSTRACT

Organic carbon was budgeted for an experimental marine ecosystem which received 21.2 mol C m^{-2} of allochthonous sewage sludge plus 12.4 mol C m^{-2} *in situ* net daytime production over a 99 day experiment. The fate of carbon, in order of importance, was remineralization, storage in the sediments and export. Sediment carbon metabolism was dominated by sulfate reduction which resulted in the dissociation of organic carbon remineralization from oxygen consumption and energy cycling. The sediments were inefficient in processing sedimented carbon and its associated chemical energy. About 70% of the energy reaching the sediments as organic carbon remained as accumulated carbon and sulfide minerals at the end of the experiment (71% of remaining energy was in the form of unrespired C and with the remaining 29% of energy stored as precipitated sulfides). Sediment oxygen consumption was a poor estimator of benthic metabolism. Total CO_2 flux from the sediments was, however, balanced by the sum of sediment oxygen consumption plus oxygen equivalents stored as sedimentary sulfides.

Sludge additions drove the experimental ecosystem to a eutrophic state with periods of severe oxygen depletion, death of macrofauna, hydrogen sulfide concentrations in excess of 1 mmolar in surface sediments, and the presence of a white filamentous bacterial mat over the sediment surface.

1. Introduction

Carbon and energy budgets modeling flows and transfers in ecosystems have revolutionized the field of ecology beginning with Lindeman's (1942) analysis of trophic energy transfers. These early studies, including the whole system studies of Odum (1957) and Teal (1957), emphasized metazoan processing of carbon and energy with the transfer of mass and energy to higher trophic levels. Aerobic respiration metabolized organic carbon using a molar equivalence of oxygen to yield water and carbon dioxide with a maximum yield of energy. However, much of the carbon remineralized in aquatic ecosystems, particularly sediments, is mediated by

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Table 1. Calculation of free energies used in budget.

Reaction	Standard free energy* (kcal)	Actual free energy** (kcal)
Aerobic Respiration:		
"CH_2O" + O_2 = CO_2 + H_2O#	−115.0	−114.5
Sulfate reduction:		
"CH_2O" + ½SO_4^{2-} + H^+ = ½H_2S + CO_2 + H_2O#	−30.3	−28.7
Sulfide oxidation:		
½H_2S + O_2 = ½SO_4^{2-} + H^+	−84.7	−85.6

*The standard free energy is the free energy under the idealized conditions of all products and reactants having an activity of one.

**Actual free energy (ΔG) of the reaction lA + mB = nC + oD is given by the equation: $\Delta G = \Delta G° + RT \times \ln[(C)^n(D)^o]/[(A)^l(B)^m]$, where $\Delta G°$ is the standard free energy of the reaction, R is the gas constant (0.001987 kcal deg^{-1} mol^{-1}), and T is absolute temperature (294° K). Activities of chemical species were approximated by *in situ* molar concentrations (top cm of sediment) and microelectrode profiles taken from Jørgensen and Revsbech (1983; for sulfide oxidation): $[SO_4^{2-}] = 2.2 \times 10^{-2}$, $[H_2S]_{anoxic} = 1 \times 10^{-3}$, pH = 7.3, $[TCO_2] = 2.3 \times 10^{-3}$, $[CO_{2(aq)}] = 1.24 \times 10^{-4}$, $[O_2]_{oxic} = 5 \times 10^{-5}$, $[O_2]_{suboxic} = 5 \times 10^{-6}$, $[H_2S]_{suboxic} = 5 \times 10^{-5}$. Free energy of formation (kcal $mole^{-1}$) for the respective species are: $SO_4^{2-} = -177.34$, $CO_{2(aq)} = -92.31$, $H_2O = -56.69$, $H_2S = -7.9$.

#"CH_2O" is used to represent generic organic matter metabolized by the bacterial community. We have assigned this organic material a free energy of formation of −34 kcal mol^{-1} (typical of sugars) and an activity of one.

anaerobic microbes (Teal, 1962; Williams, 1981; Van Es, 1982; Howarth and Teal, 1979; Martens and Klump, 1984).

Carbon cycling can be temporally or spatially displaced from oxygen and energy cycling in systems dominated by anaerobic metabolism, (Howarth and Teal, 1980, Howarth, 1984). The bacterial community using sulfate as a terminal electron acceptor is capable of utilizing only 25% the chemical energy potentially available in the organic substrate; the rest is transferred to the inorganic molecule hydrogen sulfide (Table 1). When sulfides produced from sulfate reduction oxidize back to sulfate, oxygen is consumed with energy and oxygen is reunited in balanced stoichiometry with the original input of organic carbon.

If all the hydrogen sulfide produced during sulfate reduction were quickly reoxidized there would essentially be no net effect on total energy or mass elemental cycling in the system. All that would change would be the types of organisms which dominated mass and energy flow (sulfide oxidizing chemoautotrophic bacteria could be a large component of heterotrophic production; Howarth, 1984). However, sulfides in anoxic sedimentary environments are involved in a variety of processes, most notably iron geochemistry (Goldhaber and Kaplan, 1974; Berner, 1984). The formation of iron sulfide minerals is a significant process in nearshore marine ecosystems since it represents a pool of oxygen equivalents and chemical energy (derived from organic matter) tied up in an inorganic phase which can be stored in

the sediments on seasonal and geological time scales (Jørgensen, 1977, Howarth and Teal, 1979). Furthermore, this storage can be a large fraction of the sulfide produced with as much as 75% of annual production permanently buried in rapidly sedimenting and non-bioturbated sediments (Berner and Westrich, 1985; Chanton and Martens, 1987a).

Eutrophication affects carbon and energy cycling in estuarine and coastal systems by increasing organic sedimentation and by influencing the relative roles of aerobic and anaerobic metabolism in sediments (Jørgensen, 1982; Howarth, 1984; Mackin and Swider, 1989, Sampou and Oviatt, 1991). If a larger percentage of organic carbon metabolism flows through sulfate reduction, the importance of interactions between C, O, S cycles increases. In the same scenario, inorganic sulfur compounds become increasingly more important as a currency of energy flow. Metabolic and geochemical reactions predict a variety of interactions between carbon (C), oxygen (O), and sulfur (S) cycling, and energy flow (E) in mixed oxic/anoxic environments, unfortunately, observations which illustrate these relationships are rare.

This study examined the form and function of an experimental ecosystem receiving daily additions of sewage sludge. A whole system carbon budget modeled flow and processing of organic material within the system. An analysis of sediment C, O, S and energy cycles illustrated the importance of the biogeochemical interrelationships between these elements in an oxic/anoxic environment.

2. Methods

a. The experiment. An experiment was conducted during the summer of 1984 to examine the effects of daily additions of sewage sludge and inorganic nutrients on shallow, mixed marine ecosystems. Energy and carbon were budgeted in one mesocosm, the highest sewage sludge treatment (8S). Data will be presented from control mesocosms for comparative purposes.

The mesocosms were large cylindrical tanks (1.83 m dia., 5.49 m height) filled with 13 m^3 seawater overlying a functioning benthic community (2.5 m^2 area, 37 cm depth). The mesocosms were physically scaled to Narragansett Bay in terms of sunlight, temperature (±2°C ambient bay temperature), flushing (3.7% volume exchange d^{-1}) and tidal mixing (rotating plungers mix the water column 2 h on and 4 h off, resuspending bottom sediments to roughly 3 mg/l) (Pilson *et al.,* 1979; Nixon *et al.,* 1980; Oviatt *et al.,* 1982). Water column light extinction usually allowed less than 1% of surface irradiance to reach the bottom, thus maintaining the sediments in a heterotrophic condition. Fouling on the mesocosm sides was minimized through biweekly scrubbing.

b. Sludge treatment. Anaerobically digested sludge was collected weekly from the Cranston, Rhode Island sewage treatment facility. Percent solids varied in the weekly sludge sample, but on average, the 8S treatment received 28.4 mmol total N

and 214 mmol C m^{-2} d^{-1} as sewage sludge during the morning mixing cycle. The experiment ran for 99 days (June 11–Sept 18, 1984). Treatment 8S refers to a total nitrogen loading of 8 times the areal averaged inorganic nitrogen loading to Narragansett Bay (1X = 2.88 mmol N m^{-2} d^{-1}, Nixon, 1981) and was of similar experimental design to previous MERL eutrophication experiments (Oviatt *et al.,* 1986b; Sampou and Oviatt, 1991). However, compared to inorganic salt nutrient additions, sewage sludge also had a substantial input of allochthonous carbon associated with the nutrient addition (Oviatt *et al.,* 1987). Premixing the sludge with 200 ml of water before daily additions increased dispersion within the mesocosm. The sludge was not toxic with respect to heavy metals nor halogenated hydrocarbons (Oviatt *et al.,* 1987). Detailed composition of the major and minor constituents of the sludge are given in Oviatt *et al.* (1987).

c. Production and respiration. Primary production was measured using ^{14}C incorporation into particulate organic matter integrated over the depth of the water column (Lambert and Oviatt, 1986). Daily rates were calculated by assuming 57% of the daily production occurred during the incubation period (1000 to 1400 hours) (Oviatt *et al.,* 1986a; 1987). Reproducibility of the ^{14}C estimate of primary production was better than 10%.

Oxygen was sampled on consecutive dawn, dusk, dawn and used to calculate net system daytime production and nighttime system respiration (Oviatt *et al.,* 1986a). System rate calculations were explicitly corrected for oxygen diffusion across the air/water interface using an empirically derived relationship dependent on temperature and the difference between *in situ* and 100% saturation oxygen concentrations (Oviatt *et al.,* 1986a, 1987). The equation used was:

$$D\ (\text{mmol}\ m^{-2}\ h^{-1}) = f \times (O_2 - O_2\text{sat.}\ (\text{mmol}\ l^{-1}))$$

The gas exchange coefficient (f) was empirically derived and dependent on temperature (P. Rocques and S. Nixon unpubl. data). System daytime production was calculated from the equation:

$$SYS_{prod}\ (\text{mmol}\ O_2\ m^{-2}\ d^{-1}) = ((O_2\text{dusk} - O_2\text{dawn}\ (\text{mmol}\ l^{-1})) + (D \times \text{hours daylight})) \times 5000\ l\ m^{-2}$$

System nighttime respiration was similarly calculated from the second dawn and dusk oxygen concentrations. Net daytime water column oxygen production and nighttime respiration were calculated from system rates corrected for benthic exchanges. Precision of the production and respiration measurements was 8 mmol O_2 m^{-2} (1 std. dev.; calculated from a Winkler dissolved oxygen precision of 0.05 mg l^{-1} × 5000 l m^{-2}).

Total CO_2 (TCO_2) concentrations were derived from measurements of pH,

alkalinity, salinity and temperature using the method of Strickland and Parsons (1972) with an improved salinity and temperature correction (Oviatt *et al.,* 1986a). pH of the sample was measured within 1 h of sampling in a temperature controlled (set at ambient temperature) bath. Precision was ±0.01 pH units (1 std. dev.).

Total alkalinity (TA) was calculated by the method of Culberson *et al.* (1970). Precisely 25 ml of 0.010 M HCl were added to 100 ml sample water. The pH of this solution was measured within 2 days at 25°C.

Total benthic metabolism was also analyzed by TCO_2 IR photometry following methods similar to Johnson *et al.* (1983). Water samples were collected and transferred into 2 ml glass ampules. The necks of the ampules were sealed and placed in a 103°C oven for 2 hours. Ampules were stored at room temperature until analysis. Duplicate 200 μl subsamples were taken immediately after cracking the ampule neck and analyzed according to Johnson *et al.* (1983). Replicate subsamples were preceded and followed by an injected 35 or 45 μl standard of 0.1% anhydrous sodium carbonate to compensate for instrument drift. The mean coefficient of variation was 1.8% with a standard error of 18 μmol C l^{-1} for 7–9 replicates during the analysis of samples.

d. Benthic fluxes. Benthic oxygen and carbon dioxide flux measurements were done on a monthly basis by capping the entire sediment surface with a specially designed chamber (Oviatt *et al.,* 1982). Flux methodology and chamber operation have been described in detail by Kelly *et al.* (1985). Replication of sediment oxygen consumption (SOC) between the 3 control mesocosms of this experiment was very good (C.V. < 10%) (Keller *et al.,* 1987). Total CO_2 flux from the sediments was measured by both pH-alkalinity calculations and IR photometry. Short incubation times resulted in a relatively large error to signal ratio for benthic TCO_2 flux (36% C.V. for IR photometry, error was not estimated for pH-Alk measurements).

e. Carbon analyses. Sludge carbon, particulate carbon and sedimentary organic carbon were all measured on a Carlo Erba Model 1106 CHN elemental analyzer. A subsample was collected from the weekly batch of sewage sludge and percent solids calculated from a wet weight-dry weight difference. Carbon was analyzed on the dried (60°C) sample. Weekly particulate carbon samples were prepared by filtering 50 ml of water (sampled during the morning mixing cycle prior to sludge addition) through a 13 mm diameter precombusted Whatman GF/A glass fiber filter. The filters were dried at 60°C and combusted on the CHN analyzer. Sediment samples were collected every 2–3 weeks using pole-mounted flow through corers (Frithsen *et al.,* 1983; Sampou and Oviatt, 1991). Sediments were sliced at 1 cm intervals (the surface cm was sometimes split into 0 to 0.5 cm and 0.5 to 1 cm slices) and homogenized. A subsample was dried (60°C) and ground to a fine powder. Inorganic carbon was removed from the sediments by fuming 20–50 mg sediment subsamples

with concentrated HCl inside an evacuated desiccator for 15 hours (Sampou, 1989). An Acetanilide standard curve was run with every batch of samples (71.09% C). The coefficients of variation for the sludge, particulate carbon and sedimentary carbon were 3%, 10% and 3%, respectively.

Biweekly dissolved organic carbon (DOC) was measured using a method modified from Menzel and Vaccaro (1964). Four replicate 10 ml subsamples of filtered water (passed through precombusted Gelman A/E filters) were pipetted into precombusted DOC ampules with phosphoric acid and potassium persulfate. The ampules were sealed by flame and placed in a 110°C oven for 2½ hours. Carbon dioxide liberated by the acid + persulfate digestion was carried from the ampule in a stream of N_2 gas and analyzed on an infrared gas analyzer. A standard curve was run using sucrose concentrations spanning the concentrations of DOC found in the mesocosms. The coefficient of variation for 6 replicates was 2.1%. Sample variability (C.V.) was less than 5%.

f. Carbon accumulation and export. Changes in percent carbon in surface sediments implied a net accumulation or remineralization of organic matter which could be expressed on a mass per area basis. Expressing carbon in these units would then enable direct comparisons with other system storage and rate measurements (i.e., primary production, phytoplankton biomass, benthic respiration, etc.). Sediment percent carbon was converted to g C cm^{-3} using porosity and dry sediment density. Mass C m^{-2} can then be calculated from changes in carbon concentration in surface sediments summed to a chosen depth. However, a difficulty arose when using a depth reference in centimeters for sediment systems with large seasonal and treatment porosity changes. A change in porosity from 0.75 to 0.95 would overshadow an increase in carbon concentration from 2.1% to 5.2%. There exists 5 times more solid sediment at 0.75 porosity, so even though the carbon concentration was only 40% of the carbon rich sediment, the total grams of carbon in the surface 1 cubic centimeter would be greater. A downcore integrated carbon measurement was normalized using a depth parameter independent of centimeters. Depth was normalized to 1.31 g carbon free sediment (S_{cf}) cm^{-2} which was the maximum observed depth (cm) of elevated carbon concentrations (3 cm; 8/22/84). On this date and for all others the surface 1.31 g cm^{-2} included all detectable C enrichment. The g C in association with this surface 1.31 g S_{cf} cm^{-2} was then calculated for each date, and converted to moles C m^{-2} in the surface 13.1 kg m^{-2} of sediment. This depth normalization proved to be useful in quantifying seasonal changes to the mass of sedimentary carbon along a eutrophication gradient (Sampou and Oviatt, 1991).

Import or export of PC and DOC in the mesocosm was calculated from water column concentrations (measured every 7 days) and the measured exchange of water piped from Narragansett Bay. For example, the weekly exchange of particulate

carbon was calculated using the equation:

$$\text{Export } (\mu\text{mol C l}^{-1}\ 7\text{d}^{-1}) = ((\text{PC}_{\text{BAY}}) - (\text{PC}_{8\text{S}})) \times \text{Flow}_{7\text{d}}$$

g. Sulfur cycling. Sulfate reduction was used to estimate anaerobic metabolism in the sediments of 8S. Sulfate reduction rates were measured 6 times over the experiment. Methods used were a composite of Jørgensen (1978) and Howarth and Marino (1984) for inoculation and extraction of reduced sulfur end products, respectively. Cores (2.5 cm dia. × 15 cm) were inoculated with 5–10 μcuries of ^{35}S-SO_4 at each depth (0.5, 1.5, 2.5, 4.5, 6.5, 11.5 cm) within 20 minutes of sampling. Incubations were run at *in situ* temperature with either aerobic or anaerobic overlying water (matching ambient mesocosm conditions) for 3 to 6 hours. Extraction of radiolabelled sulfate and reduced sulfur compounds (acid volatile and aqua regia digestible sulfides) followed the procedures of Howarth and Marino (1984). The methods were validated by a variety of checks, including, linearity of reduction rates over time, a consistent low time zero recovery blank in the aqua regia digestion (0.052% of initial ^{35}S-SO_4), and a comparison between reduction rates determined by chromium reduction and aqua regia in a previous experiment (Sampou, 1989; Sampou and Oviatt, 1991). The coefficient of variation for replicated sulfate reduction measurements was 40% at rates less than 100 nmol cm^{-3} d^{-1} and decreased to 20% at rates greater than 1000 nmol cm^{-3} d^{-1}. Integration of rates to a depth of 15 cm (below which rates were indistinguishable from zero) yielded an areal metabolic rate. Sulfate was determined by gravimetric precipitation with barium chloride.

Redox potential (Eh) was measured with a Methrohm combination "Eh" platinum electrode, corrected for silver-silver chloride reference electrode potential at the temperature of measurement (Sawyer and Roberts, 1974). The electrode was cleaned and then standardized in a quinhydrone-pH 7 buffer solution prior to each series of measurements. The Eh probe was allowed to equilibrate in seawater overlying the sediments prior to sediment profiling. Sediment measurements were recorded at 1 centimeter intervals beginning at 0.5 cm. Readings were allowed to stabilize at each depth (15 min.).

Concentration of hydrogen sulfide was monitored every 2–3 weeks in the surface sediments. Cores were obtained using a pole mounted corer (6.7 cm dia.) and transferred to the lab for immediate processing. Sediment sections (1 cm thick) were extruded and sliced into 250 ml centrifuge bottles which were purged with nitrogen gas and capped. Porewater was obtained by centrifugation (at ambient tank temperature). Sulfide in the porewater was reacted with a mixed diamine reagent within 30 minutes of coring and analyzed spectrophotometrically (Cline, 1969) with handling modifications necessary for microvolume (2 ml) technique (Lambert and Oviatt, 1986). The range of replicate porewater sulfide analyses was less than 10% of the measured value. The relative precision at concentrations less than 50 μM was

roughly half as good as at higher concentrations (range; 20% of value). Free sulfides were measured at 0.5, 1.5, 2.5, 3.5, 4.5, 6.5, 10.5 cm depths.

Sediments were collected from 8S at the beginning and end of the experiment and measured for total reduced sulfides. Sediment cores (6.7 cm dia.) were extruded inside a N_2 filled glove bag, sliced at 1 cm intervals and mixed. Subsamples (20 cm^3) were transferred to glass vials, freeze-dried, ground (all work was done inside a glove bag) and stored frozen in an N_2 filled desiccator. Total reduced sulfur (combined iron monosulfides, elemental sulfur and pyrite) was analyzed by chromium reduction on 50 to 200 mg sediment subsamples (Zhabina and Volkov, 1978; Howarth and Jørgensen, 1984; Canfield *et al.,* 1986; Sampou, 1989). Three replicates were run for each sediment sample. Standard curves were prepared daily by running a standard sediment containing 2% pyrite. In agreement with Canfield *et al.* (1986), recovery of sulfides averaged better than 95% in pyrite amended sediment. The average coefficient of variation for the determination of total reduced sulfur was 7% ($n = 15$).

Integration of solid sulfides downcore to a depth of 7.52 g dry sediment cm^{-2} yielded a mass of reduced sulfur. The initial mass of reduced sulfides was subtracted from the final mass to yield accumulation of reduced sulfide through the experiment.

Whole experiment estimates for production, respiration, benthic exchanges and storage were calculated by trapezoidal integration between individual measurements and expressed as moles m^{-2} $99d^{-1}$.

3. Results

a. Dissolved gases. Dissolved oxygen and total dissolved inorganic carbon in 8S were very different than control concentrations and indicated a system dominated by heterotrophic processes. Dissolved oxygen was undersaturated and fluctuated into severe oxygen depletion during the last two months of the experiment. Concentrations of TCO_2 increased throughout the experiment and rose to substantially higher concentrations than control (300 μmolar difference at the end of the experiment (Fig. 1)).

b. Production and allochthonous loading. In situ production increased in the 8S mesocosm relative to control. ^{14}C daytime production ranged from 33 to 199 mmol C m^{-2} d^{-1}. Water column daytime oxygen production varied from near zero to 300 mmol O_2 m^{-2} d^{-1} (Fig. 2). Cumulative daytime production for the whole experiment was estimated to be 12.3 mol C m^{-2} $99d^{-1}$ and 15.1 mol O_2 m^{-2} $99d^{-1}$ for the two methods, respectively. Oviatt *et al.* (1986a) reported a production quotient of 1.2 (PQ = (O_2 produced)/(CO_2 fixed)) from an earlier eutrophication experiment which is identical to the observed PQ of this experiment.

Daily addition of sludge represented a substantial input of allochthonous organic material to the 8S system which generally exceeded in situ production (Fig. 2).

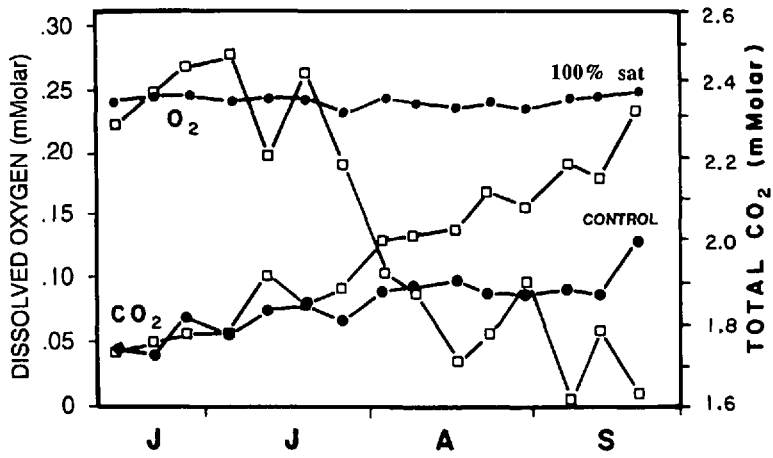

Figure 1. Dissolved oxygen and total carbon dioxide concentrations in the 8S mesocosm (□). Concentration of oxygen at 100% saturation and Total CO_2 concentration in a control mesocosm are graphed for comparison (●).

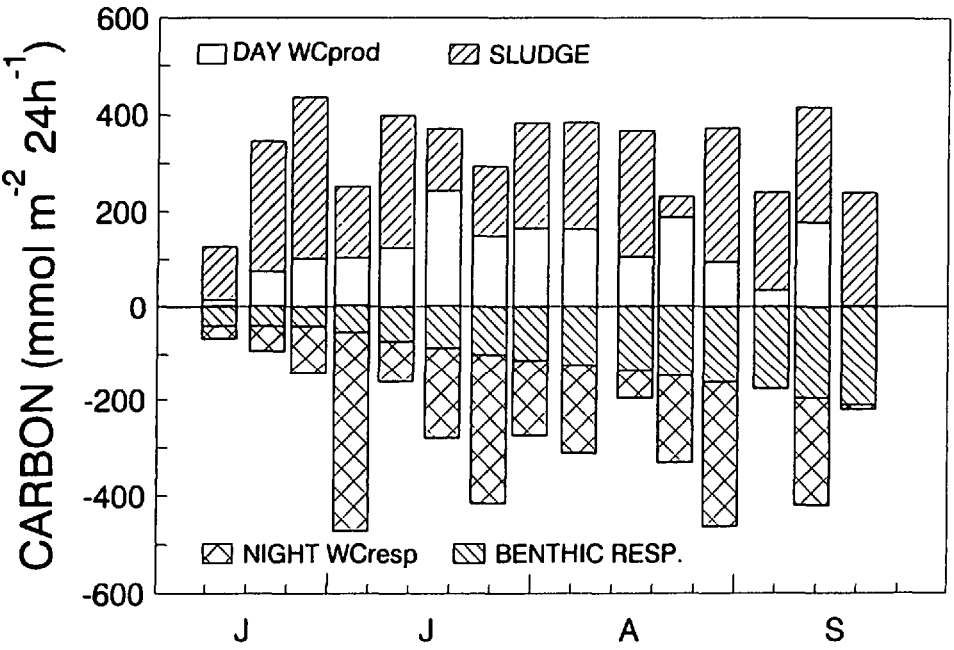

Figure 2. Production and respiration of carbon in the 8S mesocosm. Allocthonous sludge carbon plus *in situ* daytime net water column production (WC_{prod}) and benthic respiration plus night respiration (WC_{resp}), (WC_{prod}, WC_{resp}, calculated from diel changes in water column dissolved oxygen using a PQ of 1.2, an RQ of 0.8, respectively). Weekly variability of daily allochthonous sludge additions reflects week to week differences in % composition of the sewage sludge. Weekly benthic respiration rates interpolated from monthly TCO_2 fluxes.

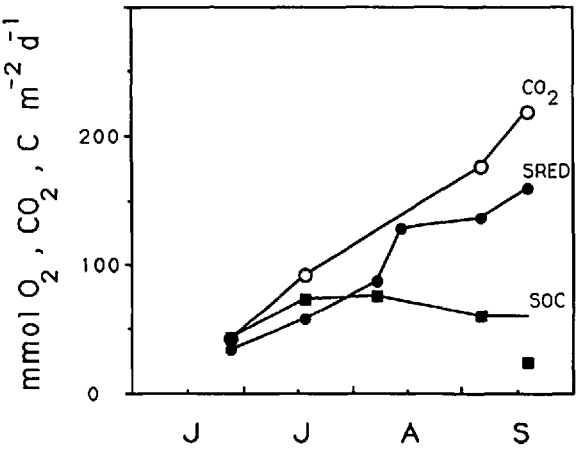

Figure 3. Sediment oxygen consumption (SOC), benthic TCO_2 flux (CO_2) and sulfate reduction metabolism (SRED; in carbon units). True SOC on September 19 was greater than measured (see text for discussion). Total CO_2 was the average of fluxes estimated by IR photometry and pH-alkalinity calculations. Sulfate reduction rate calculated from downcore profiles (Fig. 4c) integrated to a depth of 15 cm.

Weekly variations in the rate of carbon loading were due to week to week variability in the percent solids of the sewage sludge (Oviatt *et al.,* 1987). A total of 21.2 mol C m^{-2} 99d^{-1} of sludge carbon was added to 8S.

c. DOC and PC. Dissolved organic carbon was largely unaffected by the treatment of sewage sludge. Incoming bay water ranged from 118 to 456 μmol C l^{-1} (average of 210 μmol C l^{-1}) while DOC in 8S varied between 197 to 458 μmol C l^{-1} (average of 240 μmol C l^{-1}). Elevated PC concentrations were likely the result of increased phytoplankton biomass. Incoming bay waters averaged 29 μmol C l^{-1} of particulate carbon versus an average of 127 μmol C l^{-1} within the 8S mesocosm. The net export of PC and DOC from 8S was 1.8 and 0.8 mol C m^{-2} 99 d^{-1}, respectively.

d. Respiration. Water column night respiration varied from near zero to 347 mmol O_2 m^{-2} d^{-1} (Fig. 2) and was correlated with fluctuations in phytoplankton populations (Sampou, 1989). The water column was responsible for respiring 13.4 mol O_2 m^{-2} 99d^{-1} (equivalent to 10.7 mol C m^{-2} 99d^{-1} using a respiratory quotient of 0.8, inverse of the PQ calculated in this experiment).

Benthic respiration was measured both as sediment oxygen consumption (SOC) and by the flux of carbon dioxide from the sediments. SOC almost doubled in the first month of the experiment from 43 mmol O_2 m^{-2} d^{-1} (rates typical of control sediments) to 76 mmol O_2 m^{-2} d^{-1}. However, following maximum uptake rates in July, SOC remained constant (Fig. 3). The very low sediment oxygen consumption measured at the end of the experiment underestimated actual SOC since the concentration of oxygen inside the benthic chamber went to zero before the end of

the incubation. Sediment oxygen demand of hydrogen sulfide fluxing out of the sediments (assuming complete oxidation to SO_4) was calculated to be near 60 mmol O_2 m^{-2} d^{-1} for the last 3 weeks of the experiment (Sampou, 1989). Integrated sediment oxygen uptake was 6.3 mol O_2 m^{-2} $99d^{-1}$.

Benthic metabolism was measured by total CO_2 flux using IR photometry and pH-alkalinity calculations. The two values were averaged to give an estimate of benthic total CO_2 flux (Fig. 3). Flux of TCO_2 increased fivefold over the 99 day experiment from 41 to 218 mmol C m^{-2} d^{-1}. The integrated flux was 12.2 mol C m^{-2} $99d^{-1}$.

Sediment anaerobic respiration increased dramatically in the surface sediments of the 8S mesocosm (Fig. 4c). By the end of the experiment, sulfate reduction rates were an order of magnitude higher than June rates. Increased sulfate reduction metabolism was restricted to the surface 5 cm of sediment. There were no treatment effects in deeper sediments. Sulfate reduction rates (integrated to a depth of 15 cm) increased from 25.4 to 76.3 mmol SO_4 reduced m^{-2} d^{-1} (Fig. 3). A total of 4.5 mol SO_4 was reduced m^{-2} over the experiment (equivalent to 9.0 mol C m^{-2} $99d^{-1}$; 2 moles C oxidized for every mole SO_4 reduced).

e. Carbon storage in sediments. Supply of organic carbon to the 8S system from allochthonous loading and *in situ* production exceeded remineralization and resulted in a net accumulation of organic material in the sediments. Organic carbon increased steadily in surface sediments of 8S from control concentrations (2.2% carbon) to over 5.0% (Fig. 4a). The standing stock of organic carbon in the surface 13.1 kg m^{-2} of sediment at the beginning of the experiment was 21.8 mol C m^{-2} (corresponding to a depth of 2 cm). By the end of the experiment, the depth to 13.1 kg m^{-2} of sediment had increased to 2.8 cm (increasing porosity) and the pool of organic carbon had increased to 33.5 mol C m^{-2}. An independent estimate of sludge carbon accumulation in the surface sediments was calculated from the change in the del^{13}C of organic matter. That estimate of 10.8 mol C m^{-2} (Oviatt *et al.*, 1987; Gearing *et al.*, 1991) was in excellent agreement with the increase of 11.7 mol C m^{-2} of total organic carbon calculated in this study.

f. Sedimentary sulfur cycling. There was a major shift to highly reducing conditions in 8S due to the large production of sulfide from anaerobic respiration. Eh in control sediments was typically near zero in the surface few centimeters (Sampou, unpublished; Sampou and Oviatt, 1991). Eh in the surface sediments of 8S decreased to less than −200 mv by September (Fig. 4b). Free hydrogen sulfide was detected in surface sediments August 14 (free sulfide was never detected in control sediments at depths shallower than 10 cm (Sampou, unpublished data)) and increased to 1100 μmolar concentrations by September (Fig. 4d).

Total reduced sulfur also increased in the sediments of 8S. In June, concentrations of total reduced sulfur increased from 49 μmol S g^{-1} dry sediment in the 0–1 cm sediment slice to an asymptotic upper concentration of 112 μmol S g^{-1} dry sediment

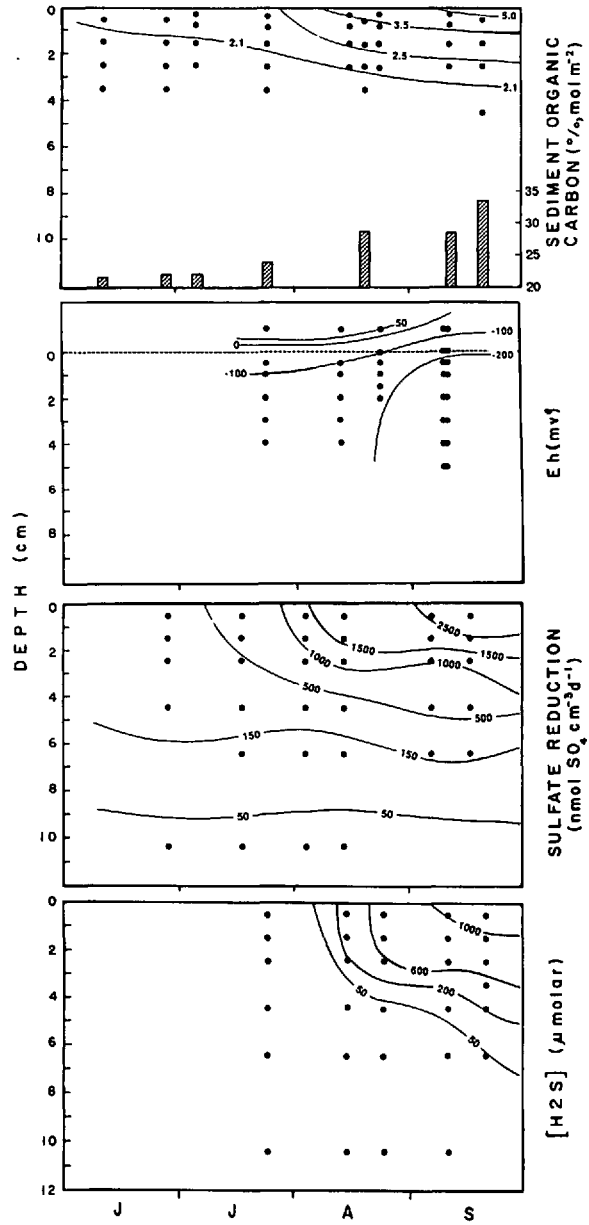

Figure 4. Synoptic view of biological and chemical changes in 8S mesocosm through the experiment. (a) Downcore sedimentary carbon concentrations for 8S mesocosm and total mass of carbon in the surface sediments, units are percent organic carbon (%) and mol C m^{-2} 13.1 kg^{-1}. (b) Redox potential of 8S sediments (mv). (c) Sulfate reduction rates (nmol SO_4 reduced cm^{-3} d^{-1}). (d) Hydrogen sulfide concentrations (μmolar). Isopleths for all graphs calculated from measured values (●) at respective depths.

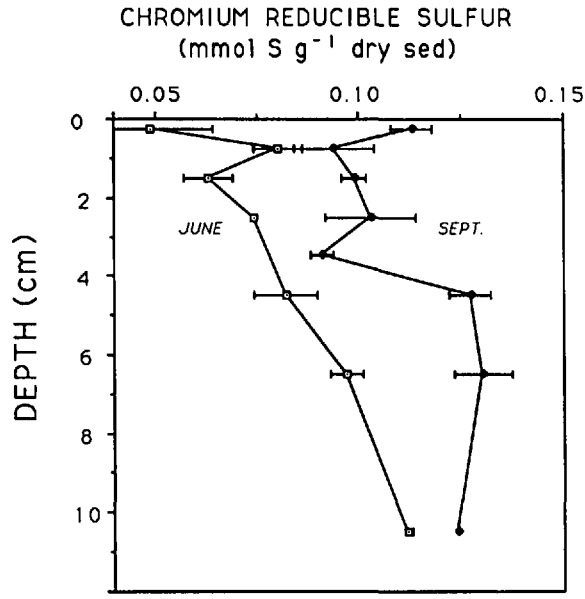

Figure 5. Total sedimentary sulfides (as chromium reducible sulfur) in the 8S mesocosm at the start (June) and end (September) of the experiment. Errors bars are ±1 S.E.

at 10.5 cm depth (Fig. 5). By the end of September, concentrations of solid sulfides were elevated in surface sediments and increased only slightly with depth. Integrating total reduced sulfur downcore to a depth of 7.52 g dry sediment cm^{-2} (corresponding to a depth of 8.2 cm and 11.0 cm for June and Sept, respectively) yielded pool sizes of 0.615 and 0.892 mmol S cm^{-2} for the two respective sampling dates. Net accumulation of reduced sulfur in the sediments over the course of the experiment was 2.8 mol S m^{-2}.

4. Discussion

a. Carbon budget. Balancing the sources and sinks of organic carbon in 8S provided a framework for interpretation of carbon cycling in a highly eutrophic ecosystem (Table 2). Sources of organic carbon were in situ production and allochthonous sludge loading. Losses from the system were export of dissolved and particulate carbon, system respiration (which was further divided into water column and benthic respiration) and storage of organic carbon in the sediments.

Sludge accounted for 63% of the 33.6 moles m^{-2} of organic carbon which were added to, or produced within, the mesocosm. Export as either dissolved or particulate carbon was small, 2.6 mol C m^{-2} (8% of total inputs). Most of the carbon staying in the system was respired with 10.7 and 12.2 mol C m^{-2} remineralized in the water column (nighttime) and the sediments, respectively. One third of the total inputs

Table 2. Carbon budget for 8S sludge mesocosm.

Carbon inputs: Sludge additions, Primary production		
Carbon sinks: Respiration (benthic and water column), Export; POC or DOC, Sedimentary storage		
Sludge addition:	21.2 (3%)*	
Day production:	12.4 (10%)	
Total inputs:		33.6
Night water column respiration:**	−10.7 (6%)#	
Benthic respiration:	−12.2 (36%)	
Export PC:	−1.8 (10%)	
DOC:	−0.8 (5%)	
Sedimentary C storage:	−11.6 (4%)	
Total losses + storage:		−37.1

*All units are mol C m^{-2} $99d^{-1}$. Error estimates (C.V.) in parentheses.

**Based on integrated night water column oxygen consumption of 13.4 mol O_2 m^{-2} $99d^{-1}$ using an R.Q. of 0.8.

#Negative numbers denote losses (export or respiration) or long term storage.

remained within the system with a net storage of 11.6 mol C m^{-2} unrespired carbon in surface sediments.

The carbon budget was roughly balanced, with loss, remineralization plus storage slightly exceeding inputs plus production (−37.1 versus 33.6 mole C m^{-2}, respectively) (Table 2). Death of the macrofaunal community during the experiment would have contributed a one time input of organic carbon into the carbon budget. However, based on the following calculations macrofaunal biomass could not have accounted for much more than 1 mol C m^{-2}. Estimates of macrofaunal biomass at the start of the experiment was 0.4 mol C m^{-2} (Keller *et al.*, 1987). Inclusion of large-bodied organisms sampled quantitatively at the end of the experiment (8S benthos was deficient compared to control biomass) yielded a maximum estimate of 0.8 mol C m^{-2} macrofaunal biomass to add to the source side of the carbon budget (Keller *et al.*, 1987).

The relative input of sludge versus primary production to the benthos and the subsequent fate of these two carbon pools was examined in the sediment subsystem. Total input of organic carbon to the sediments was estimated from the combined loss due to respiration plus net accumulation (total of 23.8 mol C m^{-2}). Oviatt *et al.* (1987) estimated that 85% of the added sludge settled to the sediment surface within 24 hours. Gearing *et al.* (1991) likewise concluded that most of the added sludge rapidly settled to the bottom. An estimate for sludge sedimentation should therefore have been close to 18.0 mol C m^{-2}. Based on changing del^{13}C values of sedimentary carbon, Oviatt *et al.* (1987) also estimated that 10.8 mol sludge C m^{-2} remained in the sediments. Benthic metabolism was stimulated by both *in situ* production and sludge (sludge carbon accounted for about 60% of benthic respiration), yet virtually all (93%) of the accumulated carbon in the sediments was sludge (10.8 sludge versus

Table 3. Sediment carbon, oxygen, sulfur and energy budget.

Carbon inputs: Organic sedimentation (respiration + storage)
Respiration: Total benthic respiration (TCO_2), Sediment oxygen uptake, Sulfate reduction
Sedimentary storage: Organic carbon accumulation, Sedimentary sulfide storage

	Carbon	Oxygen	Sulfur	Energy*
Carbon input				
Sedimentation:	23.8[♦]			2725
Respiration				
Total CO_2 flux:	12.2 (36%)			
Sediment oxygen uptake:		6.3 (10%)		
Sulfate reduction:	9.0[#]		4.5 (20%)	258
Aerobic respiration:**	3.2	3.2		366
Sulfide oxidation:[##]		3.4[@]	1.7	291
Sedimentary storage				
Sulfide storage:		5.6[@]	2.8	479
Carbon accumulation:	11.6 (4%)			1300

*Energy yield or stored, calculated from free energies of reaction (Table 1). Organic carbon has been assigned the full energy associated with its oxidation to $H_2O + CO_2$.

[♦]All units are moles m^{-2} $99d^{-1}$ except 'Energy' which is kcal m^{-2} $99d^{-1}$. Error estimates (C.V.) in parentheses.

[#]Carbon remineralized via sulfate reduction based on the molar ratio of 2C oxidized:1S reduced.

**Carbon remineralization via aerobic respiration estimated as difference between total respiration (measured TCO_2) and sulfate reduction. Oxygen consumed during aerobic respiration estimated using an R.Q. near 1.

[@]Oxygen equivalents as reduced sulfides assuming two mol O_2 needed to oxidize one mol S^{-2} (Table 1).

[##]Calculated as the difference between sulfate reduction rate and sulfide storage. Hydrogen sulfide flux across the sediment/water interface was calculated to be 1.3 mol S m^{-2} 99 d^{-1} based on Fickian diffusion (Sampou, 1989).

11.6 total). Organic carbon produced *in situ* was preferentially used by the benthos and did not accumulate in the sediments.

b. Carbon, sulfur, oxygen and energy cycling in the sediments. Simultaneous tracking of carbon, sulfur and oxygen dynamics illustrated important interrelationships between carbon decomposition, sulfur and oxygen cycling, and energy flow in the mixed aerobic/anaerobic environment of the 8S sediments and overlying water (Table 3). Carbon remineralization was dominated by anaerobic respiration (74% of benthic carbon metabolism was by sulfate reduction) which dissociated carbon cycling from both oxygen dynamics and a major percentage of energy cycling. The disparity between sediment TCO_2 flux and oxygen uptake exemplified C-O-S interactions. Sum integrated SOC (mol m^{-2} $99d^{-1}$) was only 52% of the molar flux of TCO_2 and together with the high respiratory quotients observed in the latter part of the experiment (>3.6) suggested substantial storage of oxygen equivalents in the sediments. This was matched by a significant increase in the concentration of

reduced sulfides in the sediment which was equivalent to roughly 5.6 mol O_2 m^{-2} $99d^{-1}$ of potential SOC (assuming 2:1, O_2:S^{-2} molar ratio). Adding these oxygen equivalents which accumulated as sulfides with measured SOC resulted in a combined total of 11.9 mol O_2 m^{-2} 99 d^{-1} which compared very closely to the TCO_2 flux of 12.2 mol CO_2 m^{-2} $99d^{-1}$. A benthic respiratory quotient near 1 would be predicted from carbon metabolism assuming no storage of sulfides nor oxidation of ammonium to nitrate.

Energy cycling was significantly displaced (spatially and temporally) from carbon heterotrophy as a result of sulfate reduction dominating benthic metabolism since much of the chemical energy originally contained in organic carbon was transferred to the energy-rich endproduct H_2S. Of the 915 kcal m^{-2} $99d^{-1}$ released through all paths of sediment respiration, 32% was associated with oxidation of sulfides (Table 3). More than 60% of the sulfide produced by sulfate reduction remained in the sediments at the end of the experiment with a chemical energy potential of 479 kcal m^{-2}. This represented a substantial shunt of energy away from living organisms and trophic transfer into temporary or long-term inorganic storage. Of the total energy sedimenting to the benthos (2725 kcal m^{-2} 99 d^{-1}), 66% remained in the sediments as unrespired carbon (11.6 mol C m^{-2}; 1328 kcal m^{-2}) and sulfide minerals (2.8 mol S m^{-2}; 479 kcal).

Observations suggested that chemoautotrophic secondary production via sulfide oxidation was probably occurring in 8S. Concurrent with the detection and buildup of free sulfides in the surface sediments of 8S, was the presence of a white filamentous bacterial mat at the sediment surface. These *Beggiotoa*-like bacteria were first seen August 16, and increased to a thick mat covering the entire benthos by the end of the experiment (E. Klos, personal communication). The function of sulfide oxidizers (and their chemoautotrophic fixation of biomass) as an important transfer of inorganic chemical energy back into organic trophic interactions has been suggested previously (Howarth and Teal, 1980; Howarth, 1984). Hydrogen sulfide oxidation was estimated to be the dominant pathway of sulfide oxidation in this study (Table 3), so it was possible that some of the energy passing through the sediment system as H_2S could have been transferred to higher aerobic trophic states via sulfide oxidizers. Unfortunately, a quantitative estimate of carbon fixation by the bacterial mat was not done.

c. Evolution to a sulfide dominated system. Major ecological changes occurred in the 8S system as a result of increased rates of anaerobic respiration and accumulation of sulfides in surface sediments. The third week of Aug represented a pivotal change in the benthic community structure. Macrofauna numbers had increased threefold over control abundances to 315,000 individuals m^{-2} (dominated by *Spionidae* polychaetes; Keller *et al.,* 1987). Sulfate reduction metabolism increased dramatically between Aug 3 and Aug 14 with rates almost tripling from 1050 to 2820 nmol cm^{-3} d^{-1}. Hydrogen sulfide was first detected in the surface 1 cm of sediment on Aug 14. By

Aug 16 *Beggiotoa*-like sulfide oxidizing bacteria were observed on the sediment surface. The whole system experienced severe oxygen depletion (DO < 15 μmolar) on Aug 16. By Aug 24, hydrogen sulfide had risen to 900 μmolar in the surface 1 cm of sediment, sulfide oxidizing bacteria were found on the surface of all the sediment cores taken and the surface mat of polychaete tubes was in the process of decay. Some macrofauna were visible and active, although showing signs of stress. Two weeks later (Sep 5) water column anoxia (DO < 3 μmolar) occurred and subsequent sampling of the benthos showed rotting polychaete carcasses, no intact worm tubes and extended listless bivalves on the sediment surface (behavior indicative of severe sulfide/oxygen stress) (Jørgensen, 1980). Porewater hydrogen sulfide concentrations were in excess of 1100 μmolar and the surface sediments were very fluid and black. Theede *et al.* (1969) documented increased mortality (species specific) of most macrofauna at sulfide concentrations similar to that in the surface sediments of 8S. A quantitative macrofaunal population census at the end of the experiment (Sep 19) showed an almost total lack of fauna excepting the bivalve *Nucula annulata* and mud anemone *Cerianthiopsis americanus* (Maughan, 1986). In a period of one month the 8S mesocosm degraded from an active mixed aerobic/anaerobic benthos heavily populated by opportunistic polychaetes to a bacterial dominated system with sulfides (not organic carbon) increasingly becoming the currency of energy exchange.

The 8S mesocosm was a model ecosystem which exhibited a dramatic change in its form and function over the course of the 99 day experiment. This system was not in equilibrium with respect to major elemental cycles nor species present. Since the experiment was conducted over the summer, the rate of carbon accumulation was probably at the annual minimum, while the storage of sediment sulfides could have been near maximum (Rudnick and Oviatt, 1986; Jørgensen *et al.,* 1990, Sampou and Oviatt, 1991). The sediments began the experiment with a large potential for sulfide precipitation, which probably exceeds the annual range of sulfide mineral concentrations characteristic of a system receiving heavy carbon loading for many years (Cornwell *et al.,* 1990).

5. Conclusions

1. The 8S mesocosm received a total of 33.6 mol C m^{-2}, 63% of which was allochthonous sludge inputs. Respiration of the carbon was equally divided between water column nighttime respiration and benthic remineralization (10.7 and 12.2 mol C m^{-2}, respectively). Export of organic carbon from the system as dissolved organic carbon and particulate carbon was minimal (8% of inputs). A large fraction of sludge carbon remained in the system stored in surface sediments.

2. Anaerobic respiration dominated benthic carbon remineralization, and the formation of reduced sulfur compounds via sulfate reduction uncoupled carbon metabolism from oxygen and energy cycling. Sediment oxygen consumption was a poor estimator of sediment metabolism in the latter part of the experiment. High respiratory quotients were due to the burial of sulfide as oxygen equivalents. Energy

processed by the benthos was almost equally divided between organic carbon oxidation and sulfide oxidation. However, a majority of energy which reached the benthos as organic matter (65%) remained as unrespired carbon and stored energy equivalents in inorganic sulfide minerals.

3. A eutrophic marine benthos may be characterized by a simplification of biological trophic structure (death of macrofauna), dominance by anaerobic bacterial carbon remineralization, increased importance of sulfur cycling and the uncoupling of carbon remineralization from oxygen cycling and energy flow. Chronic allochthonous carbon inputs had the capacity to bring about these drastic changes in the functioning of a coastal ecosystem.

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