

Decomposition of organic matter in aggregated seston from the Elbe estuary: redox dependency and production of low molecular weight DOC compounds

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ABSTRACT: Early microbial degradation processes and accumulation of carbonyl compounds and carboxylic acids in seston aggregates under oxic and suboxic environmental conditions were studied. In laboratory experiments, aerobic decomposition of seston material increased after aggregation and maximum rates were reached after about 70 h. Seston material that became refractory to aerobic degradation was mineralized anaerobically with nitrate as the terminal electron acceptor at a rate amounting to about 50% of the maximum rate during the previous aerobic incubation. During both early aerobic and anaerobic degradation of seston, a decrease in particulate organic carbon (POC) and the C:N ratio was observed. A net production of glyoxylate and glycolaldehyde occurred under anaerobic heterotrophic conditions and concentrations up to 4 and 30 $\mu\text{g l}^{-1}$, respectively, were detected in the field when dissolved oxygen concentrations were below 3 mg l^{-1} . Glycolaldehyde was identified as an indicator of anaerobic degradation processes which occurred in the open water of the Elbe estuary for suspended seston aggregates ≤ 2 mm in diameter. Results indicate a strong coupling between aerobic and anaerobic processes in the aggregates whereby anaerobic net production of DOC could significantly enhance O_2 consumption.

KEY WORDS: Suspended matter · Nitrification · Oxygen and nitrate respiration · Degradation · DOC · Anaerobic conditions · Elbe estuary

INTRODUCTION

Recent investigations of marine seston aggregates (marine snow) reaching a size of several cm in diameter revealed that within their spatial structure steep redox gradients occur which allow sulfate reduction to take place (Alldredge & Silver 1988, Shanks & Reeder 1993). In addition, both strictly aerobic and anaerobic bacteria were found to be associated with the marine snow (Bianchi et al. 1992). Limnic and estuarine seston aggregates are much smaller and only reach approximately 5 mm in diameter; however, even within these size ranges, anaerobic regions have been detected (Eisma 1993, Grossart & Simon 1993). The impact of differences between aerobic and anaerobic conditions on the degradation of POC is not well understood (Lee 1992). Some authors argue that the kinetics of organic matter decomposition is similar in the presence and

absence of O_2 and that there should be no influence of O_2 on carbon preservation. Others argue that decomposition is more efficient with O_2 and, hence, organic matter will be preferentially oxidized in its presence, and preserved in its absence (Canfield 1994).

Due to experimental difficulties, the processes and interactions controlling organic matter degradation within seston aggregates have, to our knowledge, not been studied. Methods of suspension generally used to determine degradation rates in the laboratory do not take into account intact aggregates. In the field, anaerobic degradation processes are difficult to quantify in open waters where oxygen concentrations are high. This is explained by the analytical methods used to measure the heterotrophic microbial processes, by changes in the organic matter composition and by the consumption of terminal electron acceptors. The inorganic end products of the anaerobic respiration

processes, which include ferrous iron, methane and sulfide, are rapidly oxidized under aerobic conditions or easily become insoluble compounds (Gerringa 1991, Balistrieri et al. 1992), while the end products of denitrification occur at high background concentrations in the atmosphere.

To overcome most of the methodological problems described above, a new laboratory device was used to study successive aerobic and anaerobic degradation in 1 mm layers of settled seston material from the Elbe estuary, Germany, by monitoring the heterotrophic consumption of oxygen and nitrate. The production of dissolved organic compounds was determined and oxocarboxylic acids and carbonyl compounds (C_1 to C_3) were used as indicators of the respiration processes occurring within the aggregated seston. The results were compared with those for field samples with varying oxygen concentrations taken along a longitudinal profile of the Elbe estuary.

MATERIAL AND METHODS

Study area and sampling. The Elbe estuary has a length of 142 km and is mostly well mixed (Fig. 1). In June 1992, during a 2 d cruise, 10 water samples were taken along a longitudinal profile from km 630 to 665 in the freshwater region of the estuary (Fig. 1). Within this region O_2 depletion occurs regularly during early summer, with concentrations falling to below 3 mg l^{-1} . This situation was chosen to study accumulation of the same dissolved organic species as were observed in the laboratory studies using different oxygen concentrations. Water samples were taken with a horizontally orientated sampler (Hydrobios, Kiel, Germany) from 2 m below the water surface and prepared for analyses of dissolved and particulate substances as described below.

For the laboratory studies during different seasons in 1992, estuarine water was sampled from a station at Teufelsbrück (km 630) located about 500 m downstream from Hamburg harbour (S1) and at a riverine station (km 585) further upstream (S2) (Fig. 1). About 20 l were collected from the upper 0.5 m of the water column during ebb tide. Suspended particulate matter

(SPM) was fractionated and concentrated from the sample by a sedimentation method described in detail by Kerner & Krogmann (1994). A specially shaped funnel was used which allowed the separation of suspended particles capable of sedimentation at a rate of $\geq 0.02 \text{ cm s}^{-1}$ from permanently suspended particles of $\leq 0.1 \text{ mm}$ diameter (Dyer 1986). Sedimenting material was used to prepare Batches A and B in July, C and D in September, and K and L in November, and subsamples were analysed for all biochemical parameters described below. During sampling, the water at the study sites had a pH ranging between 6.9 and 8.3, and contained between 2.4 and $12.7 \text{ mg O}_2 \text{ l}^{-1}$ and 80 to $176 \text{ mg Cl}^{-1} \text{ l}^{-1}$. Temperature ranged between 3.4 and 22.2°C . Additional physical and chemical data for the water at the sampling sites are given on the basis of monthly longitudinal surveys by Arge (1992).

Method of incubation. A round polycarbonate incubation cell (internal diameter = 40 mm, internal height = 22 mm) was separated horizontally into 2 equal chambers by an inflexible membrane (Fig. 2, no. 14) made of Al_2O_3 (Anotec Separation Ltd. Anopore, pore size = $0.2 \mu\text{m}$, height = $60 \mu\text{m}$). A constant flow of synthetic river water was maintained by a peristaltic pump (Gilson, Minipuls 2) from 2 stock vessels (15 l) connected to both chambers in the cell through holes in both the top and bottom disks (Fig. 2, no. 20). The synthetic water, containing 5.6 mM NaCl, 4.1 mM MgSO_4 , 0.8 mM CaSO_4 , 0.16 mM Na_2HPO_4 , 0.25 mM KH_2PO_4 , 0.2 to 0.3 mM NaNO_3 and 0.2 to 0.5 mM NH_4Cl , was of comparable inorganic composition to that of the Elbe water at the study sites (Arge 1992). The synthetic water, free of inorganic carbon, had a pH of between 6.4 and 6.8 depending on the $\text{NH}_4\text{-N}$ concentrations. To produce a difference in the chloride concentrations in the chambers overlying and underlying the seston layer, the chlorinity of the synthetic water at the inlets differed by $\sim 400 \text{ mg Cl}^{-1} \text{ l}^{-1}$. The stable chloride concentrations reached during experiments in the different chambers were used to calculate the thickness of the seston layer from the diffusion of chloride through the layer counterbalanced by the mass transport of chloride from the respective chambers of the incubation cell (Kerner & Gramm 1995).

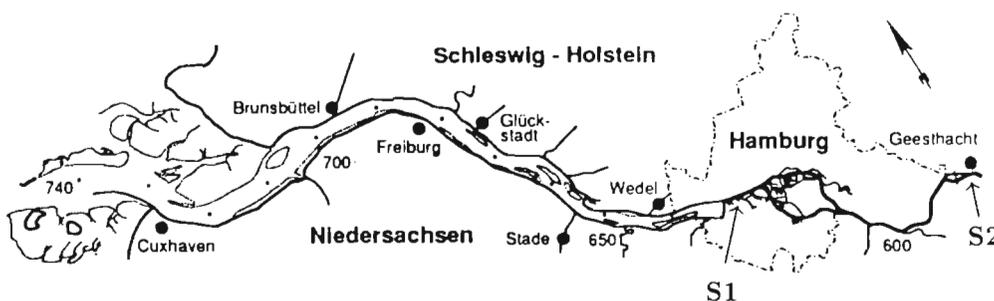


Fig. 1 The Elbe estuary, Germany, showing the sampling stations (S1, S2). Numbers are km markers

Anaerobic pore water was simulated in the chamber underlying the layer using synthetic water in which the oxygen content was eliminated by constant aeration with N_2 . The oxygen concentration of the water in the upper chamber, simulating Elbe water, was controlled by the oxygen content in the respective stock vessel. Different experimental substages (Table 1) were created by varying the concentrations of O_2 in the respective stock vessel by elimination with a defined gas mixture of N_2 and O_2 (MKS, Multigas Controller 147). At the beginning of the experiments (Stage E1) the oxygen concentration was maintained at $8.7 \text{ mg } O_2 \text{ l}^{-1}$. Subsequently an anaerobic incubation was initiated, with nitrate added as the terminal electron acceptor. At the end of the experiments, oxygen concentration in the stock vessel feeding the upper chamber was again raised to concentrations between 6.7 and $8.7 \text{ mg } O_2 \text{ l}^{-1}$ (Table 1). All experiments were conducted at a temperature of 15°C under dark conditions and an argon atmosphere to eliminate any intrusion of O_2 . Bacteria-free ($0.2 \mu\text{m}$ filtered) deionized water (Milli-Q, Millipore) was always used for dilution and rinsing procedures. The use of stable temperatures and synthetic water is a compromise between a perfect simulation of natural

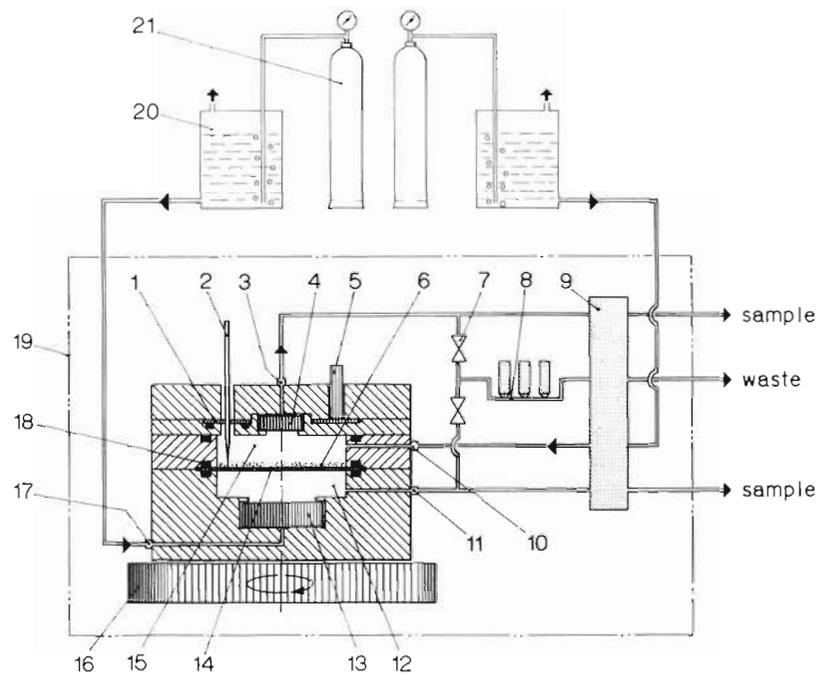


Fig. 2. Schematic diagram of the laboratory device for incubation of seston layers. (1) Opening of turntable; (2) O_2 microelectrode; (3) outlet; (4) stirring disc; (5) turntable; (6) sestet material; (7) valve; (8) flow-through cell (measurement of O_2 , pH); (9) peristaltic pump; (10) inlet; (11) outlet; (12) pore water; (13) stirring disc; (14) inflexible membrane; (15) bottom water; (16) magnetic stirrer; (17) inlet; (18) viton ring; (19) glove box; (20) stock vessel; (21) gas tank

conditions and the design of an experiment conducted under controlled conditions that are reproducible.

Experimental procedure. Before the start of the experiments, the membrane in the incubation cell was

Table 1. Conditions used in successive redox stages (E1, E2, etc.) of laboratory incubations of seston layers. Batches L, D and A contained material sampled prior to the start of a given substage; the parallel batches K, C and B contained material from the beginning of the experiments

Month Batch (stage)	Sampling site	Duration (h)	Flow rate (ml min^{-1})	Layer (mm)	pH \pm SD, outflow	O_2 (mg l^{-1}), inflow
November						
K (E1-5)	S1	432	0.24	0.99	6.52 ± 0.03	Same as for Batch L
L (E1-3)	S1	265	0.24	0.97	6.49 ± 0.04	8.7 (E1), 2.4 (E2), 1 (E3)
L (E4)	S2	121	0.24	1.52	6.62 ± 0.01	0.0
L (E5)	S2	47	0.24	1.45	6.52 ± 0.02	8.7
September						
C (E1-3)	S1	332	0.29	0.93	6.51 ± 0.06	Same as for Batch D
D (E1)	S1	192	0.29	0.70	6.49 ± 0.08	8.7
D (E2)	S1	100	0.29	1.10	6.61 ± 0.05	0.0
D (E3)	S1	42	0.29	0.80	6.55 ± 0.07	6.7
July						
B (E1-3)	S1	356	0.46	1.62	6.61 ± 0.18	Same as for Batch A
A (E1)	S1	146	0.46	1.38	6.49 ± 0.12	8.7
A (E2)	S1	164	0.46	1.68	6.82 ± 0.05	0.0
A (E3)	S1	47	0.46	1.21	6.67 ± 0.08	8.4

evenly covered with sedimenting particulate matter obtained as described above. Similar amounts of seston were allowed to settle in 2 separate containers for parallel incubations and sufficient material was used in order to produce similar uniform depths on the membrane in all experiments (Table 1). At the end of each redox stage in the experiments (Table 1), the particulate matter in one of the parallel incubations (Batches L, D, A) was completely resuspended, removed, and prepared for analyses of chemical composition as described below. Prior to the next experimental stage, the emptied cell was filled with a defined amount of seston material newly sampled from the Elbe as described above. The material was incubated under the same experimental conditions as Batches K, C, and B, which contained aged seston material from the beginning of the experiments (Table 1). Use of this procedure allowed us to conclude, from similar reactions in the parallel batches containing different material, that degradation processes were only controlled by the redox conditions.

During the experiments, Teflon-coated magnetic stirring disks located at the top and bottom of the container constantly mixed both water columns (height = 11 mm) but with a minimum of turbulence to prevent resuspension of the settled seston (Fig. 2, nos. 4 & 13). Flow rates in both chambers were equal and constant during each experiment (Table 1). For analyses, samples of at least 5 ml of water were collected from the separate chambers at irregular intervals while experiments were being conducted.

Analytical procedures. The standard deviation of replicate chemical analyses of the same sample was always $\leq 5\%$. Cl^- , NO_3^- , NO_2^- , and NH_4^+ were analysed in filtered (Minisart, pore size 0.45 μm) water samples stored at -20°C in a flow injection analyzer (Tecator, Aquatec 5020) according to the methods described by Grasshoff et al. (1983). The detection limit was 5 mg l^{-1} for chloride, 1 $\mu\text{g N l}^{-1}$ for nitrite, 30 $\mu\text{g N l}^{-1}$ for nitrate, and 10 $\mu\text{g N l}^{-1}$ for ammonium.

Determinations of oxygen and pH during the laboratory experiments were conducted directly at the outflows (Fig. 2, no. 8) using a glass flow-through cell containing specific probes (Eschweiler and Co., Kiel). The detection limit for oxygen was 0.01 mg l^{-1} . In the field studies, O_2 concentrations in the Elbe water were determined at the sampling sites with an O_2 -sensitive probe (WTW, Oxi-Digi 91).

Carbonyl compounds in water samples that had been filtered (Whatman GF/C) and stored after addition of 3% (w/v) HgCl_2 (150 μl to 50 ml filtrate) were measured by HPLC after derivatization of 5 ml samples with 2,4-dinitrophenylhydrazine. Preliminary experiments revealed no detectable losses of the organic substances by complexation with HgCl_2 . The hydrazones of carbonyl compounds and oxocarboxylic acids (C_1 to

C_4) were separated in a gradient elution (LiChrosorp, RP18-5, Merck) and detected using a UV detector (Merck, L-3000) at 360 nm. The analytical procedure is described in detail by Edelkraut & Brockmann (1990). Concentrations were calculated from calibration curves for acetaldehyde, acetone, formaldehyde, glycolaldehyde, glyoxylate and pyruvate using external standards (Merck p.a.). The detection limits ranged from 17 ng l^{-1} for glycolaldehyde to 80 ng l^{-1} for acetone.

Organic carbon and nitrogen in the particulate subsamples were determined with a Carlo Erba Elemental Analyzer, Model 1108. Samples prepared by filtration on pre-ashed (450°C) and pre-weighed Al_2O_3 filters (Anopore, pore size = 0.2 μm) were dried at 70°C (Altabet 1990). Inorganic carbonates were removed by foaming the samples on the filters with concentrated HCl. The detection limit of both N and C was below 5 μg .

For chlorophyll *a* (chl *a*) analyses, samples on GF/F filters (Whatman) were immediately extracted with acetone and stored in the dark at -20°C . Prior to analysis, the samples were homogenized at -20°C in a cell mortar cooled with liquid CO_2 . Separation of the filtered extract was achieved using an isocratic HPLC method (Daemen 1986), and chl *a* concentration was determined with a fluorescence detector (Milton Roy, SM 4000) at 430 and 663 nm. Calibration was conducted using external standards (Sigma).

RESULTS

Laboratory studies

Particulate matter

The biochemical composition of the seston material used in the experiments varied significantly (Table 2). The C:N ratios were always well above the Redfield ratio of 6.7 for living organic matter (Hecky et al. 1993). The seston layers contained between 5 and 17 mg C , and between 0.5 and 61% of the carbon was algal matter, assuming a constant C:chl *a* ratio of 66.7.

As can be seen from the loss of organic carbon, degradation processes occurred during both aerobic and anaerobic incubations (Table 2). The mineralization of carbon was not accompanied by an equivalent decrease in the N content of the particulate matter. Hence, the C:N ratios of the seston material decreased during the incubations. From the experimental design it is concluded that the changes in the C:N ratio during the experiments reflect either a selective use of a C pool depleted in N relative to the bulk material or a build-up of particulate organic compounds rich in N.

Table 2. Changes in the composition of seston layers during laboratory incubations under successive, defined redox conditions (E1, E2, etc.). Analyses were carried out on material from batches K, D and B at the beginning and end of each experiment, and on material from batches L, D and A at the beginning and end of each redox stage

Month Batch (stage)	Dry wt (mg)		Loss (End/Start)	Start			End			Chl <i>a</i> (µg)		C:Chl <i>a</i>	
	Start	End		C (%)	N (%)	C/N	C (%)	N (%)	C/N	Start	End	Start	End
November													
K (E1-5)	89.3	66.9	0.75	7.0	0.89	9.1	–	–	9.1	18.3	–	342	–
L (E1-3)	89.3	58.3	0.65	7.0	0.89	9.1	6.3	0.94	7.8	18.3	6.2	342	592
L (E4)	94.2	70.2	0.75	12.4	1.47	9.8	10.45	1.29	9.4	16.6	12.9	704	571
L (E5)	67.1	56.6	0.84	12.2	1.56	9.1	10.52	1.51	8.1	25.4	–	322	–
September													
C (E1-3)	233	173	0.74	6.0	0.50	13.9	5.10	0.51	11.7	10.1	3.9	1384	2262
D (E1)	233	220	0.95	6.0	0.50	13.9	5.13	0.51	11.7	10.1	3.4	1384	3319
D (E2)	97.2	83.7	0.86	7.3	0.84	10.2	6.3	0.65	11.3	20.6	12.5	344	422
D (E3)	57.3	48.0	0.84	8.5	0.99	10.0	–	–	10.5	23.9	4.8	204	–
July													
B (E1-5)	183	130	0.71	9.4	0.81	13.5	7.3	0.75	11.4	33.6	10.1	511	940
A (E1)	183	137	0.75	9.4	0.81	13.5	7.8	0.77	11.8	33.6	10.3	511	1037
A (E2-3)	80.9	73.6	0.91	10.1	0.9	13.1	9.9	0.95	12.2	74.7	28.6	109	255
A (E4-5)	58.4	42.9	0.73	15.0	1.62	10.8	7.9	1.03	8.9	40.5	16.8	216	202

Algal matter, determined by chl *a* measurements, was decomposed by about 70% during the first 150 to 200 h of aerobic incubation. During the same time interval, an increase in the ratio of C:chl *a* indicated a preferential use of the algal material in decomposition (Table 2).

Environmental conditions

At a constant O₂ level in the inflow, the oxygen concentrations reached in the chambers were only controlled by biochemical consumption processes in the seston layer. Thus, the excellent reproducibility of the experiments under aerobic conditions became obvious from the similar pattern of oxygen concentrations in the parallel chambers (K/L C/D, and B/A) containing the same material (Figs. 3a, 4a & 5a). A decrease was observed and minimum concentrations were always reached 70 h after the start of aerobic incubation. At this time during the incubation, anaerobic conditions were detected in the bottom part of the layer during the July experiment only (Fig. 3a). During the experiment in November, lowering the oxygen concentration in the inflow to 1 mg O₂ l⁻¹ resulted in anaerobic conditions in both seston layers (Fig. 5a).

Nitrate was provided at concentrations above 2 mg N l⁻¹ during all experiments to prevent nitrate reduction limitation, and suboxic environmental conditions were thus maintained in anaerobic incubations. Accumulation of nitrite in both the sediment and the bottom water occurred only under anaerobic conditions in the seston layer, when the reduction of nitrite was the rate-limiting step in nitrate reduction (Figs. 3b, 4b & 5b).

Under this condition, concentrations of up to 0.15 mg l⁻¹ NO₂-N were reached in November, 0.06 in September, and 0.5 in July, before reduction of nitrate balanced that of nitrite.

The pH value remained constant at about 6.5 during all phases of the experiments and changes therefore did not affect the microbial processes. Changing from aerobic to anaerobic conditions during the incubations resulted in a slight decrease in the pH values (Table 1).

Conversion processes

From the net production of nitrate determined during aerobic incubation, the oxygen consumed in nitrification was calculated using a conversion factor of 2. Heterotrophic oxygen consumption (HOC) was calculated from the total oxygen consumed minus that used in nitrification. Mineralization of organic carbon was computed during aerobic incubation from HOC and during anaerobic incubation from the nitrate consumption, using conversion factors of 1 and 1.25, respectively. The results showed that nitrification accounted for the total oxygen consumption at the beginning of aerobic incubation and after about 120 h (Fig. 6a). When maximum oxygen consumption rates were reached after about 70 h, nitrification still accounted for more than 30% of the total. Thereafter, the seston material became refractory to aerobic degradation as suggested by the decrease in HOC and nitrification was again equal to the total oxygen consumption after 150 h of aerobic incubation. Under the subsequent anaerobic conditions, the degradation rates with nitrate as the terminal electron acceptor were 40 to

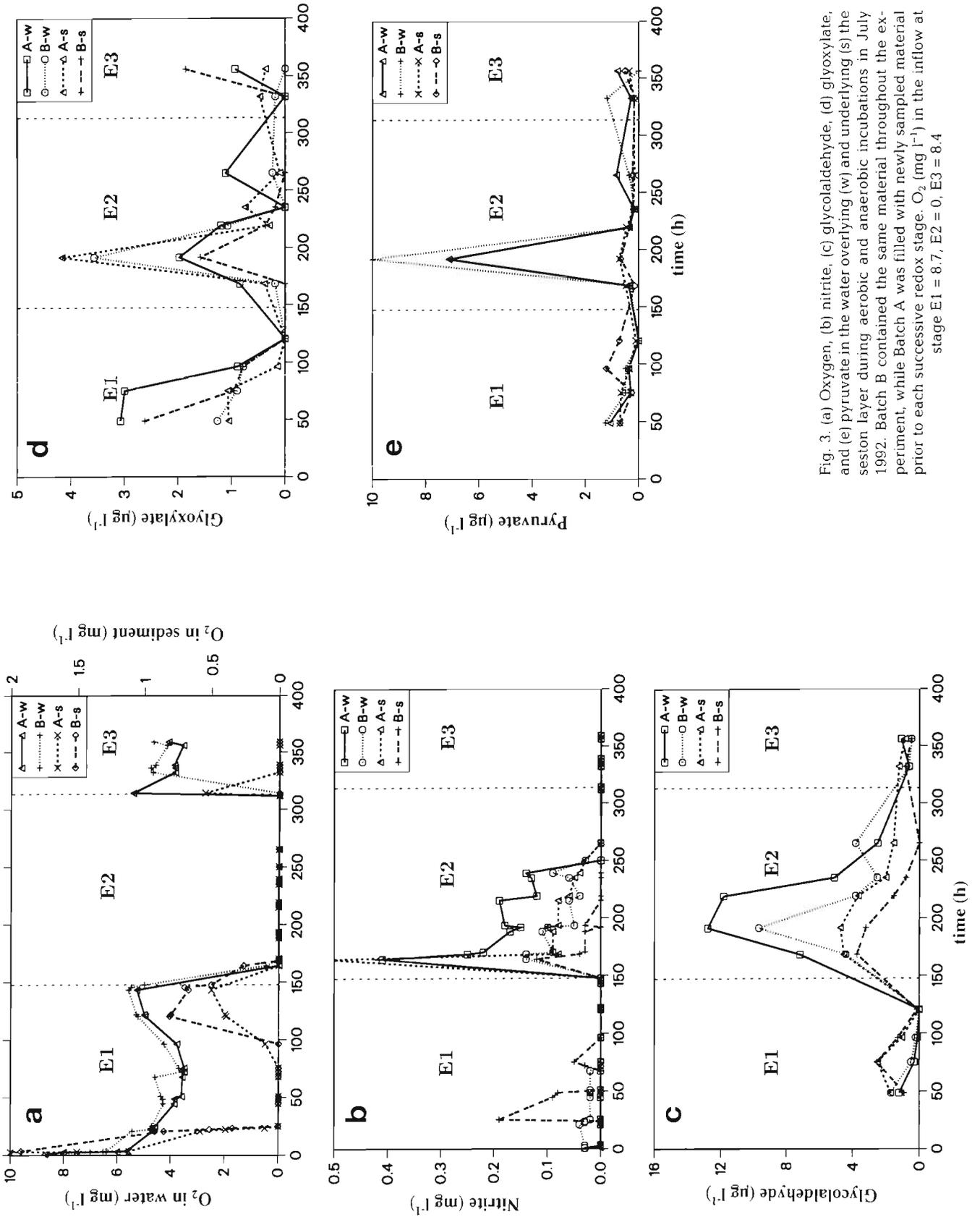


Fig. 3. (a) Oxygen, (b) nitrite, (c) glyoxaldehyde, (d) glyoxylate, and (e) pyruvate in the water overlying (w) and underlying (s) the sediment layer during aerobic and anaerobic incubations in July 1992. Batch B contained the same material throughout the experiment, while Batch A was filled with newly sampled material prior to each successive redox stage. O_2 (mg l^{-1}) in the inflow at stage E1 = 8.7, E2 = 0, E3 = 8.4

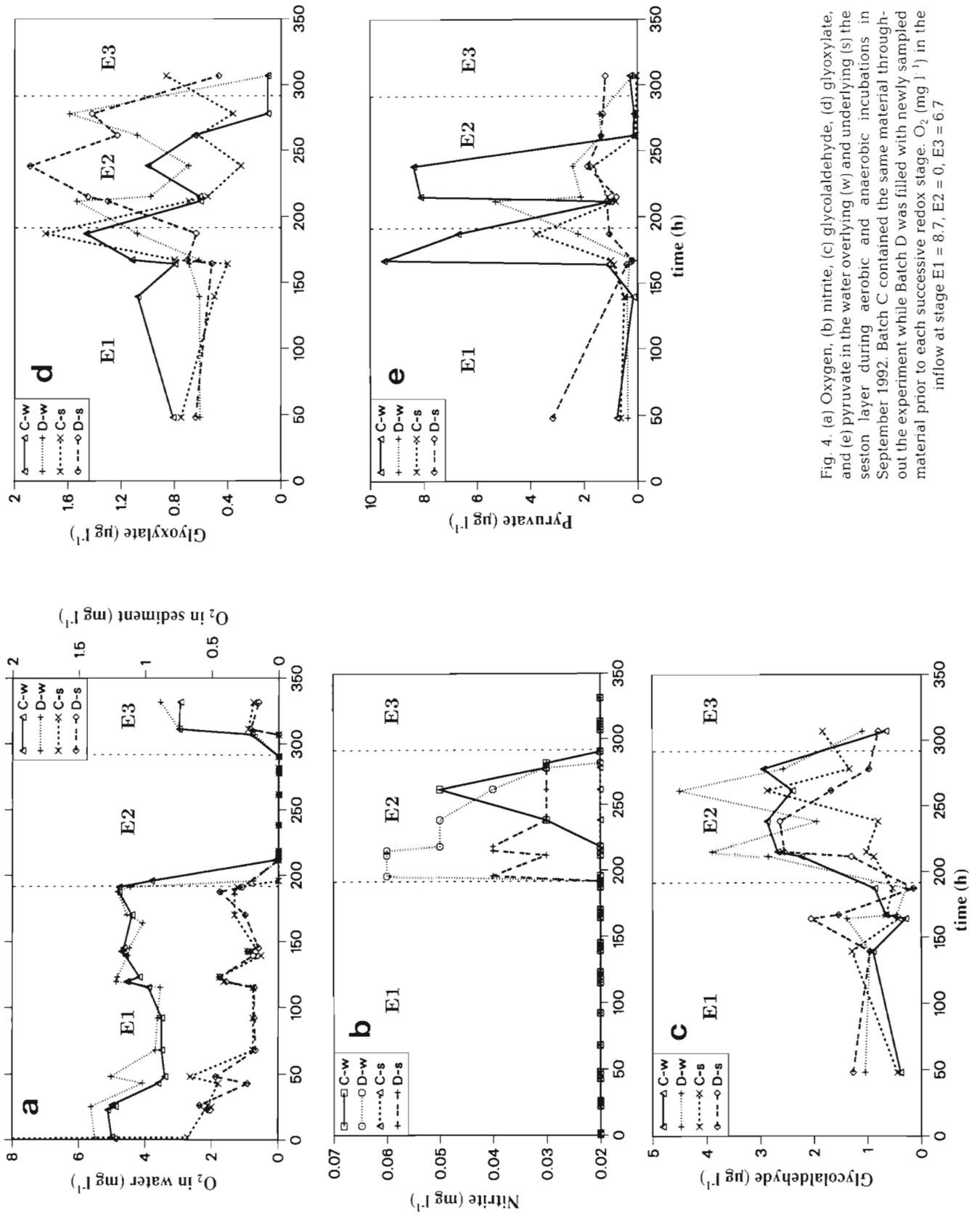


Fig. 4. (a) Oxygen, (b) nitrite, (c) glycolaldehyde, (d) glyoxylate, and (e) pyruvate in the water overlying (w) and underlying (s) the seston layer during aerobic and anaerobic incubations in September 1992. Batch C contained the same material throughout the experiment while Batch D was filled with newly sampled material prior to each successive redox stage. O_2 (mg l^{-1}) in the inflow at stage E1 = 8.7, E2 = 0, E3 = 6.7

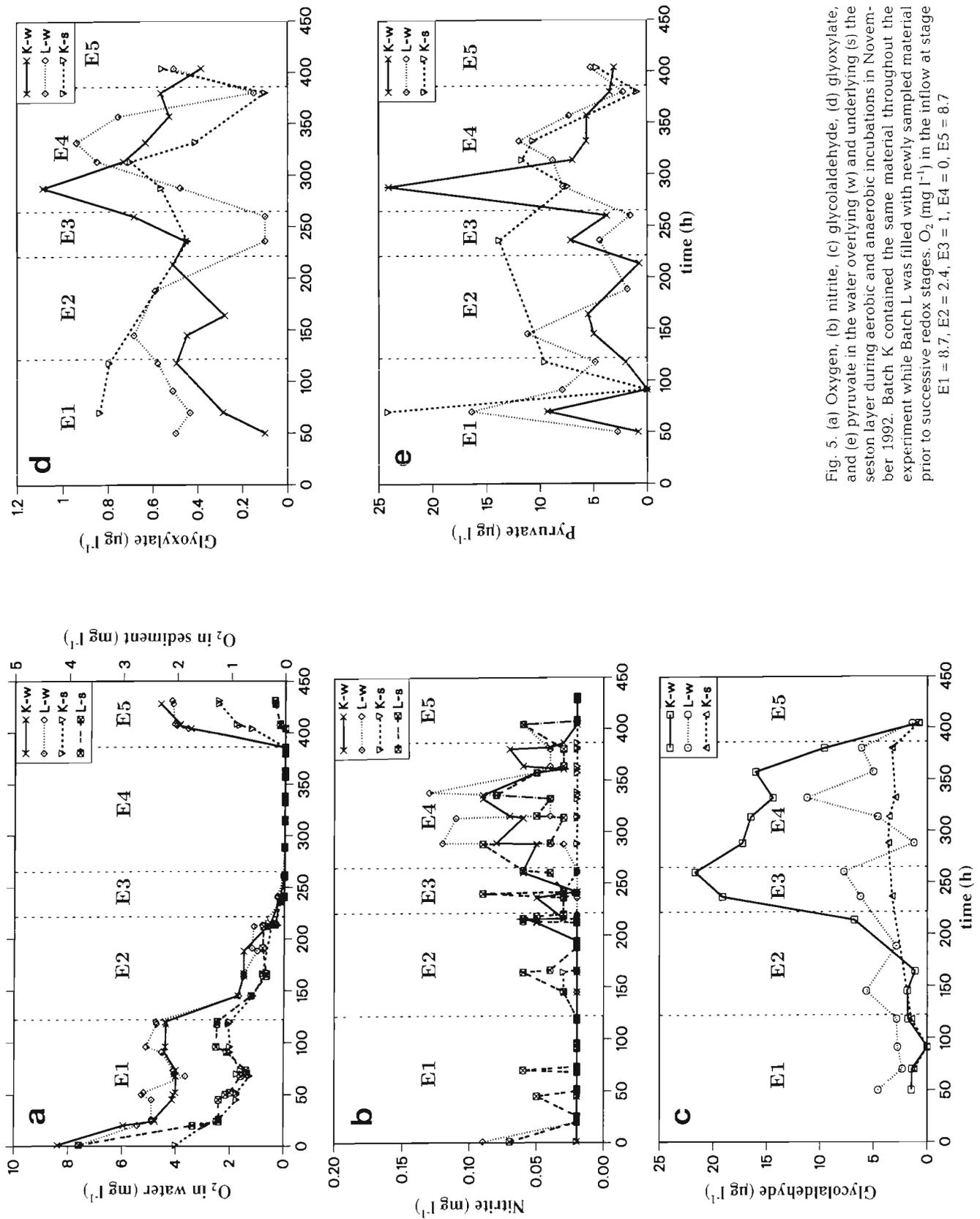


Fig. 5. (a) Oxygen, (b) nitrite, (c) glycolaldehyde, (d) glyoxylate, and (e) pyruvate in the water overlying (w) and underlying (s) the seston layer during aerobic and anaerobic incubations in November 1992. Batch K contained the same material throughout the experiment while Batch L was filled with newly sampled material prior to successive redox stages. O_2 (mg l^{-1}) in the inflow at stage E1 = 8.7, E2 = 2.4, E3 = 1, E4 = 0, E5 = 8.7

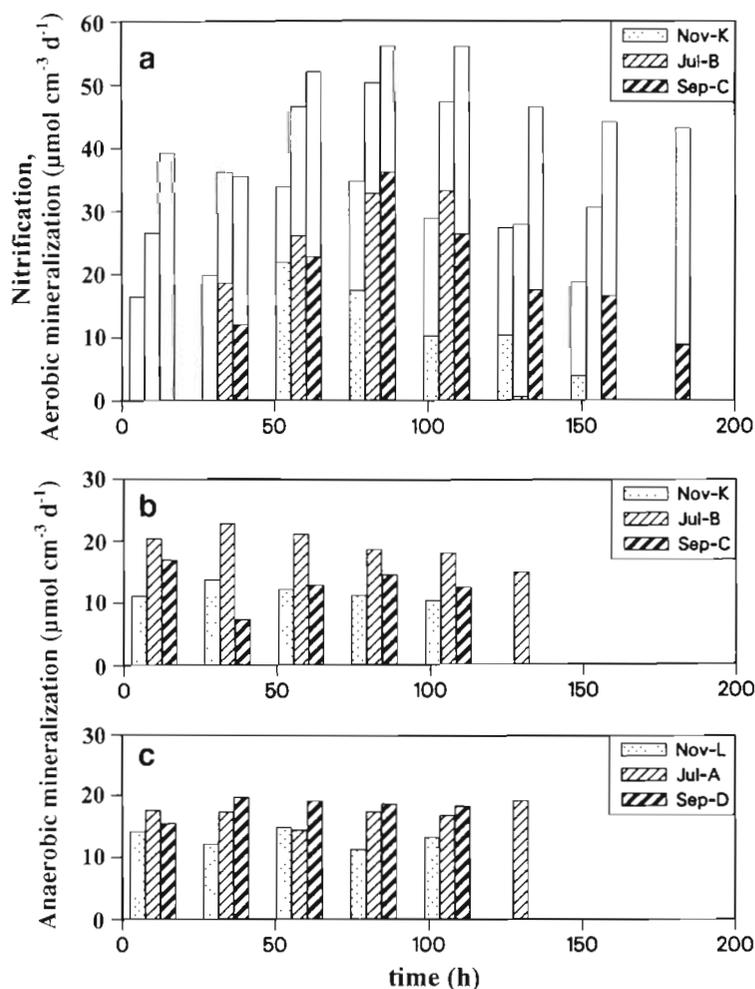


Fig. 6. (a) Nitrification (unshaded portions of bars) and mineralization rates (shaded portions) within the seston layer of Batches K, C, and B calculated from oxygen consumption during different seasons. Anaerobic mineralization rates were calculated from nitrate reduction in the seston layers (Batches K, C, and B) previously incubated aerobically (b), and in layers formed by seston material (Batches L, D, and A) sampled prior to anaerobic incubation (c)

70% of the maximum rates with oxygen as the terminal electron acceptor (Fig. 6b). Nitrate reduction in the batches containing 'fresh' seston from the Elbe (L, D and A) occurred at rates similar to those in the 'aged' seston layers (Batches K, C, and B), and in both batches degradation rates remained constant even after 200 h of continuous anaerobic incubation (Fig. 6b, c). Thus, anaerobic mineralisation in the seston layers soon after aggregation of the seston was quite independent of differences in the organic composition of the material.

In all experiments oxygen consumption was initiated, without a time-lag, upon re-aeration after anaerobic conditions had been maintained for several days (Figs. 3a, 4a & 5a). The total oxygen consumption rates attained, calculated from the oxygen concentrations,

were 64 to 88% of those determined under aerobic conditions at the start of the experiments (Fig. 6).

Dissolved organic substances

No systematic differences in the concentrations of the dissolved substances were detected between the parallel batches containing 'aged' (K, C and B) and 'fresh' (L, D and A) seston material during the different seasons (Figs. 3, 4 & 5). During aerobic incubations minimum concentrations of dissolved organic substances coincided with a decrease in oxygen consumption (Figs. 3, 4 & 5). Lowering the oxygen concentrations in the inflow to 2.4 mg l^{-1} had no effect on the concentrations of dissolved organic substances in the water above and below the seston layer, as long as aerobic conditions prevailed within the seston layer (Figs. 3, 4 & 5).

An initiation of anaerobic conditions in the seston layer was followed by an increase of glycolaldehyde after about 20 h (Figs. 3c, 4c & 5c). Concentrations up to 5 times those under aerobic conditions were reached after about 50 h of anaerobic incubation. This accumulation of glycolaldehyde under anaerobic conditions lasted for about 100 to 150 h. Concentrations decreased thereafter but remained above those found under subsequent aerobic incubation.

Anaerobic conditions also affected the release of glyoxylate and pyruvate, and higher concentrations were generally detected in the water above and below the seston layer compared to those found under aerobic incubation. However, an accumulation of these substances was not found during a longer period of anaerobic incubation (Figs. 3d, e, 4d, e & 5d, e). Acetaldehyde, acetone, and formaldehyde showed even more irregular concentration patterns and remained generally at about $1 \mu\text{g l}^{-1}$, similar to the concentration observed under aerobic conditions.

Field study

Chl *a* increased from km 630 downstream while the amount of organic carbon decreased (Fig. 7b). Thus, algal biomass did not control the C:N ratios, which increased from 7.0 to 11.4, indicating degradation of

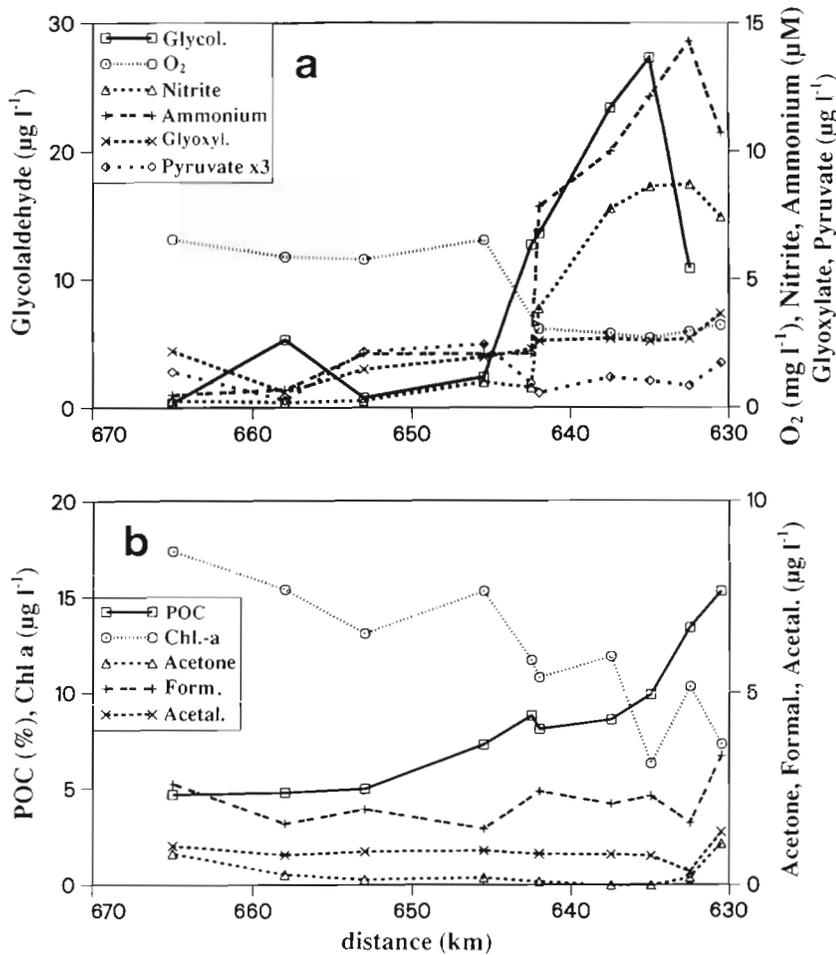


Fig. 7. (a) Dissolved oxygen, nitrite, ammonium, glycolaldehyde, glyoxylate, and pyruvate, and (b) organic carbon, chl a, acetaldehyde, formaldehyde, and acetone, along the longitudinal profile of the freshwater region of the Elbe estuary in June 1992

SPM during the transport downstream. In the O₂ deficient region (between km 630 and 642) nitrite and ammonium increased to concentrations of about 9 and 15 μM, respectively (Fig. 7a). The distributions of nitrite and ammonium were positively correlated with each other ($r = 0.98$, $p \leq 0.001$) and were closely followed by glycolaldehyde, with maximum concentrations up to 28 μg l⁻¹ at km 638 (Fig. 7a). Glycolaldehyde remained resistant to microbial consumption, and concentrations between 0.4 and 5.3 μg l⁻¹ prevailed within the profile where increased oxygen concentrations occurred. Glyoxylate was also enhanced at low oxygen concentrations but was rapidly consumed down to about 0.6 μg l⁻¹ further downstream (Fig. 7a). Pyruvate concentrations did not reveal a similar pattern in distribution, and concentrations were in the range of 0.1 to 0.8 μg l⁻¹. The same was true for acetaldehyde, acetone and formaldehyde with concentrations of about 1 μg l⁻¹ (Fig. 7b).

DISCUSSION

After aggregation, nitrification accounted for the total oxygen consumption in sedimenting seston material from the Elbe estuary during different seasons, while heterotrophic processes were inhibited by a lack of substrates as discussed below. Given that ammonium is not limiting, nitrification might bring about practically anaerobic conditions within seston aggregates (Carlucci & McNally 1969). Aerobic respiration was initiated about 20 h after aggregation and further reduced the aerobic layer in the seston to the upper 1 mm. Thus, even in O₂ saturated open waters of the Elbe estuary, seston aggregates of ≤2 mm might include anaerobic layers.

Release of organic substances

As in other waters, the concentrations of acetone, acetaldehyde and formaldehyde determined in the Elbe estuary generally remained at about 1 μg l⁻¹ (Takami et al. 1985, van Hoof et al. 1985, Whittle & Rennie 1988). These concentrations were in the same range as those detected in the laboratory experiments under both anaerobic and aerobic conditions. By exclusion of other factors described in the literature, the release of dissolved organic substances from the 1 mm seston layer was produced during the laboratory experiments by microbial processes coupled with the degradation of organic matter (Otsuki & Hanya 1972, Mague et al. 1980, Kieber & Mopper 1987, Nagata & Kirchman 1991). For the above mentioned DOC compounds the constantly low concentrations indicate that consumption was adapted to production and that there was no undetected source of DOC formation in either the field or laboratory studies (Billen et al. 1980, Sundh 1992).

Pyruvate and glyoxylate increased in the laboratory experiments when anaerobic conditions were initiated. In the field, no net production of pyruvate was detected even in regions of the Elbe estuary where oxygen concentrations were below 3 mg O₂ l⁻¹. Thus, in the field, high consumption rates may have masked an increased production of pyruvate under reduced oxygen conditions. In contrast, glyoxylate concentra-

tions along the Elbe estuary were inversely correlated with O_2 but not correlated with chl *a* concentrations. Previous studies have indicated that glyoxylate is synthesized and released by algae during photorespiration (Aaronson 1978, Bjørnsen 1988). Therefore, algal production of glyoxylate is found at high oxygen and low CO_2 concentrations and is favoured by an increase in radiation and temperature (Stewart & Codd 1981). The observed production of glyoxylate in the Elbe must be explained by the formation of acetate, under low oxygen concentrations, as an end product of fermentation (Michelson et al. 1989) and the subsequent production of glyoxylate by bacteria living on acetate as the organic substrate (Schlegel 1992). A significant input of glyoxylate apart from that produced by phytoplankton activities in the water column of the New York Bight (USA) apex was also assumed by Edenborn & Litchfield (1987). They found that at elevated temperatures glyoxylate uptake and turnover by heterotrophic bacteria exceeded the estimated production by phytoplankton.

Accumulation of glycolaldehyde

In the present investigation, glycolaldehyde was the only organic substance which, after release, remained quite unaffected by biochemical attack. The formation of glycolaldehyde depended on the anaerobic degradation of a specific organic matrix but was independent of the nitrate-based respiration rates. Likewise, anaerobic sediments from the Elbe estuary exhibited practically no capacity for accumulating glycolaldehyde (Edelkraut 1994). We postulate the formation and release of glycolaldehyde in a Strickland reaction that includes oxidative desamination of serine to 2-oxo-3-hydroxy-propionic acid with a subsequent decarboxylation (McInerney 1988). This possible fermentation pathway, in which amino acids are used both as terminal electron acceptors and donors, could explain the dependency of the formation of glycolaldehyde both on the oxygen concentrations and on the specific nature of the organic matter.

Using glycolaldehyde as an indicator, anaerobic degradation was detectable in the open waters of the Elbe estuary. From nitrite concentrations, which significantly correlated with glycolaldehyde, it has been concluded that nitrate is the terminal electron acceptor in the anaerobic processes (Betlach & Tiedje 1981). Coupled to these processes, there was an increase in the ammonium concentrations which could lead to nitrification within seston aggregates at a maximum rate amounting to at least 45 to 74 % of the total oxygen consumption, a process which is otherwise limited to 20 % by the dissolved ammonium concentrations in the Elbe estuary (Kerner et al. 1995).

Dynamics in POC degradation

Middelburg (1989) reviewed studies on early microbial degradation of marine detritus and described degradation as starting with an initial adaptation of no reactivity followed by high rates and a linear decrease with time. Similarly, HOC started in the seston layer about 20 h after aggregation; rates a maximum reached after approximately 70 h and decreased to minimum values after about 150 h. These dynamics in the degradation rates were followed by a decrease in organic C and chl *a* content and are explained by changes in the biological availability of the organic matter (Canfield 1994). However, the same organic matter that resisted oxic degradation was mineralized with nitrate as the terminal electron acceptor over a period of more than 200 h at rates of between 40 and 70 % of the maximum aerobic values. Furthermore, seston of different biochemical composition, sampled from the same region of the Elbe estuary as the 'aged' material used during the experiments, exhibited very similar anaerobic reactivities. These findings indicate that degradation under suboxic environmental conditions is less dependent on easily degradable organic matter than is aerobic degradation. Recently Kerner (1993) showed that anaerobic microbial respiration processes in sediments depended on organic matter of low molecular weight which is produced during fermentation. That DOC might have an important impact on the nitrate respiration in the aggregated seston was shown by the net production of some low molecular weight organic substances which were observed during anaerobic incubation. Fermentation processes are known to have a high potential for decomposing highly refractory organic matter and, thus, would account for the constancy of heterotrophic nitrate respiration rates in the seston as described above.

Moreover, low molecular weight DOC compounds formed during anaerobic decomposition are consumed aerobically when both aerobic and anaerobic layers are in close contact. This is true for seston aggregates, and anaerobic net production of DOC might enhance oxygen consumption rates, which in turn would reduce the thickness of the aerobic layer. That aerobic degradation is enhanced by anaerobic processes in the field is also suggested from O_2 microprofiles in sediment surface layers where oxygen consumption rates were found to increase with depth, with highest rates at the anaerobic/aerobic interface (Kerner & Gramm 1995).

CONCLUSIONS

Our laboratory and field experiments have shown that, within aggregating seston, oxygen respiration is

controlled by the availability of easily degradable organic matter and undergoes changes within hours. In contrast, anaerobic nitrate respiration remains unaffected by the composition of the organic matter and degradation occurs at high rates even in seston refractory to aerobic degradation. Anaerobic conditions within seston aggregates of ≤ 2 mm diameter are produced both by nitrification and oxygen respiration. Nitrification accounts for the total oxygen consumption early after formation of seston aggregates and after about 120 h, both points at which aerobic heterotrophic processes are inhibited by a lack of organic substrates. The production of low molecular weight DOC compounds exceeds consumption only under anaerobic conditions. DOC produced in anaerobic layers of seston aggregates that diffuses into the aerobic layers might significantly enhance oxygen respiration rates. Glycolaldehyde was the only DOC compound under investigation found to resist degradation processes and can be used as an indicator of anaerobic processes in natural open waters.

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