Organic matter degradation in the deep sea:
results from sediment trap studies and surface sediment sampling

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Niko Lahajnar
aus Hamburg

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Prof. Dr. Venugopalan Ittekkot

und   Dr. Martin G. Wiesner

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Prof. Dr. H. Schleicher

Dekan

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Abstract

The oceans play a key-role in global evolution and modern biogeochemical processes. They comprise the earth's largest reservoir of elements and closely interact with the atmosphere, biosphere, and surface lithosphere. As all elements virtually pass through the marine system at some point in their cycles, studies of transport mechanisms across the ocean boundaries and compound specific fluxes within the water column are one of the prerequisites to understand biogeochemical cycles. Major efforts have been undertaken to elucidate organic matter cycling in the deep sea as, for instance, downward particulate organic matter fluxes represent the only effective way of removing biologically fixed CO_2 from the atmosphere. To date, the most effective way of measuring particle fluxes in the ocean is to deploy sediment traps as they provide data on both the magnitude and composition of organic matter fluxes.

Here, four studies from five deep-sea areas have been combined in order to record the amount of transported material as well as to understand the mechanisms of organic matter transport and degradation in the ocean's interior. These studies encompass samples from a marginal sea of the Pacific Ocean (South China Sea - SCS), tropical sites in the northern Indian Ocean (Arabian Sea and Bay of Bengal), low-productivity areas such as the eastern Mediterranean Sea and temperate zones in the northeast Atlantic Ocean. All investigations have used long-term particle flux data obtained from bottom-tethered sediment traps and surface sediment samples. Special emphasis has been laid on evaluating organic matter degradation by analysing nitrogen-bearing organic matter (amino acids and hexosamines). Studies on early diagenetic alteration have been performed by using broad amino acid spectra that have been linked to stable isotope ratios of bulk nitrogen ($\delta^{15}N$). In addition, organic matter fluxes have been related to dissolved organic carbon (DOC) fluxes at the sediment-water-interface of deep-sea sediments in the Indian and Atlantic Ocean thus describing an important link during early diagenesis of organic compounds.

Particle flux studies in the northern, central and southwestern part of the SCS represent the first long-year and basin-wide particle flux investigations conducted in this area. In the northern and central part annual bulk fluxes were in the order of 70 to 125 mg m^{-2} d^{-1}, organic matter and amino acid fluxes follow the trend of bulk material. Flux rates were higher during the NE and SW monsoon than during the intermonsoons. However, bulk and organic matter *compositions* were not markedly susceptible to seasonal changes implying that

the increase in productivity during the monsoons does not lead to substantial organic matter changes. Organic matter degradation in the deep SCS deduced from amino acid spectra are highest compared to other tropical and monsoon-influenced regions.

During the study period two strong El Niño/Southern Oscillation (ENSO) events occurred in 1987/88 and 1998/99, respectively. Higher than normal sea surface temperatures associated with low wind speeds led to reduced particle fluxes in the central basin as well as enhanced organic matter degradation as discerned by amino acid analyses. It turned out that particularly proteinogenic basic amino acids, above all histidine, trace organic matter degradation in sediment trap samples and surface sediments. Most-likely, El Niño conditions also suppressed winter upwelling and subsequent (potentially) stimulated downward organic matter fluxes in the northeastern SCS off Luzon. At the same time annual particle fluxes in the southwestern part along the central coast off Vietnam exceeded 240 mg m^{-2} d^{-1} with short-term flux peaks above 500 mg m^{-2} d^{-1}; however, bulk particle composition and compound specific analyses point to severe mixing with laterally advected material from the adjacent continental margin. Thus, measured seasonal flux patterns along the Vietnamese coastline rather reflect resuspension caused by physical oceanographic processes than upwelling-induced enhanced productivity.

Surface water processes also play an important role in the eastern Mediterranean Sea off Crete. δ^{15}N values between 1.2 and 2.5 ‰ - close to atmospheric ratios - in sinking particulate organic matter indicate a hydrological shift in the 1990s accompanied by plankton community alteration to predominating N$_2$-fixing diazotrophs. Preferential remineralisation of light nitrogen leads to increasing δ^{15}N values in settling particles in the water column. These findings are important basic information to explain food-chain structures. For instance, studies on mesozooplankton assemblages, feeding on particulate matter, from shallow (700 m) and deep (2700 m) waters document an increasing length of the food chain with increasing water depth.

Biogeochemical and isotopical alteration of organic matter has also been investigated in the northern Indian Ocean (Arabian Sea and Bay of Bengal). The influence of land-derived (riverine) material in coastal areas and dinitrification processes in some parts of the open ocean are responsible for a wide range of δ^{15}N values (<4 ‰ in the northern Bay of Bengal, ~8 ‰ in the equatorial open ocean and >11 ‰ in the central Arabian Sea) in sedimentary organic matter. Isotopic nitrogen ratios from long-term sediment trap deployments reveal an isotopic shift of about 2-3 ‰ between sinking particles in the deep water column (500-1000 m above ground) and surface sediments, indicating preferential

utilisation and remineralisation of light nitrogen. The isotopic enrichment of residual nitrogenous organic matter in open-ocean sediments significantly correlates with the degree of degradation as discernable from amino acid spectra. This relationship between organic matter alteration and isotopic signature has to be taken into account for paleoceanographic and paleoclimatological interpretations.

Organic matter remineralisation rates at the sediment-water-interface have been quantified in surface sediments from the Arabian Sea and NE Atlantic Ocean. Dissolved organic carbon concentrations have been measured in bottom waters and in the underlying upper 10 cm of deep-sea sediments. About 21 - 25 % of sedimenting particulate organic carbon is converted to DOC, the majority (up to 75 %) is respired to CO_2, and only 2.5 - 6 % is buried. The conversion from solid to dissolved constituents leads to DOC concentrations between 509 and 1526 µmol L^{-1} with maximum values occurring in the uppermost sediment horizon. In contrast to the sediments, DOC concentrations in bottom waters are one magnitude lower (47 - 122 µmol L^{-1}). This leads to a gradient-controlled benthic DOC flux from the sediments into the ambient bottom waters. Calculated DOC flux rates between 47 and 224 µmol m^{-2} d^{-1} are highly correlated to annual vertical particulate organic carbon fluxes derived from sediment trap deployments and thus appear to be a function of regional productivity. Based on this assumption DOC flux rates of 70 - 103 x 10^{12} g y^{-1} for the entire deep-sea (>2000 m) have been calculated which is the first global estimate. Including shelf and continental margin areas, marine sediments release about 260 x 10^{12} g DOC y^{-1} and thus represent an important potential source of DOC in the oceans.

Zusammenfassung

Die Ozeane sind für die Entstehungsgeschichte der Erde von zentraler Bedeutung, spielen aber ebenso bei den biogeochemischen Prozessen der Gegenwart eine elementare Rolle. Sie stellen das weltweit größte Reservoir für die meisten Elemente und chemischen Verbindungen dar und sind dabei eng mit der Atomsphäre, Biosphäre und Oberflächen-Lithosphäre verknüpft. Da fast alle Stoffe während ihres Kreislaufs das marine Milieu durchlaufen, ist es für das Verständnis von biogeochemischen Zyklen eine Grundvoraussetzung, die Stoffflüsse innerhalb der Ozeane und deren Transportmechanismen über ihre Grenzen hinweg zu verstehen. Es wurden und werden daher unter anderem umfangreiche Forschungsprojekte mit dem Ziel durchgeführt, den Kreislauf von organischem Material in der Tiefsee zu erforschen, da zum Beispiel das vertikale Absinken von partikulären organischen Verbindungen die einzig effektive Möglichkeit darstellt, biologisch umgesetztes CO_2 der Atmosphäre zu entziehen. Eine der effektivsten Möglichkeiten, den Partikelfluss in den Ozeanen zu untersuchen, ist der Einsatz von am Meeresgrund verankerten Sinkstofffallen, denn sie geben sowohl Auskunft über das Ausmaß als auch über die Zusammensetzung der organischen Partikelflüsse.

Die vorliegende Arbeit setzt sich aus vier Veröffentlichungen zusammen, die insgesamt fünf Tiefseegebiete mit dem Ziel beschreiben, den Transport von partikulärem organischen Material zu quantifizieren und die dabei ablaufenden Abbauprozesse in der Tiefsee besser zu verstehen. Die Veröffentlichungen bestehen aus einer Studie über ein pazifisches Randmeer (Südchinesisches Meer), tropenbeeinflusste Gebiete im nördlichen Indischen Ozean (Arabisches Meer und Bucht von Bengalen), Niedrigproduktivzonen wie z.B. das östliche Mittelmeer und gemäßigte Regionen im nordöstlichen Atlantik. Alle Forschungsergebnisse basieren auf langjährigen Partikelflussaufzeichnungen sowie auf Proben aus Oberflächensedimenten. Besonderer Schwerpunkt wurde in diesem Zusammenhang auf den Abbau von organischem Material anhand stickstoffhaltiger Verbindungen (Aminosäuren und Aminozucker) gelegt. Dabei wurde die Degradation und die diagenetische Veränderung mittels Aminosäurespektren beschrieben und mit Ergebnissen stabiler Stickstoffisotope ($\delta^{15}N$) verknüpft. Zusätzlich wurde im Indischen und Atlantischen Ozean der Transport des absinkenden organischen Materials mit den Flüssen von gelöstem organischen Kohlenstoff an der Sediment-Wasser-Grenzschicht in Beziehung gesetzt und damit ein wichtiger Abbauvorgang organischer Verbindungen quantifiziert.

Die Untersuchungen von Partikelflüssen im nördlichen, zentralen und südwestlichen Teil des Südchinesischen Meeres sind die ersten beckenweiten Langzeitstudien in diesem Gebiet. Im nördlichen und zentralen Teil beläuft sich der Partikelfluss dabei auf 70 bis 125 mg m^{-2} d^{-1}, wobei die Flüsse des organischen Materials (Aminosäuren) diesen Trend nachzeichnen. Die Flussraten sind im Allgemeinen während des Nordost- bzw. Südwestmonsuns höher als während der Intermonsunphasen, die Zusammensetzung des partikulären Materials hingegen zeigen keinen deutlichen saisonalen Unterschied, was darauf schließen lässt, dass die Monsune keinen entscheidenden Einfluss auf die Zusammensetzung des Materials haben. Der anhand von Aminosäuren bestimmte Abbaugrad des organischen Materials im Tiefenbereich des Südchinesischen Meeres ist im Vergleich zu allen anderen tropischen und Monsun beeinflussten Untersuchungsgebieten am größten. Während des Beprobungszeitraums kam es zu zwei stark ausgeprägten El Niño Ereignissen in den Jahren 1987/88 und 1998/99. Höhere Wasseroberflächentemperaturen einhergehend mit geringen Windgeschwindigkeiten führten zu einem verringerten Partikelfluss im zentralen Becken sowie zu einem generell höheren, mittels Aminosäuren bestimmten Abbaugrad des organischen Materials. Dabei stellte sich heraus, das besonders die proteinogenen basischen Aminosäuren, allen voran Histidin, den Abbau des Materials in den Sedimentfallen und Oberflächensedimenten gut widerspiegelten. Höchstwahrscheinlich führten die El Niño Bedingungen auch zu einer Unterdrückung des Wasserauftriebs und damit potentiell erhöhten vertikalen Flussraten von organischem Material im nordwestlichen Teil vor der Küste Luzons. Zur gleichen Zeit betrug im südwestlichen Teil entlang der zentralvietnamesischen Küste die mittlere Partikelflussrate über 240 mg m^{-2} d^{-1} mit kurzzeitigen Flussimpulsen von über 500 mg m^{-2} d^{-1}. Die Zusammensetzung des aufgefangenen Materials lässt hierbei aber den Rückschluss zu, dass es in dieser Region zu einer beträchtlichen Vermischung mit lateral advektiertem Material vom Kontinentalhang kommt. Daher sind die gemessenen Partikelflüsse - aufgrund von ozeanographischen Randbedingungen - zum erheblichen Teil ein Ausdruck wieder in Suspension gebrachten Sediments und nicht die Folge einer durch Auftrieb induzierten erhöhten Produktivität.

Oberflächenprozesse spielen auch im östlichen Mittelmeer vor Kreta eine wichtige Rolle. Stickstoffisotopenverhältnisse (δ^{15}N) im absinkenden partikulären organischen Material zwischen 1,2 und 2,5 ‰ - Werte nahe dem atmosphärischen Standard - lassen auf eine hydrologische Veränderung in den 1990iger Jahren in Verbindung mit einer Änderung der Planktonzusammensetzung hin zu diazotrophen Stickstofffixierern schließen. Die

bevorzugte Remineralisierung von leichtem Stickstoff führt zu einem Anstieg von $\delta^{15}N$-Werten im absinkenden Material der Wassersäule. Diese Ergebnisse stellen dabei eine wichtige Grundlage dar, um die Struktur der Nahrungskette zu verstehen. In dieser Studie - basierend auf Mesoplanktongruppen aus 700 bzw. 2700 m Wassertiefe, die das partikuläre absinkende Material als Nahrungsquelle verwenden - wird aufgezeigt, dass hierbei die Verlängerung der Nahrungskette mit zunehmender Wassertiefe zu beobachten ist.

Biogeochemische und isotopische Veränderung des organischen Materials wurde auch im nördlichen Indischen Ozean (Arabisches Meer und Bucht von Bengalen) erforscht. Der Eintrag von Landmaterial durch Flüsse in die Küstenregionen sowie Abbauprozesse in einigen Teilen des offenen Ozeans führen zu einer großen Bandbreite an $\delta^{15}N$-Werten in den Sedimenten (<4 ‰ im nördlichen Teil der Bucht von Bengalen, ca. 8 ‰ im äquatornahen offenen Ozean und >11 ‰ im zentralen Arabischen Meer). Die Isotopenverhältnisse der Proben aus Langzeitverankerungen zeigen einen Anstieg der Isotopensignatur von etwa 2-3 ‰ zwischen absinkendem partikulären Material in tiefen Wasserschichten (500-1000 m über Meeresgrund) einerseits und den darunter liegenden Oberflächensedimenten andererseits, was für einen bevorzugten Abbau von leichtem Stickstoff spricht. Die Anreicherung mit schwerem Stickstoff im verbleibenden stickstoffhaltigen organischen Material im offenen Ozean korreliert deutlich mit seinem Abbaugrad, was anhand der Aminosäurespektren aufgezeigt werden konnte. Diese Beziehung zwischen dem Abbau organischen Materials und der Isotopensignatur stellt einen wichtigen Aspekt für die paläoozeanographische und paläoklimatologische Rekonstruktion dar und muss bei deren Interpretationen berücksichtigt werden.

Der Abbau von organischem Material an der Sediment-Wasser-Grenzschicht konnte in den Oberflächensedimenten des Arabischen Meeres und des Nordost-Atlantiks quantifiziert werden. Dafür wurden Konzentrationen gelösten organischen Kohlenstoffs (*Dissolved Organic Carbon* - DOC) im Bodenwasser und den ersten 10 cm von Tiefsee-Sedimenten gemessen. Es stellte sich heraus, dass ca. 21-25 % des eingetragenen partikulären organischen Kohlenstoffs in gelösten Kohlenstoff umgewandelt werden, der Großteil (bis zu 75 %) jedoch zu CO_2 abgebaut wird und dass nur 2.5 - 6 % tatsächlich langfristig im Sediment eingelagert werden. Die Umsetzung von festen zu gelösten Verbindungen führt zu DOC Konzentrationen zwischen 509 und 1526 μmol L^{-1}, wobei die höchsten Konzentrationen in der obersten Sedimentschicht auftreten. Im Gegensatz zum Sediment sind die DOC-Konzentrationen im darüber liegenden Bodenwasser eine Größenordnung geringer (47-122 μmol L^{-1}). Diese Tatsache führt zu einer durch das Konzentrationsgefälle gesteuerten

Abgabe von DOC aus dem Sediment in das Bodenwasser. Die berechneten DOC-Flussraten von 47 bis 224 µmol m^{-2} d^{-1} zeigen dabei einen deutlichen Zusammenhang zu dem durch Sedimentfallenverankerungen ermittelten Jahresmittelfluss an vertikal eingetragenem partikulären organischen Kohlenstoff und stellen somit ein Abbild der regionalen Produktivität dar. Basierend auf dieser Annahme konnten DOC-Flussraten von 70-103 x 10^{12} g y^{-1} für die gesamte Tiefsee unterhalb 2000 m Wassertiefe errechnet werden - die erste globale Abschätzung überhaupt. Unter Mitberücksichtigung der Schelf- und Kontinentalhanggebiete emittieren marine Sedimente ca. 260 x 10^{12} DOC pro Jahr und agieren daher als eine wichtige potentielle Quelle für DOC in den Ozeanen.

1. Introduction

The oceans cover about 71 % of the earth's surface and thus comprise the largest reservoir for most elements. The field of *Marine Biogeochemistry* attempts to merge the achievements from physics, chemistry, biology, geology and oceanography in order to elucidate the cycling of elements and chemical compounds in the ocean. It soon became obvious that the marine system plays a key role for global processes in the past, present and future as it is intimately interconnected with the atmosphere and solid earth. In this regard, surface processes in the euphotic zone (approximately the top 50-200 m) impact the ocean's interior and even strongly affect the biogeochemistry of surface sediments in the deep sea. These diverse pools are linked by the transport of inorganic nutrients and organic matter through the water column. Transportation is mainly achieved by three processes: (1) physical sinking and rising of water masses as stated by the concept of the global ocean conveyor (e.g., Broecker, 1991); (2) active vertical migration of zooplankton and micronekton causing (downward) transport of organic matter (e.g., Hays et al., 1997; Hidaka et al., 2001) and (3) an ubiquitous gravitational settling of particulate matter, mostly heterogeneous aggregates (marine snow), from surface waters to the deep ocean (e.g., Alldredge and Silver, 1988; Eppley and Peterson, 1979; Falkowski et al., 2003; McCave, 1975; Wakeham and Lee, 1989). For instance, the export of biogenically fixed organic carbon to the ocean's interior - also named biological pump - is of special importance as it removes CO_2 from the atmosphere (Fig. 1) - a direct impact on the climate of the earth. Since organic matter is initially composed of an average stoichiometrical proportion of major elements (i.e., carbon, nitrogen, phosphorus, see Redfield, 1934; Redfield et al., 1963) and according to this dependent on the availability of biolimiting elements such as nitrogen and phosphorus, downward organic matter fluxes also lead to nutrient drawdown to deeper water levels and thus have a profound influence on the biogeochemistry of the deep-sea environment.

However, downward organic matter fluxes exponentially decrease with water depth (e.g., Martin et al., 1987). Thus, only a minor fraction of organic matter being transported to the deep sea is ultimately incorporated into the seabed and therefore removed from an active, short-term cycle; the vast majority is consumed and decomposed (by herbivorous zooplankton) or degraded (by bacteria) prior to final burial (e.g., Tréguer et al., 2003). In terms of carbon, the amount of primary production in surface waters is in the order of 50 - 60 Pg (1 Petagram = 10^{15} g) (Field et al., 1998), the export flux of
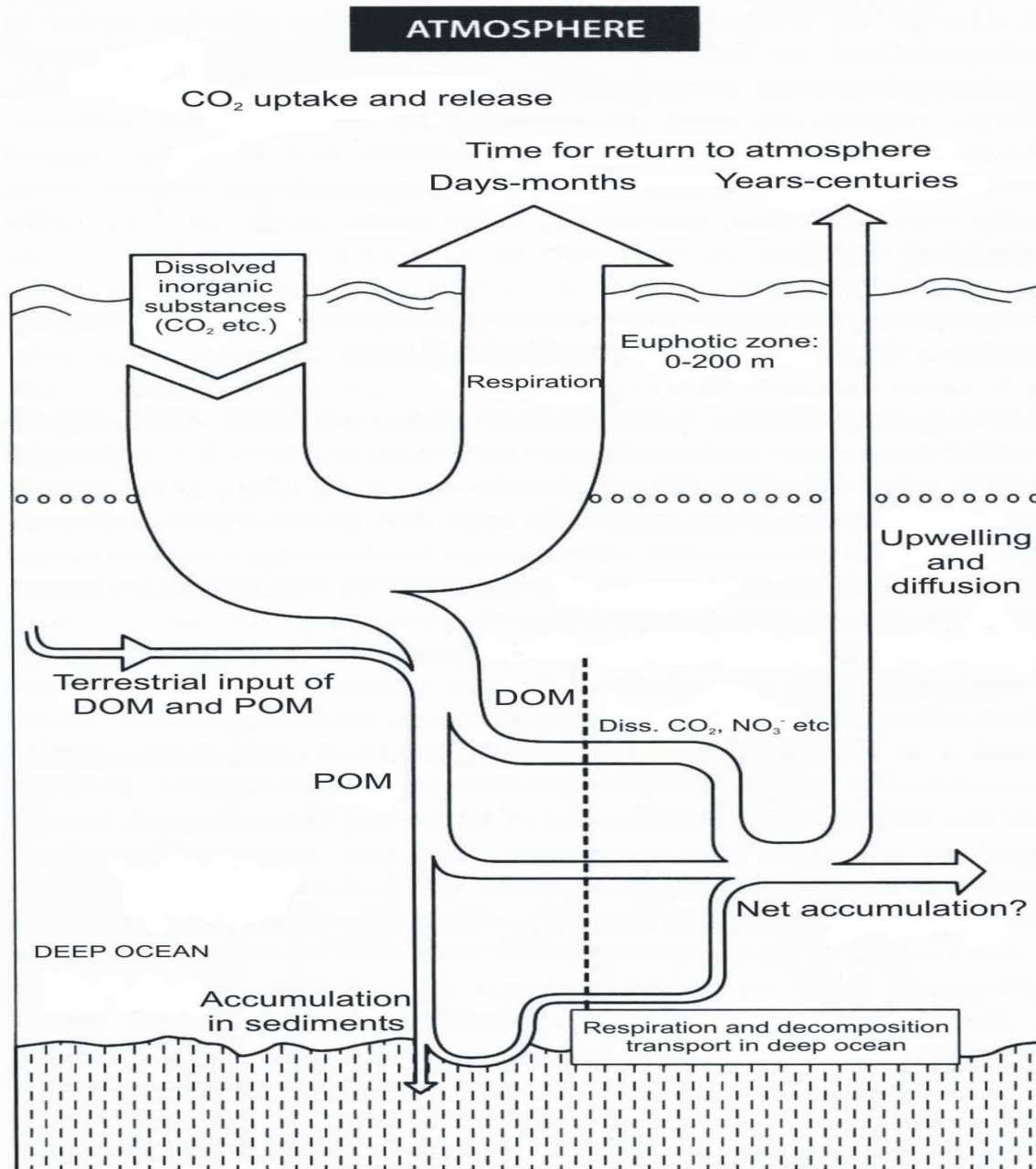
Fig. 1: A classical view of organic matter transport in the ocean, slightly modified after Tréguer et al. (2003). This scheme first shows how biologically fixed organic matter in the surface layer is potentially transported to the deep sea and to the underlying sediment. It also shows that only a very minor fraction of particulate organic matter (POM) is ultimately buried in deep-sea sediments and thus removed from the short-term (days-centuries) biogeochemical cycle (in contrast to the long-term geological cycle). Most of vertically settling particles are decomposed to dissolved organic matter (DOM) and eventually respired to inorganic substances.

particulate organic carbon, i.e. organic carbon which leaves the euphotic zone, is in the order of 10 - 16 Pg y^{-1} (Falkowski et al., 2003; Schlitzer, 2002) - about 20 % of the annual primary production. On a global scale the initial export flux is reduced to 0.34 - 0.40 Pg C y^{-1} at 1000 -2000 m water depth (Jahnke, 1996; Lampitt and Antia, 1997), indicating intense organic matter decomposition during the vertical transfer through the upper part of the ocean. Most of the remaining material is eventually decomposed at the sediment-water interface and released

to the water column, completing the short-term (days to centuries) biogeochemical cycle (Fig. 1). No more than about 0.16 Pg C y^{-1} escapes remineralisation and becomes ultimately buried in marine sediments (Bender and Heggie, 1984; Berner, 1982; Emerson et al., 1985; Hedges and Keil, 1995). This is less than 0.1 % of total produced organic matter in the surface ocean which may be permanently stored in the deep sea on a geological time-scale (Berger et al., 1989; Emerson and Hedges, 1988).

Long-year multidisciplinary research campaigns at various deep-sea sites have documented that biogeochemical pathways of organic matter alteration and turn-over rates in the deep ocean not only depend upon the magnitude of transported particulate organic matter, but also on the nature and composition of exported material. It became obvious that instead of having a unifying theory organic matter fluxes and preservation represent a multivariate problem (Pedersen, 1995). Therefore, we require solid and comprehensive information on the quantity *and* quality of organic matter in deep-sea environments.

To date, the direct and hence one of the most promising ways to study organic matter fluxes in the ocean is to deploy bottom-tethered sediment traps in the water column. They collect sinking particulate material at a defined water depth within a programmed time schedule (e.g., Honjo and Doherty, 1988). However, the correctness of absolute flux values ("trapping efficiency") is still being discussed due to the hydrodynamic impact on fluxes and the activity of zooplankton entering the trap ("swimmers") (e.g., Baker et al., 1988; Gardner and Zhang, 1997; Gust et al., 1996; Yu et al., 2001). Albeit potential biases of absolute flux rates, the trapped material - after successful retrieval - can be biogeochemically analysed for any desired variable and therefore provides an invaluable insight into the composition of settling particles. In combination with biogeochemical, atmospheric and oceanographic data from the sea surface - to an increasing degree derived from remote sensing (satellite) data - as well as in conjunction with surface sediment samples obtained from box-corers, gravity-corers or multicorers (e.g., Barnett et al., 1984), the cycling and fate of particles can be illustrated in deep-sea environments. The sediment traps thereby supply the link between deep-sea sediments and the more easily accessible surface ocean, thus making degradational processes and lateral transport mechanisms palpable.

Particle flux studies carried out since the 1980s have considerably improved our knowledge of sedimentation processes, organic matter degradation and element cycling; however, published and accessible data are still limited for

most of the oceanic regions due to the enormous financial and logistic efforts required to perform long-term surveys.

After successful sampling, how can we assess organic matter cycling and degradation in a deep marine environment? Organic matter substantially consists of amino acids as they are the basic components of enzymes and proteins and thus ubiquitously present in organic substances. Moreover, most of organic nitrogen-bearing compounds are made of amino acids so that special emphasis has been laid on organic matter alteration inferred by amino acid spectra. Amino acids are easily metabolisable but also sensitive to degradation and therewith represent an excellent indicator of early diagenetic processes as well as a diagnostic value of diagenetic stages (e.g., Dauwe et al., 1999; Degens and Mopper, 1976). The total amount and the relative concentrations of single amino acid spectra are thus powerful tools in the field of marine biogeochemistry.

In addition, the ratio of heavy to light stable nitrogen isotopes (δ^{15}N) in organic matter deciphers dissimilatory transformation processes (nitrification, denitrification) that are associated with isotopic fractionation and therefore records changes in nutrient dynamics and diagenetic effects of organic matter alteration (e.g., Altabet, 1996). Moreover, organic matter fluxes and degradation from sediment trap investigations can be compared to fluxes of dissolved organic carbon (DOC) release from surface sediments and hence describe the transition from particulate to dissolved organic substances, an important step during organic matter decomposition.

In this thesis organic matter degradation in the deep sea is investigated by sediment trap studies from the Northeast Atlantic, the eastern Mediterranean Sea, the northern Indian Ocean and the western Pacific (South China Sea). It is combined with the biogeochemistry of the water column and the sediment-water-interface. The thesis is compiled from four scientific papers, one submitted and three published between 2003 and 2005. They merge long-year sediment trap records with surface sediment data from various deep-sea regions (Fig. 2). All of them illustrate organic matter fluxes and degradational processes in the deep sea. Three publications are mainly focused on tropical, monsoon-influenced regions, and two of them deal with sub-tropical to temperate climate.

Publication 1 "Fluxes of amino acids and hexosamines to the deep South China Sea" has been submitted to *Deep-Sea Research I* in November 2005. It describes for the first time long-year and basin-wide flux studies on labile organic particulate matter in the South China Sea (Fig. 2). It is mainly focused on flux
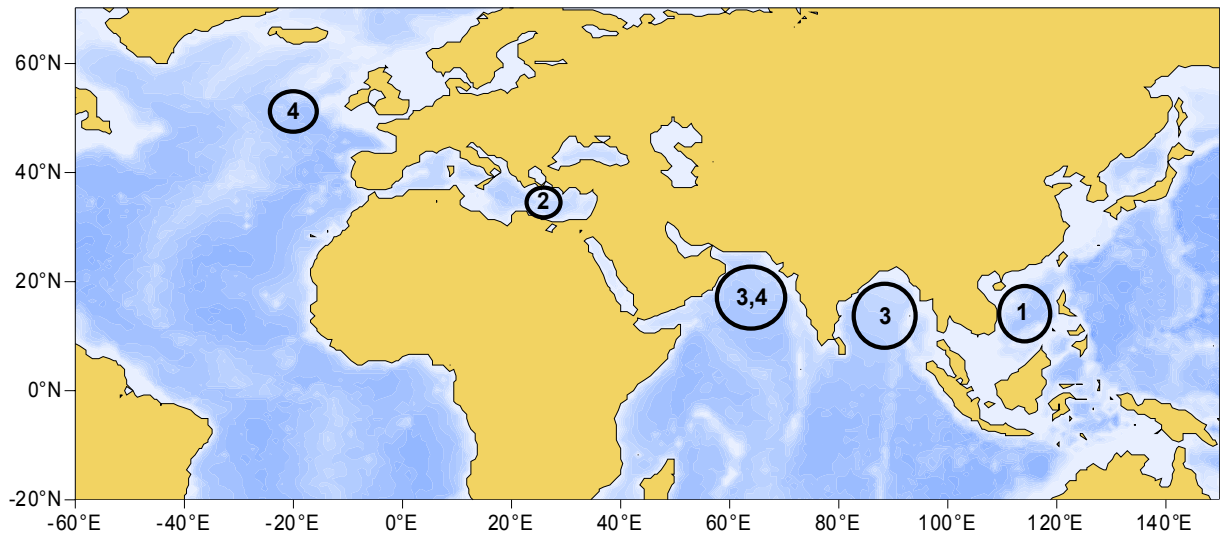
Fig. 2: Study areas and their appearance in the publications. The numbers denote the publications mentioned in this introduction.

variations, both quantitatively and qualitatively, that are related to the influence of the monsoons and to the El Niño phenomenon and their reflection in organic matter quality as evident from biogeochemical indicators based on amino acids.

Publication 2 "Vertical distribution of mesozooplankton and its δ^{15}N signature at a deep-sea site in the Levantine Sea (eastern Mediterranean) in April 1999" was published in *Journal of Geophysical Research* in September 2003. It deals with δ^{15}N ratios of particulate organic matter in the deep eastern Mediterranean Sea (Fig. 2) and its effect on zooplankton communities.

Publication 3 "Stable nitrogen isotopic ratios of sinking particles and sediments from the northern Indian Ocean" has been published in *Marine Chemistry* in September 2005. It focuses on organic matter degradation and its influence on the preservation of primary δ^{15}N signals by comparing sediment trap samples and surface sediments in the Arabian Sea and Bay of Bengal (Fig. 2). The degradational state of nitrogenous organic matter is derived from amino acid spectra.

Publication 4 "Dissolved organic carbon (DOC) fluxes of deep-sea sediments from the Arabian Sea and NE Atlantic" has been published in *Deep-Sea Research II* in July 2005. Here the transformation of particulate organic carbon to dissolved organic carbon in deep-sea sediments are described. Measured dissolved organic carbon concentrations in surface sediments have been used to calculate DOC flux rates from the sediments to the deep water column. The coupling between vertical particle flux rates and DOC effluxes at the sediment

water interface is documented and DOC flux estimates for the entire deep sea (>2000 m) are provided for the first time.

Publication 1:

Fluxes of amino acids and hexosamines to the deep South China Sea

N. Lahajnar, M. G. Wiesner, B. Gaye

submitted to *Deep-Sea Research I*

Fluxes of amino acids and hexosamines to the deep South China Sea

N. Lahajnar[a,*], M. G. Wiesner[a], B. Gaye[a]

[1]*Institut für Biogeochemie und Meereschemie, Universität Hamburg, Bundesstraße 55, D-20146 Hamburg, Germany*

Abstract

Settling particles collected by sediment traps deployed between 1987 and 1999 inside and outside the major upwelling centers of the South China Sea (SCS) were analysed to study seasonal, interannual and spatial variations in the composition and flux of labile particulate matter. The results were combined with remote-sensing and surface sediment data in order to describe the factors controlling the preservation or organic matter en route from the upper ocean to the seafloor. Amino acid (AA) and hexosamin (HA) fluxes range from 0.2 to 10.4 mg m^{-2} d^{-1} and 0.06 to 0.41 mg m^{-2} d^{-1}, respectively. Flux patterns are distinctly bimodal, closely following the fluxes of total particulate matter and maximize during the main phases of the SW and NE monsoons with rates up to three times higher compared to the intermonsoon phases. Notably, this seasonality is not seen in the composition and content of AA and HA implying that the monsoons with higher wind speeds do not lead to distinct changes in the upper water column. Organic matter degradation parameters discerned from amino acid spectra indicate intense early diagenetic alteration in the deep SCS leading to the highest decomposition rates compared to other monsoonal oceans such as the Arabian Sea and the Bay of Bengal. Probably, enhanced degradation is due to partly missing ballast material and the dissolution of bulk carbonate below the lysocline or carbonate compensation depth (CCD).

The central station recorded particle fluxes under strong El Niño (El Niño / Southern Oscillation - ENSO) conditions in 1998/99 which resulted in a reduced seasonal variability. The long-term particle record in the central basin also shows that increased organic matter degradation took place during the ENSO warm phase compared to ENSO-free conditions. Particularly proteinogenic basic amino acids seem to be susceptible to decomposition during ENSO periods. In this context the amino acid histidine also traces organic matter degradation in trap samples and surface sediments. Our study shows that bulk AA contents are significantly depleted in surface sediments (around 1 mg/g) compared to settling material (about 20 mg/g).

In addition, flux records from the northeastern station off Luzon show that temporarily occurring winter upwelling with subsequent enhanced productivity in that region is suppressed during El Niño conditions. At the same time the upwelling region along the central coast off Vietnam is characterised by pronounced seasonal flux patterns with significantly higher annual total flux rates (249 mg m^{-2} d^{-1} compared to 68 mg m^{-2} d^{-1} in the central basin) but only moderately elevated amino acid flux rates (2.9 mg m^{-2} d^{-1} vs. 1.5 mg m^{-2} d^{-1}). Bulk composition in combination with compound specific amino acid analyses strongly suggest that the region receives laterally advected material from the adjacent continental margin. Thus, seasonally varying flux rates off central Vietnam rather reflect physical oceanographic processes (i.e. changing currents along the coastline with temporarily severe resuspension of surface sediments) than upwelling-induced enhanced productivity.

1. Introduction

The relationship between production of organic matter in oceanic surface waters and its decomposition and fractionation during transit through the water column has been investigated extensively by direct measurements of vertical fluxes from sediment trap deployments in various oceanic regions (e.g., Eppley and Peterson, 1979; Haake et al., 1993b; Jahnke, 1996; Lampitt and Antia, 1997). It has been demonstrated that the quantity and quality of the organic matter arriving on the sea floor largely

*Corresponding author. Phone : +49-40-42838-7087; fax : 49-40-42838-6347

E-mail address: lahajnar@geowiss.uni-hamburg.de (N. Lahajnar)

depends on four factors: primary productivity and allochthonous particle supply, types and relative abundance of heterotrophs present, chemical composition of the particles, and the physical packaging of the particles as this determines their sinking rates (e.g., Alldredge and Silver, 1988; Asper et al., 1992; Ducklow et al., 2001; Falkowski et al., 1998; Ittekkot, 1993; Tréguer et al., 2003; Wakeham and Lee, 1989). In the euphotic zone, the major constituents of the organic matter are amino acids and hexoamines which are subject to rapid decomposition mediated by zooplankton and bacteria (e.g., Ingalls et al., 2003; Kirchman, 1992; Lee and Cronin, 1984; McClelland et al., 2003; Panagiotopoulos et al., 2002; Wakeham and Lee, 1993). Since during transit nitrogen-rich compounds are degraded faster than nitrogen-deficient components (carbohydrates and lipids), the relative abundance of amino acids and hexoamines typically decreases with increasing depth in the water column or with the ageing of the organic matter (e.g., Colombo et al., 1998; Cowie and Hedges, 1993; Degens and Mopper, 1976a; Haake et al., 1992; Keil et al., 2000; Lee and Cronin, 1984; Müller et al., 1986; Unger et al., 2005b). The release of inorganic nitrogen from remineralization of organic nitrogen compounds in turn can affect biological productivity through its role as limiting nutrient. The decomposition process can also influence the nutritional value of the particulate matter sinking to the seafloor and thus affects the growth and reproduction of benthic faunal communities.

Moreover, amino acids *per se* have different nutritive values leading to shifts in their distributions and further shifts can occur due to differences in their adsorption/desorption behaviour and resistance against degradation (e.g., Amon et al., 2001; Boski et al., 1998; Cowie and Hedges, 1992b; Dauwe and Middelburg, 1998; Hedges and Hare, 1987; Henrichs and Sugai, 1993; Lee, 1988; Sigleo and Shultz, 1993; Wang and Lee, 1993; Whelan and Emeis, 1992). The compositional modifications of amino acids and hexoamines en route and their contribution to total organic carbon and nitrogen have proved to be valuable tools for assessing the degree of organic matter degradation over a wide range of organic matter sources, sedimentation regimes and diagenetic stages (e.g., Cowie and Hedges, 1994; Dauwe and Middelburg, 1998; Degens and Mopper, 1976b; Keil et al., 2000; Whelan and Emeis, 1992). Information on the types of organisms involved in the cycling of organic matter can be obtained from the relative content and distribution of hexoamines (e.g., Haake et al., 1992; Seifert et al., 1990).

First results from time series sediment trap studies in the northern and central South China Sea (SCS) have documented that the downward flux of particulate matter displays a distinct bimodality related to the seasonality of the monsoonal climate.

In the north, the bimodal flux patterns exhibit a maximum during the NE monsoon while in the central SCS flux peaks are more prominent during the SW monsoon period (Chen et al., 1998a; Chen et al., 2002; Jennerjahn et al., 1992; Wiesner et al., 1996). This has been suggested to result from the seasonal shift in the geographic location of the wind stress maximum and hence of the site of maximal wind-driven mixing of nutrient-rich deep-waters into the surface layer. Remineralization of the organic matter was found to take place mainly in the upper few hundred meter of the water column and at the sediment-water interface (Chen et al., 1999; Chen et al., 1998b). It has been shown that one of the mechanism contributing to the preservation of amino acids in this area is entrapment in biominerals (Chen et al., 2000).

This study presents a comprehensive set of new data on the fluxes and composition of organic carbon and nitrogen-containing compounds in the SCS. The time-series covers El Niño and non-El Niño conditions and includes the upwelling areas off Luzon Island and off southeastern Vietnam as well as areas in the open SCS (Fig. 1). A comparison is made between the compositions of organic matter in settling particles at different depth levels at the sediment trap stations and in the underlying surface sediments. Results are combined with earlier data sets and remotely sensed data to describe the extent and type of transformations which detrital organic matter undergoes as it sinks from the surface waters toward the seafloor. The aim of the study is to contribute to a better understanding of the link between environmental signals produced by land-air-sea interactions in the upper ocean layer (as reflected in the initial composition of the organic matter) and those entering the sedimentary record in the deep SCS.
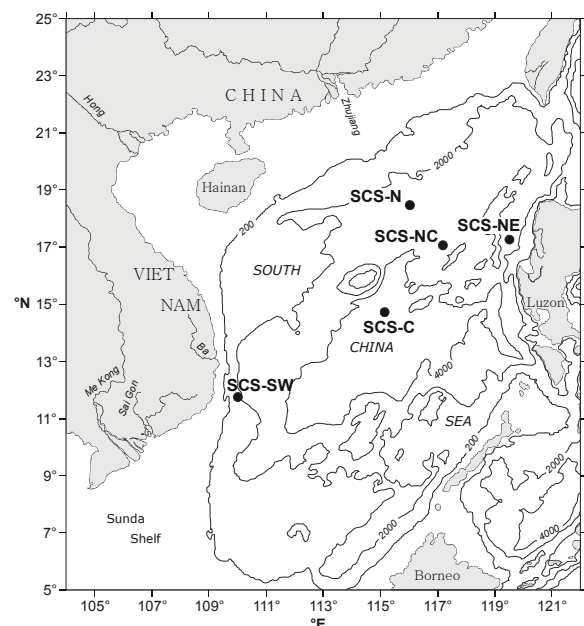

Fig. 1. Sediment trap locations in the SCS

2. Study area

The climate and hydrography in the South China Sea are primarily controlled by the East Asian monsoon system. The summer monsoon (June to August/September) is dominated by a low-pressure system over Asia, moderate (5 m s^{-1}) southwesterly winds, and high precipitation over the SCS region. The alongshore component of the winds causes cold and nutrient-rich, high-salinity water to be upwelled off southeastern Vietnam (LaFond, 1963; Wyrtki, 1961, see Fig. 2). An anticyclonic (cyclonic) gyre develops to the south (north) of the upwelling center, advecting the coastal water offshore into the central South China Sea along 12°N, collocated with a tongue of high chlorophyll concentrations (Liu et al., 2002; Wang et al., 2003; Xie et al., 2003).
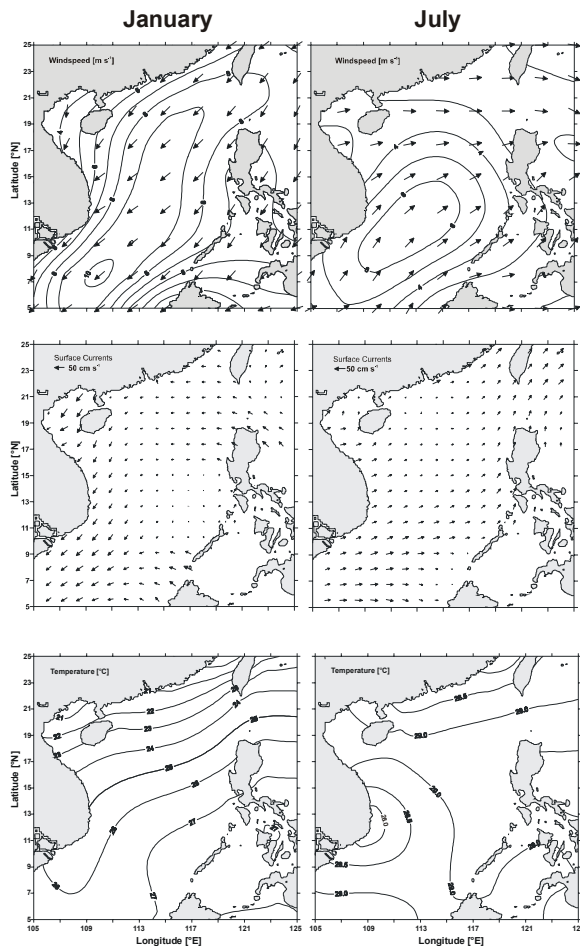

Fig. 2. Seasonally changing boundary conditions in the SCS (modified from Gerbich, 2001). Wind speed and direction, surface currents and SST distribution are shown for NE-monsoon (January) and SW-monsoon (July) phases.

The winter monsoon (October to April) is marked by high atmospheric pressure over northern Asia, strong (> 9 m s^{-1}) northeasterly winds across the SCS and enhanced precipitation in the Australasian equatorial zone. The winds force a cyclonic gyre covering the entire deep basin. Western Pacific surface water intrudes into the SCS through the Strait

of Luzon, moves along the continental slope to the south, forming a distinct tongue of low sea surface temperatures which extends to the break of the northern Sunda Shelf (Shaw and Chao, 1994; Wyrtki, 1961, see Fig. 2). When the jet impinges on the shelf break, it is uplifted due to the shoaling topography, inducing upwelling (Chao et al., 1996a; Liu et al., 2002; Shaw et al., 1996). On the east side of the SCS, off northwestern Luzon, upwelling occurs due to subsurface convergence of the northward flowing jet (Shaw et al., 1996; Udarbe-Walker and Villanoy, 2001). The two upwelling zones have been identified by their anomalously cold subsurface temperatures and high chlorophyll concentrations rather than sea surface temperatures (SST) and, as such, cannot be observed in satellite-derived SST fields; doming of isotherms occurs up to water depths of 50 m (Liu et al., 2002; Tang et al., 1999; Udarbe-Walker and Villanoy, 2001).

Outside the upwelling areas, biological productivity is largely controlled by wind-induced deepening of the mixed layer and by the formation of cyclonic (and anticyclonic) mesoscale eddies which are a constant feature of the SCS (Wang et al., 2003). Another source contributing to the nutrient and particle load is riverine discharges which display a strong seasonal signal in response to the alternating monsoons and shift in precipitation. The major supply occurs during the summer season through the rivers Mekong, Zhujiang and He (360 x 10^6 t yr^{-1} sediment discharge, Milliman and Meade, 1983). Further contributions are provided by eolian input from the loess plateaus of northern China (Fang et al., 1999) with an estimated dust deposition rate of 2.5 10^6 t yr^{-1} (Gerbich, 2001).
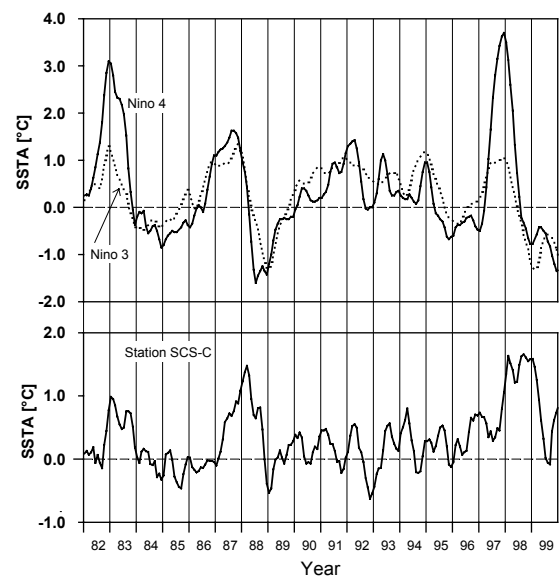

Fig. 3. Sea surface temperature anomalies (SSTAs) in the Pacific (Niño 3/4 reference region - upper part) and in the central SCS (lower part), both plotted as a five month running mean. SSTA above 1 °C are considered as El Niño events.

Interannual variations in the SCS are mostly associated with weakened circulation gyres and upwelling under weakened monsoons during El Niño. This creates higher-than-normal SSTs across the basin (Chao et al., 1996b; Ose et al., 1997) lagging behind the SST anomalies of the equatorial Pacific by about 6 months (Fig. 3). Weaker winds and reduced upwelling intensities in association with reduced precipitation and riverine discharge spin down the biological productivity throughout the SCS (Fig. 4). The coupled El Niño-monsoon system thus produces changes in the surface waters (temperature, salinity, nutrient content, fluvial sediment loads and runoff) which are expected to impact the physical, chemical and biological characteristics of particles settling through the water column and accumulating on the seafloor.
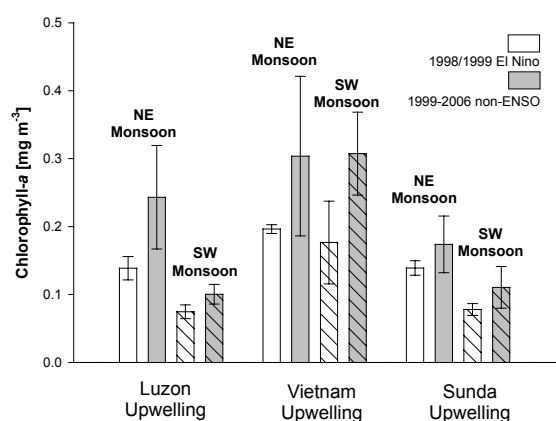

Fig. 4. Chlorophyll-a concentrations in surface waters as a proxy for primary productivity during El Niño and non El Niño conditions for three upwelling regions in the SCS. During El Niño events upwelling is reduced or suppressed which leads to lower productivity in these areas. For additional information on upwelling regions in the SCS refer to Liu et al. (2002).

3. Methods

3.1. Sample material

Bottom-tethered time-series sediment traps with a collection area of 0.5 m² (Mark VI - Honjo and Doherty, 1988) have been deployed between 1000 and 3744 m water depth at five stations in the SCS (see Fig. 1). Sampling intervals ranged between 15 and 32 days. Detailed information on location, water depth, sediment trap depth, and sampling periods is given in Table 1.

Prior to deployment, the sample bottles were filled with ambient SCS deep-sea water. Analytical grade sodium chloride (35 g NaCl l⁻¹) and mercury chloride (3.3 g HgCl₂ l⁻¹) were added in order to prevent diffusive processes and microbial activity in the trapped samples. After recovery, the samples were stored in a cooling room at 2 °C. During most of the cruises sample preparation took place onboard

directly after recovery. The supernatant was decanted while the particulate residue was passed through a 1 mm meshsize sieve. The fractions were split using a high precision rotary splitter (McLane WSD-10) and filtered onto pre-weighed Nucleopore filters (0.45 μm) and dried at 40 °C for three days. Only the <1 mm-fraction was used for flux calculation and subsequent biogeochemical analyses.

Surface sediment samples (0-1 cm) were obtained with a *Wuttke* standard box corer. An undisturbed surface sediment horizon was taken off and dried at 40 °C for three days. For further analyses, both, trap samples and surface sediments, were crushed and homogenized with an agate mortar.

3.2. Analytical methods

Total carbon and total nitrogen were measured by flash combustion using a Carlo Erba 1500 CNS analyser (Erba Science, Milan, Italy). The standard deviation of the duplicate analyses was 0.15 % for carbon and 0.005 % for nitrogen. Carbonate carbon was determined on a Wösthoff Carmhograph 6 (Bochum, Germany). Briefly, the samples were heated in 2 N phosphoric acid and the evolving CO_2 was led into a 0.05 N sodium hydroxide solution. The change in conductivity was measured and calibrated against a standard of pure $CaCO_3$. The standard deviation of this method was ±1 % or better. Organic carbon was calculated as the difference between total carbon and carbonate carbon. The type of the organic matter in terms of hydrogen index (HI, in mg hydrocarbons/g total organic carbon) was determined by rock-eval pyrolysis on a Delsi Oil Show Analyser according to the analytical procedure described by Liebezeit and Wiesner (1990) for recent sediments.

In order to achieve the best possible comparability all THAA measurements have been conducted under equal analytical conditions within a short time frame of approximately four months. For this reason several samples have been re-analysed and might slightly deviate from previously published results. Total hydrolysable amino acids (THAA) and total hydrolysable hexosamines (THHA) were analysed with a Pharmacia LKB Alpha Plus 4151 Amino Acid Analyser (Freiburg, Germany) after hydrolysis of 2-4 mg of trap samples (30-50 mg of surface sediments) with 6 N HCl for 22 h at 110 °C under a pure argon atmosphere. HCl was then removed from an aliquot by evaporation, the residue was taken up in an acidic buffer and injected into the analyzer. After separation with a cation exchange resin, the individual monomers were detected fluorometrically: taurine (Tau), aspartic acid (Asp), threonine (Thr), serine (Ser), glutamic acid (Glu), glycine (Gly), alanine (Ala), valine (Val), methionine (Met), iso-leucine (Ile), leucine (Leu), tyrosine (Tyr), phenylalanine (Phe), β-alanine (β-Ala), γ-aminobuteric acid (γ-

Tab. 1. Location, water depth, trap depths, deployment periods and collection intervals of sediment trap deployments used in this study

Station	Latitude [° N]	Longitude [° E]	Water depth [m]	Trap depths [m]			Deployment period	collection interval [days]
SCS-NE-01	17° 16'	119° 31'	2826	1225	1765	2287	08. Jul. 1998 - 30. Apr. 1999	28
SCS-N-01	18° 28'	116° 01'	3766	1000		3350	10. Sep. 1987 - 22. Mar. 1988	15
SCS-N-02	18° 28'	116° 01'	3766			3350	13. Apr. 1998 - 21. Oct. 1988	15
SCS-NC-01	17° 04'	117° 11'	4038	1465		3500	10. Dec. 1996 - 26. Nov. 1997	27
SCS-C-02	14° 35'	115° 03'	4270	1191			20. Mar. 1992 - 09. May 1993	32
SCS-C-03	14° 36'	115° 09'	4270	1191		3728	01. Jun. 1993 - 31. May 1994	28
SCS-C-04	14° 36'	115° 08'	4306	1208	2243	3774	01. Jun. 1994 - 05. Apr. 1995	28
SCS-C-05	14° 37'	115° 07'	4005		1830		01. Jun. 1995 - 24. Jun. 1996	30
SCS-C-06	14° 42'	115° 09'	4298	1225			10. Dec. 1996 - 26. Nov. 1997	27
SCS-C-07	14° 42'	115° 08'	4281	1208		3744	29. Jun. 1998 - 25. Apr. 1999	28
SCS-SW-01	11° 54'	110° 01'	1881	1246			29. Jun. 1998 - 23. Apr. 1999	28

Aba), histidine (His), ornithine (Orn), lysine (Lys), arginine (Arg), glucosamine (Gluam), galactosamine (Galam). The relative error was 4 % for total AA and 5-16 % for individual monomers. For Tau, Val, Met, and Orn the errors were usually below 15 % but in a few cases of very low THAA-contents up to 35 % due to concentrations close to the detection limit. THHA values were multiplied by 1.4 to correct for loss during hydrolysis (Müller et al., 1986).

The molar percentages of the 14 protein amino acids have been used to calculate the Degradation Index (DI) developed by Dauwe and Middelburg (1998) and Dauwe et al. (1999). Molar percentages of individual AA are standardised by the mean and standard deviations of the 28-sample data set. The DI integrates the AA weighed by the factor coefficients for the first axis of the principal component analyses (PCA) according to the formula:

$$DI = \sum_{i} \left[\frac{var_i - AVGvar_i}{STDvar_i} \right] \cdot fac.coef._i$$

where var_i is the original mole percentage of each AA_i, $AVGvar_i$ and $STDvar_i$ are the mean and standard deviations and $fac.coef._i$ is the factor coefficient of the first axis of the PCA of Dauwe et al. (1999). The DI thus represents the cumulative deviation with respect to an assumed average molar composition with negative values indicating more and positive values less degradation than the average

All internet sources in this study have been accessed between May and October 2005. In case data of the exact position of a study site were not available we used the smallest possible area (smaller than a 2° x 2° quadrangle) to cover the region of interest.

Daily data on wind speed and wind direction (above ground) were derived from the *Climate Data Assimilation System I; NCEP-NCAR Reanalysis Project* (Kalnay et al., 1996) (http://iridl.ldeo. columbia.edu/SOURCES/.NOAA/.NCEP-NCAR/ .CDAS-1/.DAILY/.Diagnostic/.above_ground/).

Weekly data on sea surface temperature (SST) and sea surface temperature anomaly (SSTA) were obtained from the *Climate Modeling Branch* of the *National Centers for Environmental Prediction* (Reynolds et al., 2002) (http://iridl.ldeo.columbia. edu/SOURCES/.NOAA/.NCEP/.EMC/.CMB/ .GLOBAL/.Reyn_SmithOIv2/.weekly/).

Chlorophyll-a concentrations in surface waters were obtained from the GES-DISC Interactive Online Visualization and Analysis Infrastructure (Giovanni) as part of the NASA Goddard Earth Sciences (GES) Data and Information Services Center (DISC) (http://reason.gsfc.nasa.gov/OPS/Giovanni/ocean.sea wifs.2.shtml).

To define monsoon and intermonsoon phases for our study we used a modified approach from Gerbich (2001) which is based on the following criteria: (a) the five day mean of the meridonal wind component must exceed 2.16 m s^{-1} (southwest monsoon) or must fall below -2.90 m s^{-1} (northeast monsoon); (b) criterion (a) must be met during five consecutive days; (c) after the onset of a monsoonal phase there must not be a period longer than 20 days during which criteria (a) and (b) are not fulfilled.

4. Results

4.1. Station SCS-NE 1998-1999

Total particulate fluxes in the shallow trap at 1225 m water depth varied between 36 and 191 mg m^{-2} d^{-1} (Fig. 5). Fluxes in the middle trap at 1765 m were between 47 and 193 mg m^{-2} d^{-1}; fluxes in the deep trap at 2287 m ranged between 64 and 199 mg m^{-2} d^{-1}.

The average particle flux during the deployment was 99 mg m^{-2} d^{-1} in the shallow trap, 121 mg m^{-2} d^{-1} in the middle and 125 mg m^{-2} d^{-1} in the deep trap. Highest fluxes were observed in the end of

September 1998 and between January and March 1999. Fluxes were significantly reduced in the shallow trap in 1999 in comparison to the deeper traps.

Generally, organic carbon fluxes followed the flux patterns of total particulate matter (Fig. 5). Organic carbon fluxes ranged between 1.52 and 7.66 mg m^{-2} d^{-1} with no distinct differences between the shallow, middle and deep trap. THAA and THHA fluxes show the same trend as organic carbon fluxes. The THAA and THHA contents of sinking matter, in contrast, reveal a depth depending reduction of labile components. Highest amounts were measured in the shallow trap (16.5-29.8 mg g^{-1}), whereas in the middle and deep trap THAA ranged between 9.8-21.9 and 8.8-13.8 mg g^{-1}, respectively. Average THAA decreased with increasing water depth (20.5, 14.3, and 11.1 mg g^{-1}, respectively). Organic matter reactivity deduced from the Degradation Index (DI) ranged between -0.35 and +0.52 with no clear depth-dependent trend.

4.2. Station SCS-N 1987-1988

Total particulate fluxes varied significantly between the shallow trap at 1000 m water depth and the deep trap at 3350 m (Fig. 5). Fluxes at 1000 m were in the range of 11-40 mg m^{-2} d^{-1} from September to November 1987, distinctly increasing up to 180 mg m^{-2} d^{-1} until February and decreasing at the end of the deployment period to 42 mg m^{-2} d^{-1}. For the deep trap, fluxes increased until November 1987 from 48 to 107 mg m^{-2} d^{-1}, decreasing until January 1988, rising again until March to 112 mg m^{-2} d^{-1} and decreased with the last sampling interval. For the deployment period between April and November 1988 only samples from the deep trap were available. Maximum fluxes were observed during May to July 1988 (107-121 mg m^{-2} d^{-1}), lowest fluxes were measured between September and October 1988 (19-33 mg m^{-2} d^{-1}). Average total particulate flux in the shallow trap was 89 mg m^{-2} d^{-1}, in the deep trap 78 mg m^{-2} d^{-1} during the first and 70 mg m^{-2} d^{-1} for the second deployment period. THAA fluxes ranged between 0.8 and 3.9 mg m^{-2} d^{-1} in the shallow and between 0.4 and 1.4 mg m^{-2} d^{-1} in the deep trap.

The organic carbon content in the shallow trap was between 3.1 and 6.4 % with a mean of 4.4 %. The THAA content varied between 12.1 and 24.0 mg g^{-1} in the shallow trap and 7.6 and 13.0 in the deep trap (Fig. 5). The THAA mean in the shallow trap (19.8 mg g^{-1}) was about two times higher than in the deep trap (10.2 mg g^{-1}) which was also valid for THHA contents (2.4 vs. 1.3 mg g^{-1}). Organic matter reactivity derived from amino acid nitrogen (THAA-N/N$_{tot}$) exhibits a significant higher particle reactivity in shallow trap samples (mean: 45 %) than in the deep trap (mean: 31 %). This is also supported by the DI with an average of +0.33 in the shallow trap versus +0.04 in the deep trap.

4.3. Station SCS-NC 1996-1997

At Station NC particle fluxes were very similar in the shallow trap at 1465 m and the deep trap at 3500 (Fig. 5). Total particulate fluxes ranged between 39 and 183 mg m^{-2} d^{-1} in the shallow trap and between 52 and 225 mg m^{-2} d^{-1} in the deep trap. A prominent flux peak occurred in January 1997 in both traps, followed by a stable flux range with a mean of about 70 mg m^{-2} d^{-1}. Organic carbon fluxes showed the same trend compared to the total flux but unlike total particle fluxes, organic carbon fluxes were slightly higher in the shallow trap (mean: 4.9 mg m^{-2} d^{-1}) than in the deep trap (3.7 mg m^{-2} d^{-1}) during most of the sampling period.

THAA fluxes peaked in January 1997 with 10.4 and 4.1 mg m^{-2} d^{-1} in the deep trap. Average THAA fluxes in the shallow and deep trap, respectively, were 2.2 and 1.2 mg m^{-2} d^{-1}. The particle flux was significantly enriched in THAA during January 1997 (56.6 mg g^{-1} in the shallow trap); this elevation was neither observed by relative AA concentrations nor by any AA indicator in the deep trap. Mean THAA concentration for the shallow trap was 19.2 mg g^{-1} and 13.1 mg g^{-1} for the deep trap. The amino acid peak in January 1997 coincided with an extremely high THAA-N/N$_{tot}$ ratio (97 % !) and a THHA peak of 4.6 mg g^{-1} (mean: 2.5 mg g^{-1}). On average organic matter reactivity was somewhat higher in the shallow trap (DI: +0.26) than in the deep trap (+0.07) but the extraordinary peak in January 1997 had no influence on this early diagenetic indicator.

4.4. Station SCS-C 1992-1999

Total particulate fluxes in the shallow trap at approx. 1200 m water depth ranged between 6 and 207 mg m^{-2} d^{-1} with an average flux of 78 mg m^{-2} d^{-1} throughout the deployments (Fig. 5). Peak fluxes occurred in June-July 1992 (169 mg m^{-2} d^{-1}), in August-September 1994 (207 mg m^{-2} d^{-1}) and in May-June 1997 (170 mg m^{-2} d^{-1}). Very low fluxes were measured from March to May 1997 (6-19 mg m^{-2} d^{-1}). During the deployment between 1998 and 1999 fluxes were in the range of 36-91 mg m^{-2} d^{-1}.

The middle trap in 1994-1995 followed the trend of the shallow trap with fluxes between 50 and 135 mg m^{-2} d^{-1}. During winter 1995/1996 maximum fluxes reached maximum values between 97-177 mg m^{-2} d^{-1}. The average flux rate (78 mg m^{-2} d^{-1}) in this water depth was slightly lower than the year before. Total particle fluxes received from the deep trap at approx. 3700 m water depth in 1993-1994 were almost similar (81 mg m^{-2} d^{-1}) to those in the shallow trap (85 mg m^{-2} d^{-1}). Between 1994 and 1995, however, mean deep fluxes (69 mg m^{-2} d^{-1}) were
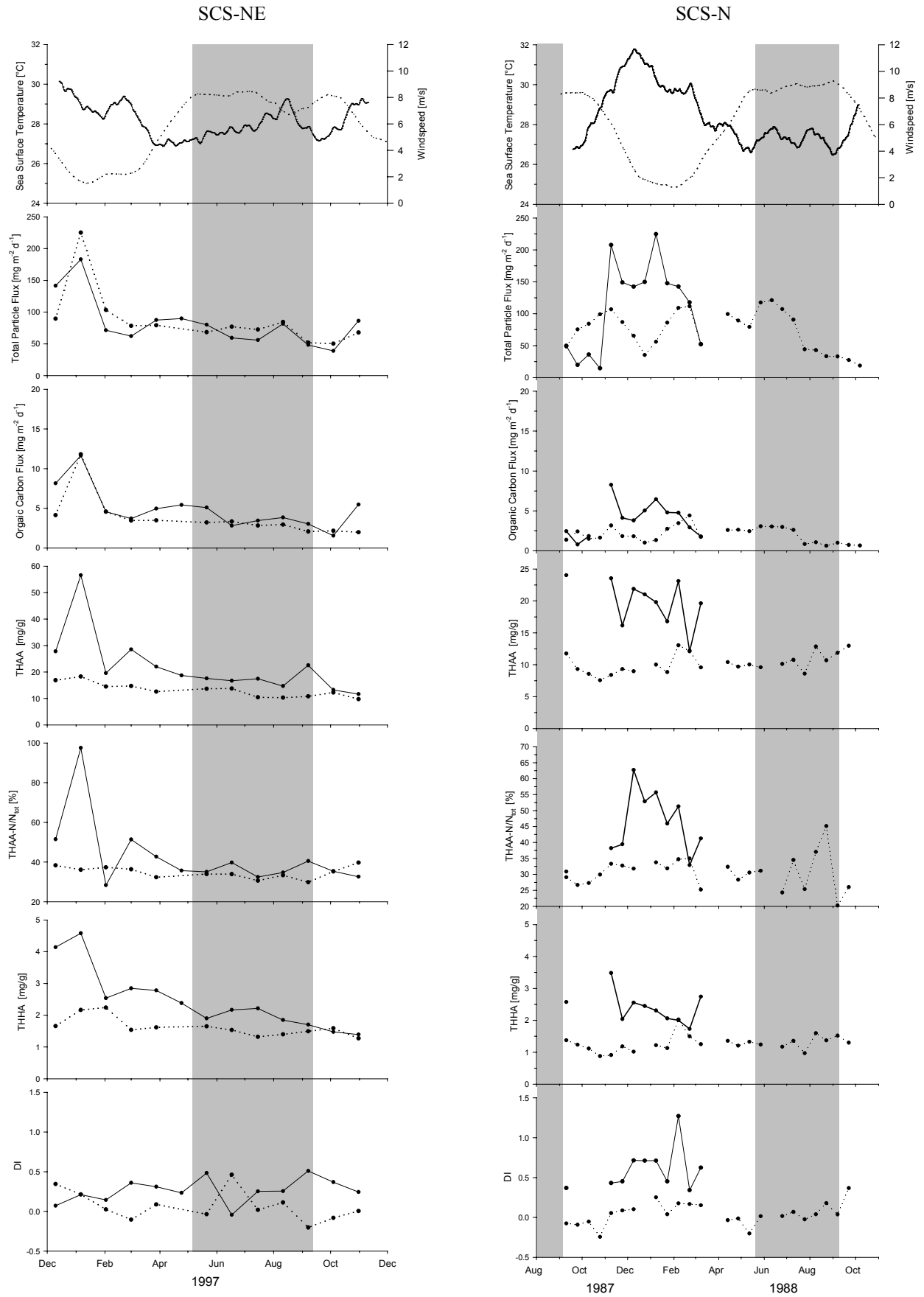
SCS-NE

SCS-N

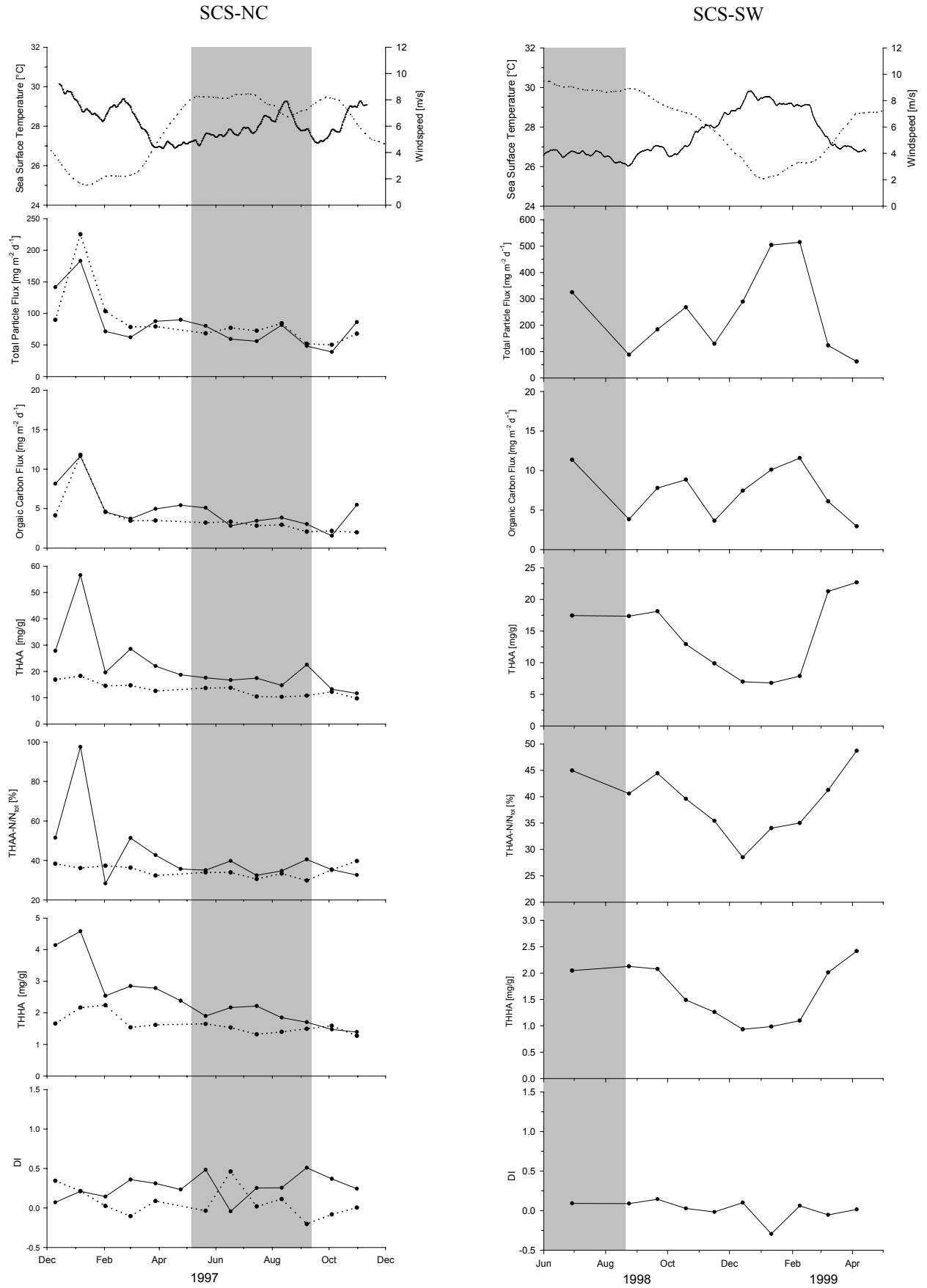Fig. 5 (continuing next page)

SCS-NC

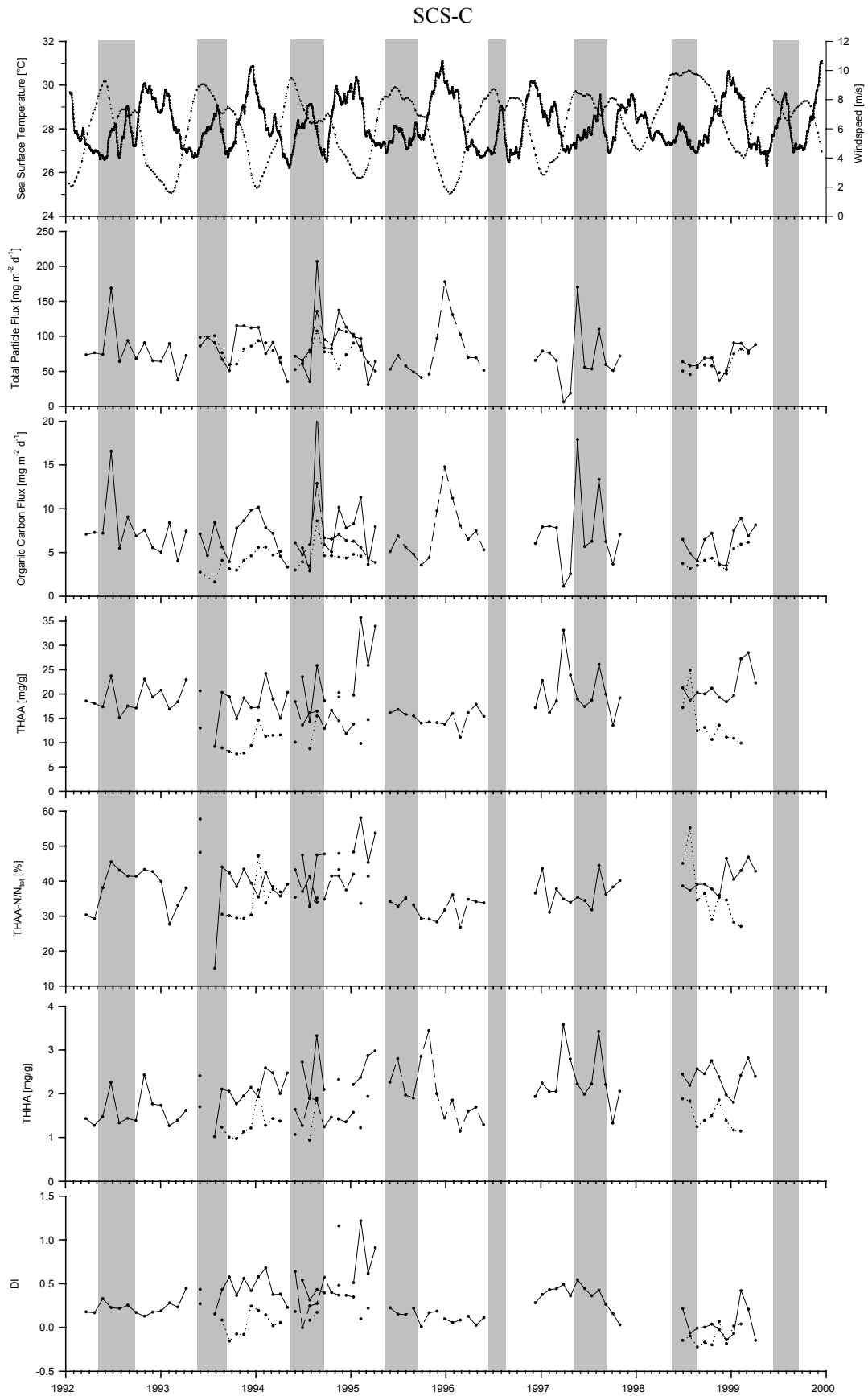SCS-SW

Fig. 5 (continuing next page)

SCS-C

Fig. 5 (continued). Sea surface temperatures (dotted lines) and wind speeds (solid lines) in the uppermost chart of each station, both based on a five weeks running mean. Total and organic carbon fluxes as well as THAA and THHA concentrations shown for all trap locations and all available trap depths. In addition, the degradational state of organic matter depicted on the basis of the ratio of amino acid nitrogen vs. total nitrogen (THAA-N/N_{tot}) and the Degradation Index (DI).

Flux data: solid line - shallow traps; dashed line - middle traps; dotted line - deep traps). Summer monsoon phases (SWM) are shaded for better orientation.

reduced compared to the shallow trap. Fluxes measured in the deep trap with a mean of 59 mg m^{-2} d^{-1} between 1998-1999 followed the trend of the shallow trap.

Organic carbon fluxes almost entirely mirrored the total particle flux patterns at all depths (Fig. 5). Average organic carbon flux at 1200 m water depth was 4.0 mg m^{-2} d^{-1} with flux peaks that occurred during the summer monsoon seasons in 1992 (9.2 mg m^{-2} d^{-1}), in 1994 (11.8 mg m^{-2} d^{-1}) and in 1997 (10.0 mg m^{-2} d^{-1}). Organic carbon fluxes in the middle and deep trap were, on average, between 3.9 and 2.4 mg m^{-2} d^{-1}, respectively. The organic carbon content varied between 3.8 and 10.2 % (mean: 5.3 %) for the shallow traps. Minimum values (4.7 %) were observed between 1993-1994, maximum organic matter concentrations (6.2 %) were measured during the 1996-1997. This was also the period of organic carbon contents with highest organic variability (3.9-10.2 %). For all deployments the average organic carbon fraction decreased with increasing depth being reduced by approx. 30 % from shallow to deep traps.

THAA fluxes ranged between 0.2 and 4.0 (average: 1.6) mg m^{-2} d^{-1} and between 0.5 and 1.7 (average: 0.7) mg m^{-2} d^{-1} in the shallow and deep trap, respectively. THAA in the shallow traps contributed with an average of 20.4 mg g^{-1} and a range of 9.2 to 35.8 mg g^{-1} to the particle flux. The amount of THAA in the deep traps was reduced by 40-50 % compared to the respective shallow traps. THAA were closely coupled to the organic carbon content but not to the flux pattern. For instance, highest THAA concentrations were measured during the transition from winter monsoon to spring intermonsoon seasons in 1995 (35.7 mg g^{-1}), 1997 (33.1 mg g^{-1}) and 1999 (27.9 mg g^{-1}). THHA-N/N$_{tot}$ varied from 15.1 % in summer 1993 to 58.1 in winter 1994/1995. Mean THHA-N/N$_{tot}$ throughout the deployment period dropped from 40.0 % in the shallow traps to 35.4 % in the middle and 36.3 % in the deep traps. THHA contents ranged from 1.0 - 3.6 (mean: 2.2), 1.1 - 3.4 (mean: 1.8) and 0.9 - 2.1 (mean: 1.4) mg g^{-1} in the shallow, middle and deep traps, respectively. Highest organic matter reactivity deduced from DI data was observed in winter 1994/1995, lowest during the winter season 1998/1999 (Fig. 5). Average DI values decreased with increasing water depths from +0.32 in shallow traps to +0.22 and +0.06 in middle and deep traps, respectively.

4.5. Station SCS-SW 1998-1999

At station SCS-SW highest flux rates were measured from January to March 1999 (504-515 mg m^{-2} d^{-1}). The average particle flux rate at Station SW was 249 mg m^{-2} d^{-1} with variable fluxes throughout the deployment (Fig. 5). Organic carbon fluxes followed this trend but were not so much pronounced

during the flux peak in winter 1998/99. Their average was 7.4 mg m^{-2} d^{-} with a variability between 3.0 and 11.6 mg m^{-2} d^{-1}. THAA fluxes ranged between 1.3 and 5.7 mg m^{-2} d^{-1} with an average of 2.9 mg m^{-2} d^{-1}. Especially during the winter monsoon season THAA and THHA contents were opposed to the flux pattern revealing minimum values in December 1998 and January 1999 (Fig. 5). THAA values dropped from about 17-18 mg g^{-1} during the summer period to about 7 mg g^{-1} in winter time. The same trend were observed for THHA concentrations (~2 vs. 1 mg g^{-1}). Decreasing THAA and THHA concentrations coincided with decreasing THHA-N/N$_{tot}$ (minimum value of 28.5 compared to an average of 39.2 %). This trend was not supported by the DI, which ranged close to the mean of +0.02 throughout the deployment, except for January 1999 (DI: -0.30).

4.6. Surface sediments at the sediment trap stations

At the open-ocean stations SCS-N (SO-50/27 at 4000 m water depth) and SCS-C (SO-50/90 at 4300 m water depth) surface sediments revealed a very uniform composition with predominantly lithogenic contribution close to 90 %. The remaining sediments consisted of biogenic opal with about 10 %. The carbonate fraction was reduced to less than 1 %, i.e. the detection limit (Lahajnar & Wiesner, in prep.). At station SCS-N and SCS-C, 0.69 % and 0.53 %, respectively, were organic carbon. About 1 mg g^{-1} was identified as THAA and about 0.3 mg g^{-1} as THHA at both stations.

Surface sediments from SO-95 17927-1 at station NE (Lahajnar & Wiesner, in prep.) also mainly constituted of lithogenic material (~85 %), but were slightly enriched in biogenic opal (12 %) and carbonate (2 %). Organic carbon contributed with 0.56 % to the sediments. THAA and THHA were slightly depleted with 0.8 and 0.13 mg g^{-1}, respectively, compared to the open-ocean stations.

Sediment sample SO-140/58 (Lahajnar & Wiesner, in prep.) close to station SW had a lithogenic fraction of about 80 %. Biogenic opal averaged at 7 %, and in contrast to the other stations, the carbonate content ranged between 10 and 13 %. Organic carbon was slightly enriched with 0.9 %. Accordingly, THAA concentrations amounted to 2.0 mg g^{-1}, THHA to 0.42 mg g^{-1}.

Compared to the sediment trap samples all surface sediments were characterized by a low organic matter reactivity. The DI values ranged from -0.59 at station SCS-NE and -1.02 at station SCS-SW and reached minimum values of -1.57 and -1.74 at the open-ocean stations SCS-C and SCS-N, respectively.

Tab. 2. Seasonal and annual total, organic carbon, THAA and THHA contents and fluxes from 1200 m water depth. SCS-C (2/3/4/6) are combined in order to describe fluxes at the shallow trap (1200 m) in the central basin. SCS-C7 is given separately for comparison with other El Niño related fluxes (SCS-SW, SCS-NE). SWM: SW-monsoon, FIM: fall intermonsoon, NEM: NE-monsoon, SIM: spring intermonsoon. Component values: organic carbon in [%], THAA and THHA in [mg/g].

	SCS-NE Content	SCS-NE Flux [mg m⁻² d⁻¹]	SCS-N Content	SCS-N Flux [mg m⁻² d⁻¹]	SCS-NC Content	SCS-NC Flux [mg m⁻² d⁻¹]	SCS-C (2/3/4/6) Content	SCS-C (2/3/4/6) Flux [mg m⁻² d⁻¹]	SCS-C7 Content	SCS-C7 Flux [mg m⁻² d⁻¹]	SCS-SW Content	SCS-SW Flux [mg m⁻² d⁻¹]
Total Flux												
SWM		92		-		72		93		61		290
FIM		104		25		45		59		62		151
NEM		91		120		116		84		67		335
SIM		102		42		76		51		79		98
Organic carbon												
SWM	6.2	5.6	-	-	5.6	4.0	5.2	4.9	5.2	3.2	3.1	10.1
FIM	5.1	5.3	5.8	1.7	5.5	2.5	4.7	2.6	4.5	2.8	4.2	6.2
NEM	4.8	4.3	3.8	4.9	5.8	7.0	4.9	4.1	5.1	3.4	2.7	8.3
SIM	5.1	5.3	4.3	1.8	6.0	4.5	6.1	2.9	4.9	3.8	4.9	4.8
THAA												
SWM	26.6	2.4	-	-	16.8	1.2	19.1	1.9	20.1	1.2	15.6	5.1
FIM	22.2	2.4	24	1.0	19.3	0.9	17.9	1.1	20.0	1.2	17.7	2.7
NEM	18.5	1.7	18.8	2.5	27.2	4.0	20.2	1.8	21.1	1.5	9.3	2.9
SIM	22.0	2.3	19.6	0.8	22.8	1.7	22.4	1.1	28.5	2.3	21.9	2.1
THHA												
SWM	2.4	0.23	-	-	2.1	0.15	2.1	0.21	2.3	0.14	1.8	0.06
FIM	2.1	0.22	2.5	0.10	1.6	0.07	1.8	0.11	2.5	0.15	2.1	0.32
NEM	2.2	0.20	2.2	0.30	2.9	0.41	2.0	0.18	2.3	0.15	1.9	0.38
SIM	2.1	0.21	2.7	0.11	2.7	0.20	2.3	0.11	2.8	0.22	2.2	0.21
Average												
Total Flux		99		96		84		80		68		249
Organic Carbon	5.2	4.9	4.4	3.9	5.8	4.1	5.4	4.2	5.0	3.4	3.5	7.4
THAA	20.5	2.0	19.8	2.2	22.1	2.2	20.2	1.6	21.5	1.5	14.1	2.9
THHA	2.9	0.22	2.4	0.27	2.5	0.24	2.1	0.17	2.4	0.16	1.6	0.35

5. Discussion

5.1. Organic matter fluxes in the open SCS (stations SCS-C and SCS-NC)

Particle fluxes at the two stations in the central SCS show a high intraseasonal and interannual variability (Fig. 6). On the basis of the defined season (chapter 3.3.) particle fluxes have been assigned to the respective monsoonal phases (Fig. 6). From 1992 until 1998 total particle fluxes are in all cases higher during the SWM or NEM than during each of their preceding or following intermonsoonal period. There is, however, neither a significant correlation of organic matter fluxes with the wind speed nor with the SST. During monsoonal periods (SWM and NEM), total particle fluxes range between 84 and 93 mg m^{-2} d^{-1} at SCS-C and between 72 and 116 mg m^{-2} d^{-1} at SCS-NC. Average fluxes during the intermonsoons are in the order of about 55 mg m^{-2} d^{-1} at SCS-C. Stimulated fluxes during the SWM can be assigned to a summer coastal jet that separates at ~12° N off Vietnam towards the Luzon Strait (Liu et al., 2002). This jet transports clay minerals and explains why in many years lithogenic fluxes peaked during the SWM period (Gerbich, 2001). In contrast, during NEM-phases station SCS-C does not receive eolian inputs (loess from continental China) as revealed from studies on the mineralogical composition (Wiesner et al., 1996).

The very striking winter flux peak at SCS-NC (Fig. 5) could be due to large-scale cyclonic eddy formation during December (Ho et al., 2000) which triggers enhanced primary productivity. Indeed, it is not the lithogenic fraction but biogenic opal that increased from around 20 % to 44-50 % in December/January (Wiesner et al., submitted). The dominating character of biogenic opal is also accompanied by a very low Asp/Gly ratio (0.55) compared to the mean of 0.72 at SCS-NC and 0.73 at SCS-C. Asp/Gly ratios < 1 often serve as a proxy for opal-dominated particle fluxes (Hecky et al., 1973; King, 1977). The biologically governed flux peak at SCS-NC is thus also characterised by elevated THAA-concentrations (27.2 mg g^{-1}) during the NEM (Tab. 2) with maximum concentrations up to 56.6 mg g^{-1} in January 1997 revealing higher productivity and better organic matter preservation.

5.2. Organic matter fluxes during El Niño conditions

5.2.1. Central South China Sea 1998-1999

The deployment during 1998-1999 (SCS-C-07) coincided with one of the strongest ENSO-events on record in the East Asian region (Kuo et al., 2004; McPhaden, 1999). Throughout the year 1998 and even at the beginning of 1999 the SCS were under the severe influence of atypically high SSTs and abnormally low wind speeds (Fig 6). However,

during the ENSO warm phase in 1998-1999 organic carbon contents and THAA concentrations did not deviate much from the long-term average in the central SCS, although total and component flux rates were reduced, particularly during the SWM and NEM (Tab. 2). The amino acid spectra (Fig. 7) do not display a marked difference between ENSO-neutral and ENSO-warm phases, except for Asp at the central station. This can be explained by enhanced carbonate fluxes during that period (Wiesner et al., submitted) as Asp is often associated with CaCO$_3$ (Carter and Mitterer, 1978; Constantz and Weiner, 1988; Ittekkot et al., 1984b; Müller and Suess, 1977). Moreover, this is the only period when the Asp concentration slightly dominated Gly (Asp/Gly: 1.1). Such a ratio can also signal strong organic matter degradation.

Indeed, by assigning the amino acid spectra to the monsoonal phases it turned out that, deduced from the DI, organic matter reactivity was reduced during the ENSO warm phase compared to the preceding years (Fig. 6). It is possible that the organic matter that was exported from the photic zone had already been decomposed (recycled) to a greater extent in the upper ocean. Concurrent lower chlorophyll-a concentrations from remote sensing support this assumption. In addition, the lithogenic fraction in the trap samples dropped to minimum values during the El Niño phase (Wiesner et al., submitted). This (partly) missing ballast material (Ittekkot, 1993) probably led to less efficient organic matter removal and slower downward fluxes and thus resulted in a lower organic matter reactivity in our trap samples. Therefore, minimum fluxes in combination with reduced lithogenic components could have enhanced THAA degradation (Haake et al., 1992; Ittekkot et al., 1984a) at the central station. However, neither the median grain size nor the composition (smectite and kaolinite) of the lithogenic material show any relationship with the amino acids as reported from other oceanic regions (Wang and Lee, 1993)

Lower organic matter reactivity in sinking particulate organic matter during El Niño conditions have also been reported from the western Equatorial Pacific (Gupta and Kawahata, 2002) but are associated with higher flux rates which is not the case in the SCS.

In this connection, most sensitive with respect to El Niño conditions are the basic AA His, Orn, Lys, and Arg. As the proteinogenic AA His, Lys and Arg drop to minimum concentrations, the relative abundance of the non-proteinogenic AA Orn rises to values twice as high as compared to the long-term mean (Fig. 6). Of all proteinogenic AA, particularly His seems to be sensitive to organic matter reactivity (Fig. 8). His concentrations [mole-%] dropped from very stable values of 2.2 between 1992-1998 to values of ~1.5 during El Niño conditions in 1998/1999. Similar but less pronounced trends have
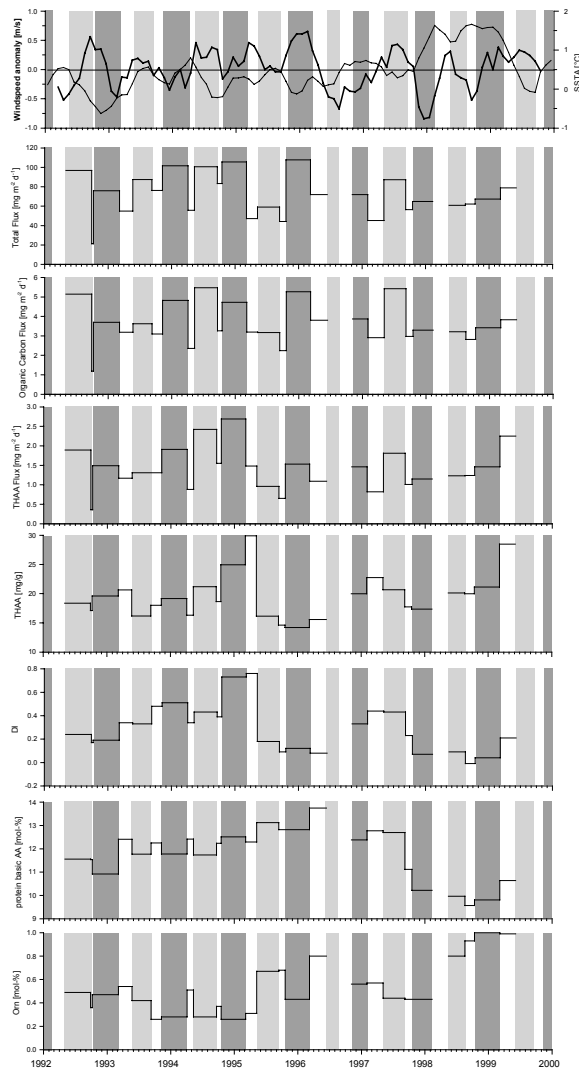
Fig. 6. Interseasonal and interannual variability of total and compound specific fluxes at SCS-C shallow. The fat line in the upper chart denotes the wind speed anomaly, the thin line sea surface temperature anomaly. Light grey periods indicate SW-monsoon, dark grey periods NE monsoon phases.
ENSO warm conditions in 1998/99 were associated with a low seasonality and increased organic matter degradation (low DI). Particularly proteinogenic amino acids were depleted during the El Niño. Contrastingly, non-proteinogenic Orn was significantly elevated compared to the long-term mean.

been observed for Lys and Arg. Neutral and acidic AA, on the other hand, are not susceptible to El Niño conditions. As primary production rates and composition changed it would be possible that this shift has influenced the relative abundance of basic AA. Organic matter is negatively charged (Henrichs and Sugai, 1993) and thus has the potential to accumulate positively charged basic AA; changing bulk organic components could lead to a reduced protection-capability of basic AA. However, this would no explain the distinct increase of Orn which is considered as an (intermediate) degradational product of Arg (Keil et al., 2000; Schmidt et al., 2004; Wakeham and Lee, 1993). Therefore, we rather account basic AA modifications during El Niño to

reduced lithogenic fluxes (i.e. to the available amount but not to the composition) since distinctly low wind speeds and surface currents during ENSO-warm conditions are responsible for a 40 % lower lithogenic (clay minerals) input (Wiesner et al., submitted). The at least partly missing supply of kaolinite and montmorillonite could prevent an efficient protection of basic AA by adsorption (Cowie and Hedges, 1992a; Hedges and Hare, 1987; Keil et al., 2000).

Other potential sources of ballast material which could have accelerated downward particle fluxes such as increased zooplankton abundance were not macroscopically detected in trap samples and can be neither deduced from Gluam/Galam (Gupta and Kawahata, 2002; Zhang et al., 1992) nor from THAA/THHA ratios (Haake et al., 1992) as Gluam/Galam ratios from shallow traps in the SCS are constant (close to 80) and THAA/THHA ratios range between 13 and 14 except for SCS-C2 with a mean ratio of 18 (Tab. 2 and Fig 7).

5.2.2. Northern South China Sea 1987/88
Sediment traps at station SCS-N were deployed during ENSO warm conditions in 1987/88 (Fig. 3). It is difficult to estimate whether the obtained fluxes are representative for this area or whether the flux signal was altered by ENSO warm conditions. Our results show that a pronounced increase between the flux rates during the NEM and the intermonsoon periods occurred (Tab. 2). Wiesner et al. (1996) found that the lithogenic components shift from clay dominated minerals during the SWM (also during SIM/FIM) to quartz- and feldspar-rich assemblages in winter times. Station SCS-N is the only site with such a lithogenic composition; hence, those minerals are presumed to be derived from Chinese loess fields (Gerbich, 2001) when strong southward winds blow from the continent towards the northern SCS. These strong lithogenic (eolian) input lead to high particle fluxes during the NEM (120 mg m^{-2} d^{-1}) that are associated with low organic carbon, THAA and THHA contents (Tab. 2).

Eolian loess transport would also explain high carbonate fluxes at station SCS-N. Carbonate-producing plankton (foraminifers and coccolithophorids) are up to 10 times less abundant compared to SCS-C (Wiesner et al., 1996). The non-biogenic carbonate source is also seen in moderate Asp concentrations (12.3 mol-%) as well as in relatively low Asp/Gly ratios (0.74) although biogenic opal (Gly source!) is virtually absent in all trap samples during the deployment of SCS-N (Jennerjahn et al., 1992).
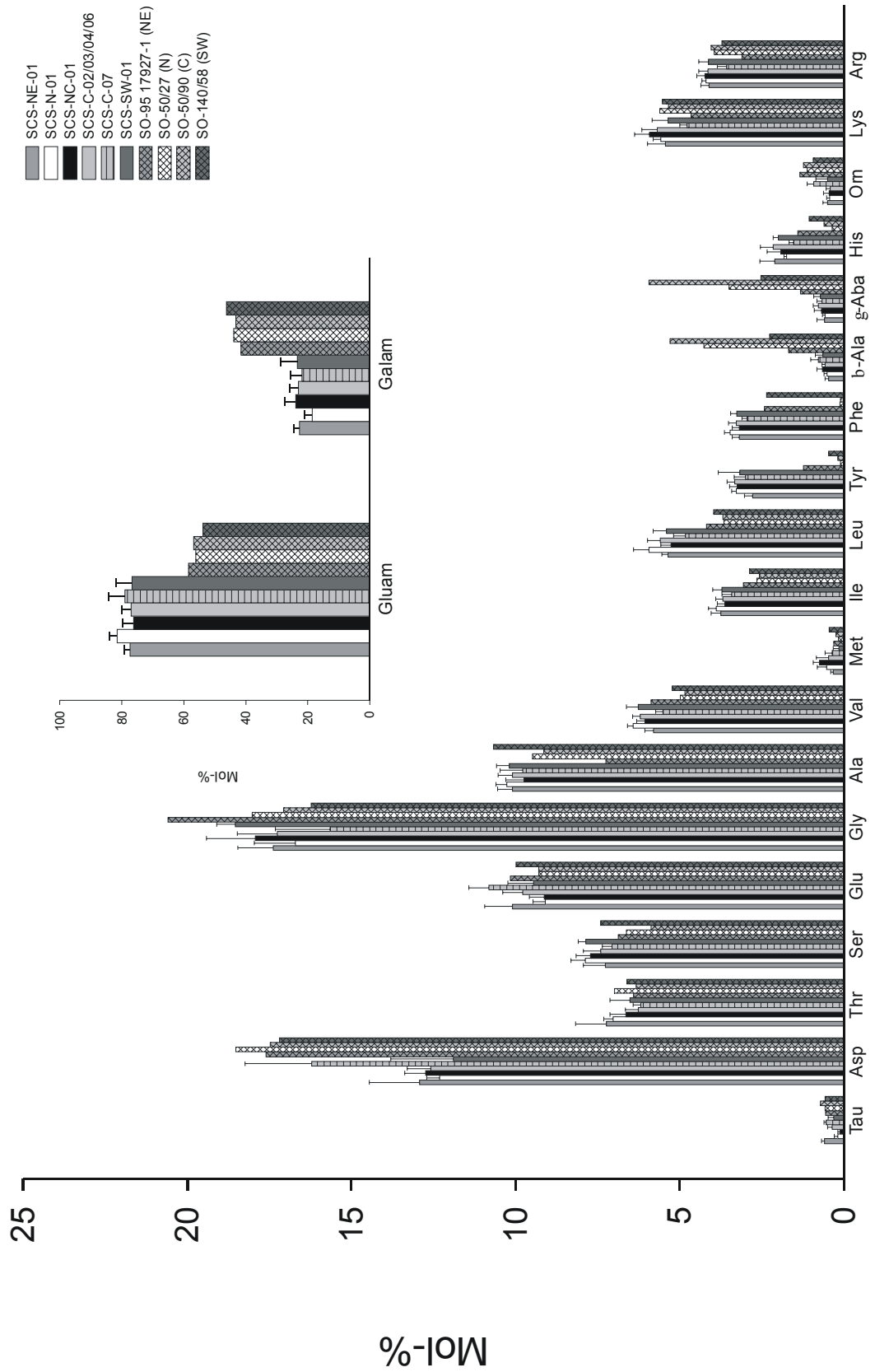
Fig. 7. Monomeric amino acid and hexosamine compositions of shallow sediment trap samples opposed to surface sediments. Error bars denote the standard deviation (1 σ) of all samples from each shallow trap-

5.2.3. NE South China Sea off Luzon 1998/99

Particle fluxes at station SCS-NE, located in the upwelling region off Luzon, deviate from the open ocean sites (Tab. 2). Due to the NEM, in winter times upwelling, sometimes only "updoming", takes place in this region (Huang et al., 1994; Liu et al., 2002; Liu and Xie, 1999; Pohlmann, 1987; Shaw et al., 1996; Tang et al., 1999; Udarbe-Walker and Villanoy, 2001; Xie et al., 2003). From remote sensing data this is also seen in elevated chlorophyll-a concentrations at the sea surface between approximately November and March. However, chlorophyll-a concentrations fell below a long-year mean throughout the year 1998 and for the first half of 1999 (except for Sep./Oct. 1998) indicating that reduced wind speeds during ENSO warm conditions in 1998 (Kuo et al., 2004) to a certain extent weakened the development of upwelling-stimulated primary production. This is in close agreement with recent findings that the extra-strong basin wide warming in 1998 might have prevented the formation of winter upwelling off Luzon (Wu and Chang, 2005).

Total fluxes do not show a clear seasonal trend at this station; flux rates are even slightly higher (~ 100 mg m^{-2} d^{-1}) during the intermonsoons than during the SWM and even during the NEM (~ 90 mg m^{-2} d^{-1}). Compared to the central SCS mean THHA concentrations (2.9 mg g^{-1}) are slightly elevated (Tab. 2) but AA indices are ambiguous. Unexpectedly, lowest THAA fluxes were measured during the NEM corroborating that a winter-upwelling triggered plankton bloom did not take place during ENSO warm conditions in 1998/99.

A comparison between the shallow and deep trap revealed an increase of total particle fluxes with depth but a decrease of organic carbon and other labile components. This is a good indication of laterally transported material. Geochemical analyses of rare earth elements point to the fact that a significant part of this lateral flux component is derived from rivers draining Luzon (Duyanen, unpublished data).

5.2.4. SW South China Sea off Vietnam 1998/99

Station SCS-SW is the shallowest study site (1881 m water depth) and closest to the continental shelf (about 100 km off central Vietnam). Total fluxes average to ~ 250 mg m^{-2} d^{-1} and reach maximum values of more than 500 mg m^{-2} d^{-1} (Fig. 5 and Tab. 2). The flux record depicts a pronounced seasonality related to both summer and winter monsoons with highest total fluxes during the NEM (335 mg m^{-2} d^{-1}) and lowest during the subsequent SIM (98 mg m^{-2} d^{-1}). Upwelling in this region caused by Ekman-pumping (e.g., Liu et al., 2004) usually occurs in June and late August, both for a time-span in the order of one week. Remote sensing data (SST) reveal, however, that upwelling was suppressed in summer 1998. Despite the influence of El Niño conditions, total (and bulk component) fluxes are still drastically higher compared to all other study sites. Low organic carbon contents (2.7 - 3.1 %) and an unusually high lithogenic fraction up to 68 % during the SWM and NEM (Wiesner et al., submitted) lead to the assumption that peak fluxes are not primarily caused by enhanced primary productivity but rather resulted from resuspension due to wind-induced ocean currents and eddy-formation. An ongoing research campaign has just shown that resuspension and lateral transport are of great importance in this area (Lahajnar and Wiesner, in prep.). Resuspension also explains why THAA concentrations are negatively correlated with bulk and THAA fluxes as resuspension takes place particularly during periods of elevated wind speeds and is thus opposed to normal conditions with higher organic matter fluxes being associated with less (microbially) degraded organic substances (Ittekkot et al., 1984b). A low Gluam/Galam ratio (2.6) and the lowest DI value (+0.016) of all sediment trap investigations between 1000-2000 m water depth in the Indo-Pacific region (Tab. 3) substantiate this assumption.

5.3. Organic matter transport and alteration in the deep South China Sea

From chlorophyll-a data obtained by remote sensing (Antoine et al., 1996) the annual primary production in the SCS ranges between 360 mg C m^{-2} d^{-1} (open ocean) and 580 mg C m^{-2} d^{-1} (upwelling regions) which is consistent with basin-wide primary production rates of 354 mg C m^{-2} d^{-1} provided by Liu et al. (2002). Recalculating primary productivity from organic carbon fluxes recorded by our sediment traps using the approaches of Suess (1980), Pace et al. (1987) or Berger et al. (1989) would lead to production rates of 100 mg C m^{-2} d^{-1} (open ocean) to 400 mg C m^{-2} d^{-1} (upwelling regions). This discrepancy could be due to a lower export ratio (the amount of organic carbon which leaves the photic zone) than the estimate of 12 % by Liu et al. (2002). Export ratios below 10 % are typically observed in oligotrophic regions (Buesseler, 1998). In addition, primary production rates calculated from remote sensing chlorophyll-a concentrations could be misleading as standard algorithms do not apply for at least some parts of the SCS due to its high load of suspended matter (R. Doerffer, written communication). Our trap studies show that particularly in the upwelling areas, which account for 30 % of the basin-wide primary productivity (Liu et al., 2002), production rates are reduced during ENSO-warm conditions. Deduced from organic carbon flux rates in 1200 m water depth our calculations point to 50 % lower productivity during upwelling than the previously estimated primary production rates of 650 mg C m^{-2} d^{-1} off Luzon in

January/February and of 1000 mg C m^{-2} d^{-1} off Vietnam in August (Liu et al., 2002). Moreover, additional flux sources (laterally transported suspended material) have to be taken into account which is especially necessary in the vicinity of continental margins (SCS-NE, SCS-N, SCS-SW) leading to a dilution and bias of the composition and extent of in-situ produced downward particle fluxes. At the open ocean sites (SCS-C, SCS-NC) this is considered to be only of minor importance.

Organic matter degradation in the SCS, however, is not related to the ambient primary production and subsequent export flux rates (Fig. 9) since climatic conditions have a great influence on organic matter degradation. That is why lowest organic matter reactivity of sinking material is found during the impact of ENSO warm conditions in 1998/99 (Fig. 10). In addition, the very high annual organic matter flux rate in combination with the lowest DI value at SCS-SW indicates that elevated fluxes off Vietnam are largely not caused by stimulated primary productivity but most-likely stem from intense resuspension of relatively degraded organic material. In the open SCS flux rates are comparable to those in the Bay of Bengal and Arabian Sea and even though organic matter contents in surface sediments are quite similar, the accumulated organic matter is by far more degraded than in other tropical and subtropical ocean regions (Tab. 3). One reason for enhanced

degradation in the deep SCS is the missing carbonate matrix below the CCD (Thunell et al., 1992) which can serve as a protection for at least some organic compounds (Ingalls et al., 2004; Klaas and Archer, 2002; Mitterer, 1968; Terashima, 1991)

Once particles have reached the sea-floor, particulate matter is accumulated in surface sediments. Unfortunately, solid accumulation rates are still missing for our study sites. Taking a general approach that less than 0.1 % of the organic carbon produced in the photic zone is finally accumulated in deep-sea sediments (e.g., Berger et al., 1989; Lahajnar, 1999), about 0.05 - 0.2 g C m^{-2} y^{-1} is incorporated into the sediments. With an organic carbon content between 0.5 and 0.9 % for our study sites, the estimated total accumulation rates would range between 9 and 25 g m^{-2} y^{-1}, depending on the primary production rates discussed above. Calculating the burial efficiency from organic carbon fluxes in sediment traps, only approximately 5 % of organic matter fluxes in 1200 m water depth are accumulated in the underlying sediment.

At all study sites in the SCS the Gluam/Galam ratio shifts from 3 - 4.5 in trapped particulate organic matter to 1.2 - 1.4 in surface sediments (Fig. 10). Gluam is mainly found in zooplankton whereas Galam is associated with bacterial productivity. In many cases Gluam/Galam ratios < 4 indicate bacteria dominated organic matter degradation (Kandler, 1979; Rixen and Haake, 1993) but particularly the drop within the sediments implies that the decomposition is largely related to microbial activity. Lower THAA/THHA ratios in the deep basin (~ 5) than in coastal areas (~9.5), both below 10 and thus zoobenthos dominated (Ittekkot et al., 1984a), indicate that benthic consumption is more efficient in SCS deep-sea sediments than in shallower waters.

Compared to bulk organic matter in the SCS, THAA are preferentially decomposed on their way from the sea surface to the deep sea and particularly during accumulation in surface sediments (Fig. 10). About 50 % of THAA are lost during the transport from shallow to deep traps. Similar decomposition rates have also been observed in the northern Pacific (Haake et al., 1993a). Organic matter concentrations decrease from 8-10 % in sediment traps to 1-1.6 % in sediments whereas THAA contents in settling particles at 1200 m water depth vary at around 20 mg/g sediment (except for SCS-SW with 14 mg/g) and decrease to ~1 mg/g in the sediments (2.3 mg at SCS-SW). This indicates that THAA decompose at much faster rates than other organic compounds. A loss of more than 80 % of THAA during the incorporation into the sediment is reported from other deep-sea areas (Haake et al., 1993a).

With regard to the complete amino acid spectra our study shows that organic matter reactivity decreases from shallow to deep traps, i.e. the organic matter is being degraded during the transport through
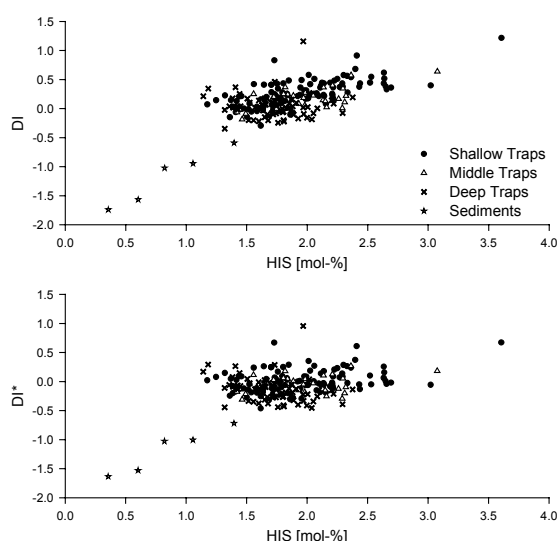

Fig. 8. Relationship between Histidine (His) and organic matter reactivity determined by means of the Degradation Index (DI). The positive correlation implies that His as a single AA monomer depicts the state of organic matter in sediment trap samples and particularly in surface sediments fairly well. However, His contributes to the DI calculation (Dauwe and Middelburg, 1998) and thus could result in a spurious correlation and misleading interpretation. Thus, DI has been calculated without His (DI*) showing that in this case the correlation is virtually unaffected.

the water column. This holds true for all sediment trap stations in tropical Asian and Pacific waters (Tab. 3).

Single AA analyses of shallow sediment trap samples and surface sediments (Fig. 6) reveal that Gly and Asp are the major AA in particulate matter, followed by Ala, Gly, Ser, Thr, Val, and Leu. Dominating Gly and Asp mol-% are also reported from the Peru upwelling (Henrichs et al., 1984), the NE-Atlantic (Horsfall and Wolff, 1997), and from the equatorial Pacific (Gupta and Kawahata, 2002; Lee et al., 2000). Lowest concentrations are accounted for the sulphur-containing AA Met and Tau as well as for the non-proteinogenic AA Orn. Neutral AA (Ser, Thr, Gly, Ala, Val, Ile, Leu) and aromatic AA (Tyr, Phe) are preferentially lost (Cowie et al., 1995; Jennerjahn and Ittekkot, 1997; Suthof et al., 2000) in SCS sediments, though Gly as a single AA does not follow this trend (Fig. 6). Gly, Ser, and Thr might be protected through incorporation in diatom cell walls (Colombo et al., 1998; Hecky et al., 1973).

The degradation process in the water column also affects the hydrogen richness of the bulk organic matter. In the northern and central South China Sea, the Hydrogen Indices range from 150 to 400 mg hydrocarbon/g total organic carbon indicating that the organic matter is a mixture of well preserved marine and terrestrial (higher plant) material or largely consists of biodegraded marine components. The values decrease from the shallow to the deep traps which is paralleled by a decrease in the ratios of Arg to Orn and Asp to β-Ala (Fig. 11) documenting downcolumn organic matter degradation. Notably, in the deep trap at the central station the Arg/Orn and Asp/β-Ala ratios are significantly lower than at the northern station (at comparable HI values) (Fig. 11). This can be explained by the position of the deep traps which at SCS-C as they are below the carbonate compensation depth (~3500 m, Thunell et al., 1992) and hence the dissolution of plankton tests releases labile components which are rapidly decomposed. The hydrogen indices are unaffected by this process reflecting that the lipids are less susceptible to degradation than the nitrogen-rich compounds.

5.4. Organic matter degradation in surface sediments

Among other indices, the ratio of aromatic to non-proteinogenic AA (Reactivity Index - RI) is a measure for the state of organic matter degradation (Jennerjahn and Ittekkot, 1997), especially in suspended and sinking matter (Unger et al., 2005a). At SCS-N and SCS-C the RI drops from values around 5 to 6 in shallow traps to virtually zero reactivity (RI: 0.03) in surface sediments (Fig. 9). In combination with very low DI values we conclude that labile components are largely decomposed within the uppermost sediment layer in the open SCS. In areas closer to the continental margins (SCS-NE and
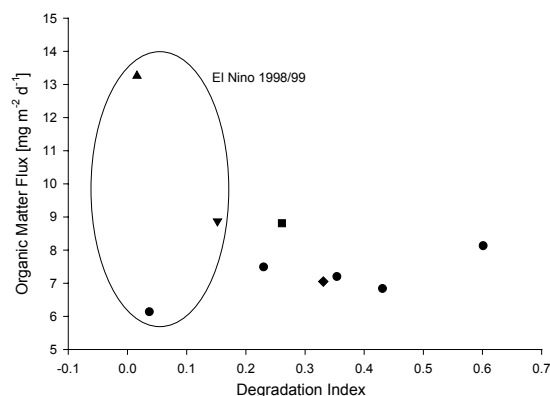

Fig. 9. Degradation Index vs. annual organic matter fluxes measured in shallow traps (circles: SCS-C 2/3/4/6/7, diamond: SCS-N, square: SCS-NC, triangle down: SCS-NE, triangle up: SCS-SW).
Highest organic matter degradation occurred during the El Niño event 1998/99. Organic matter fluxes at SCS-C are lower during ENSO conditions concomitantly with enhanced organic matter decomposition. Significantly elevated fluxes at SCS-SW were associated with distinctly degraded organic matter indicating that maximum organic matter fluxes were not derived from stimulated primary productivity but from resuspension and lateral advection of already biogeochemically degraded organic matter.

SCS-SW) the consumption and decomposition take place at lower rates.

Val, Ile, Leu, and His seem to be sensitive to organic matter degradation in SCS sediments, but in particular the rapid consumption of the aromatic AA Tyr and Phe is obvious (Fig. 7). In addition, relative concentrations of non-proteinogenic AA β-Ala, γ-Aba and Orn, which are the respective degradational products of Asp, Glu and Arg and hence a measure for the stage of organic matter alteration (Aizenshtat et al., 1973; Cowie and Hedges, 1994; Ittekkot et al., 1984b; Lee, 1988; Lee and Cronin, 1982; Morris, 1975; Terashima, 1991), significantly increase within the sediments (Fig. 7). Physical adsorption and incorporation to the sediment matrix in oxic environment backs up the preservation of non-proteinogenic AA (Cowie and Hedges, 1993; Nguyen and Harvey, 1997). A common Glu/ γ-Aba ratio in phytoplankton is in the order of 40 (Montani and Maita, 1986) and decreases in sinking particulate matter to 10 - 20 on average in SCS trap material. Glu/ γ-Aba ratios of surface sediment are reduced to values between 1.5 - 8. It has been demonstrated in this study that basic AA are susceptible to climatically induced organic matter alteration in the SCS (Fig. 6). In this regard His as a single AA also traces the decompositional trend, deduced from DI values, of labile organic particles in the deep South China Sea. Moreover, His does not only follow organic matter reactivity in trap samples ($r^2 = 0.52$) but is particularly positively correlated ($r^2 = 0.92$) to the state of organic compounds in deep-sea surface sediments (Fig. 8). This general trend holds true for

Tab. 3. Total particle fluxes, organic carbon and THAA contents as well as organic matter degradation (DI) from sediment trap studies and surface sediment sampling in monsoon-influenced and El Niño influenced regions.

Sediment Traps		Latitude	Longitude	Total Flux	Organic Carbon	THAA	DI
Station	Trap depth [m]	[° N]	[° E]	[mg m^{-2} d^{-1}]	[%]	[mg/g]	
South China Sea							
SCS-NE	1225	17° 16'	119° 31'	98.6	5.17	20.5	0.152
	1765			120.8	3.83	14.3	0.038
	2287			124.8	3.44	11.1	-0.069
SCS-N	1000	18° 28'	116° 01'	89.4	4.39	19.8	0.331
	3350			73.8	2.72	10.2	0.044
SCS-NC	1465	17° 04'	117° 11'	83.5	5.78	22.1	0.261
	3500			87.3	4.11	13.1	0.070
SCS-C	1191-1225	14° 39'	115° 08'	78.4	5.22	20.4	0.320
	3728-3774			70.3	3.39	12.2	0.061
SCS-SW	1246	11° 54'	110° 01'	248.8	3.50	14.1	0.016
Bay of Bengal[a]							
NBBT	750-970	17° 27'	89° 36'	111.0	7.61	43.2	0.95
	1730-2030			129.3	5.61	18.8	0.44
CBBT	900-950	13° 09'	84° 22'	101.1	7.22	29.7	0.58
	2230-2330			140.3	5.44	19.7	0.41
SBBT	1020-1040	04° 28'	87° 19'	93.4	7.28	40.5	1.39
	2980-3010			108.8	5.67	20.0	0.38
Arabian Sea[b]							
WAST	1080	16° 20'	60° 30'	130.0	8.28	31.4	0.85
	2080			218.8	6.94	24.3	0.28
	3020			149.1	6.56	23.7	0.36
CAST	730-1570	14° 31	64° 46'	80.8	8.39	32.6	0.49
	2900			98.4	6.28	23.6	0.26
EAST	1200-1650	15° 31	68° 43'	64.6	8.44	28.9	0.50
	2800			92.3	6.44	17.4	0.33
SAST	1090	13° 09'	67° 08'	122.0	7.89	20.9	0.055
	3050			129.5	6.67	14.6	0.052
Equatorial Pacific[c]							
EP	1357	0° 00'	175° 09'	40.0	5.2	27.2	0.21
	4363			36.0	4.2	12.9	0.19

Surface Sediments	Latitude	Longitude	Water depth	Organic Carbon	THAA	DI
	[° N]	[° E]	[m]	[%]	[mg/g]	
South China Sea						
SO-95 17927-1 (SCS-NE)	17° 19'	119° 28'	2800	0.53	0.84	-0.590
SO-50/27 (SCS-N)	18° 26'	116° 01'	3750	0.69	1.17	-1.739
SO-50/90 (SCS-C)	14° 44'	115° 10'	4300	0.56	0.94	-1.565
SO-140/58 (SCS-SW)	11° 55'	110° 01'	1906	0.89	2.03	-1.022
Bay of Bengal[d]						
GB 23 (Station NBBT)	17° 27'	89° 36'	2290	0.86	n.a.	-0.646
GB 14 (Station CBBT)	13° 09'	84° 22'	3290	1.00	n.a.	-0.556
Arabian Sea[b]						
M33 SL-2 (WAST)	16° 13'	60° 16'	4050	1.30	4.01	-0.84
M33 SL-3 (CAST)	14° 25'	64° 34'	3950	0.40	1.31	-1.18
M33 SL-4 (EAST)	15° 35'	68° 34'	3850	0.29	1.02	-1.12
M33 SL-5 (SAST)	10° 02'	65° 00'	4420	0.44	1.13	-1.17
Equatorial Pacific[e]						
EqPac	0° 00'	140° 00'	4600	~1.0	1.87	-1.30

[a]Unger et al. (2005b), [b]Gaye-Haake (unpublished data), [c]Gupta and Kawahata (2000), [d]V. Ittekkot (unpublished data), [e]Lee et al. (2000)
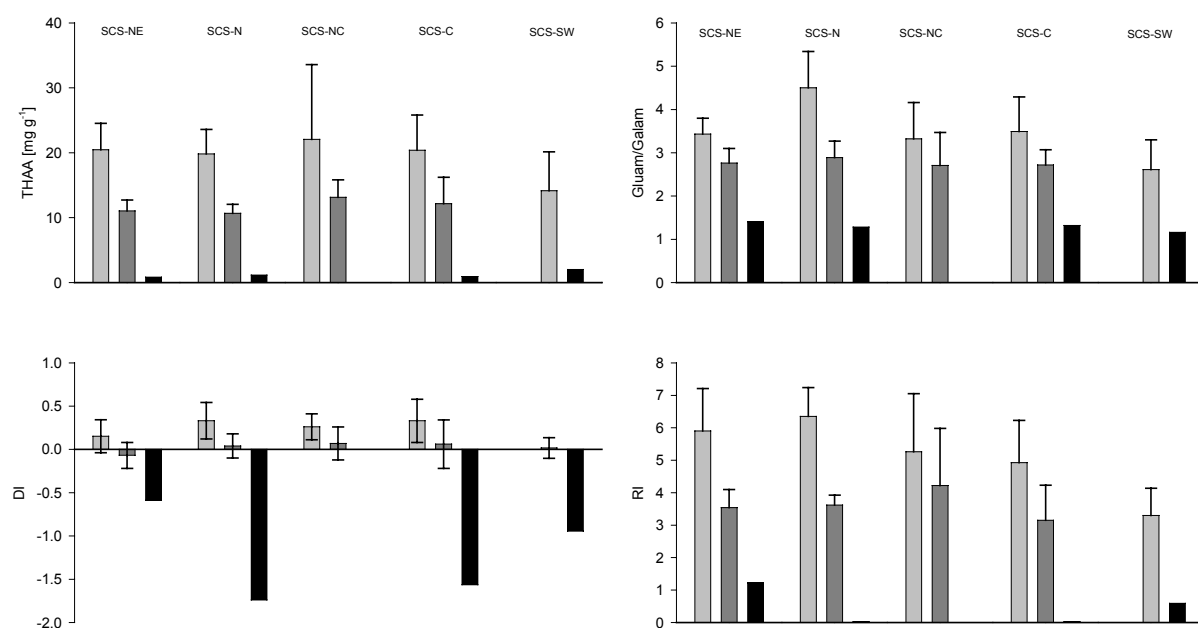
Fig. 10. Organic matter degradation in the deep SCS sea deduced from amino acid and hexosamine compositions. Light grey bars: shallow traps, dark grey bars: deep traps, black bars: surface sediments (0-1 cm). Error bars denote the standard deviation (1 σ). SCS-NC has not been sampled for surface sediments. Decreasing THAA, DI, RI, and Gluam/Galam ratios indicate that the organic matter degradation is most intense at the sediment water interface and largely mediated by microbial activity.

the proteinogenic basic AA Lys and Arg as well and depicts an inverse relationship for the non-proteinogenic AA Orn. Increasing relative Orn concentrations during early diagentic processes caused by enzymatic decomposition of Arg have also been found in other deep-sea studies (e.g., Ittekkot et al., 1984b). Proteinogenic basic AA (particularly Lys) are known for their selective degradation in marine environments (Cowie and Hedges, 1992b; Wang and Lee, 1993; Whelan and Emeis, 1992). They can be relatively enriched in conjunction with high organic matter contents (Keil et al., 2000) or can be protected by the mineral matrix of sediments (Cowie and Hedges, 1992a; Henrichs and Sugai, 1993; Keil et al., 1994).

In the SCS THAA preservation is neither correlated with the relative amount of organic ($r2 = 0.09$) nor with the lithogenic ($r2 = 0.03$) matter. Hence, preservation of labile compounds such as amino acids is coupled either to the *composition* (reactivity) of organic matter (Fig. 8) or to the coinciding varying amounts of clay minerals. Probably, it is a result of both, mineral (lithogenic) and organic material.

Particulate matter in the open SCS changes from a carbonate dominated composition in sinking material to lithogenically dominated (80 - 90 %) surface sediments. Here, carbonate is almost completely dissolved as the sea floor is below the CCD of 3000 m in the northern part (Wei et al., 1998) and 3500-

4000 m in the central part (Calvert et al., 1993; Thunell et al., 1992) of the SCS. Biogenic opal and organic matter are also considerably remineralized. Decreasing organic matter fluxes and concomitantly increasing particle residence time on the sediment surface favours microbial degradation and early diagenetic decomposition of organic substances (Calvert et al., 1993).

It has been shown that Asp concentrations are sensitive to carbonate changes as this acidic AA is adsorbed to carbonate anions (Carter and Mitterer, 1978; Ingalls et al., 2004). A significant mole-% increase of Asp (Fig. 7) in marine sediments is also reported from the Arabian Sea (Haake et al., 1992), the Bay of Bengal (Unger et al., 2005b) and from the equatorial Pacific (Lee et al., 2000) where sufficient carbonate is still present in those deep-sea sediments (Archer, 1996). Skeletal carbonate enriched in Asp and Glu (Constantz and Weiner, 1988; King, 1977; Terashima, 1991) or a $CaCO_3$-matrix that protects organic matter from decomposition (Ingalls et al., 2004), however, are missing in the central SCS as almost complete carbonate dissolution takes place in the deep basin (Calvert et al., 1993; Thunell et al., 1992; Wei et al., 1998). Despite a missing carbonate fraction in the central basin, Asp is the only proteinogenic AA whose relative abundance markedly increases in SCS deep-sea deposits (Fig. 7). The SCS, therefore, documents that AA protection or remineralization is not coupled to a single process. Perhaps clay minerals compensate the loss of
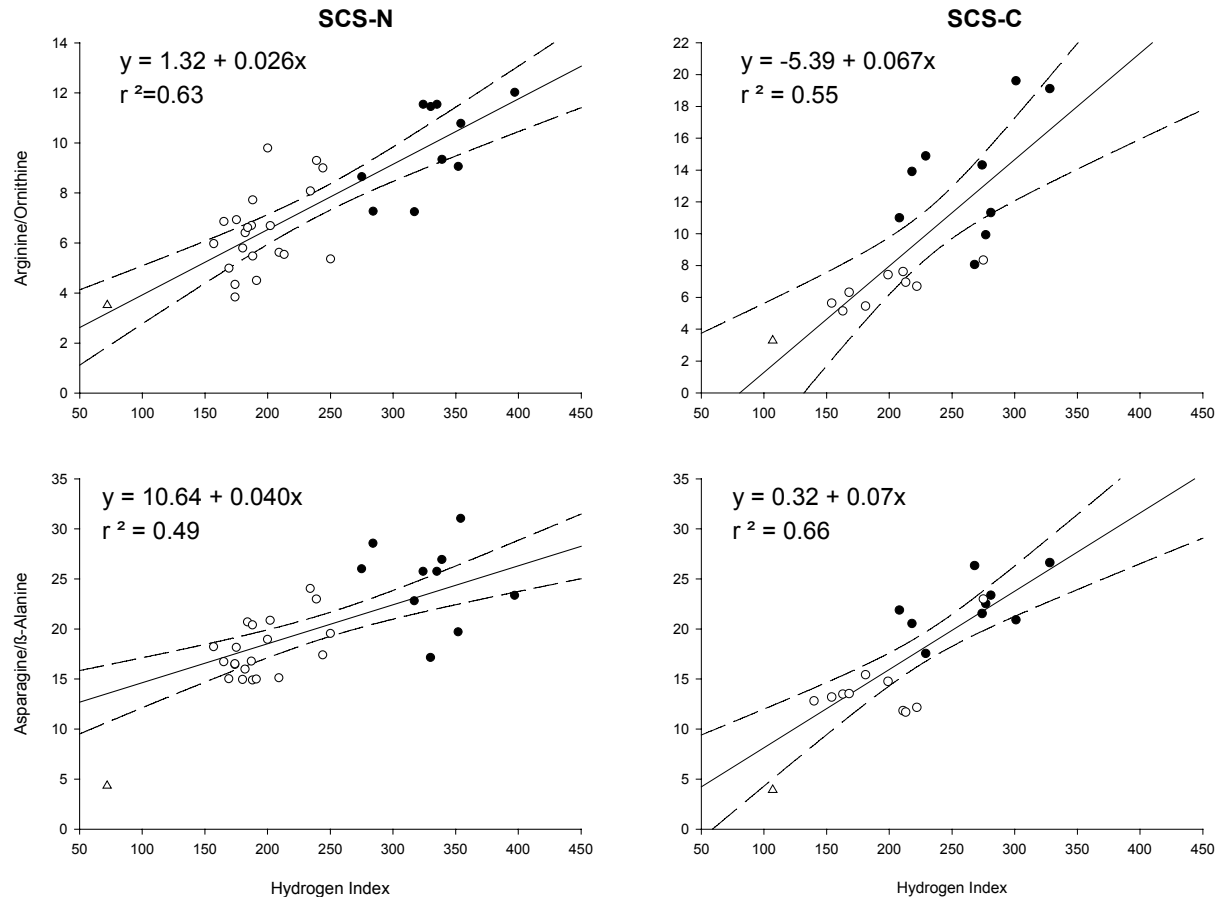
Fig. 11. Amino acid indices (Arg/Orn and Asp/ß-Ala, both molar ratios) compared to the Hydrogen Index (HI). Open circles = shallow traps, solid circles = deep traps, triangles = surface sediments. All figures indicate that nitrogen compounds are preferentially decomposed with increasing water depth whereas lipids and other organic matter are less affected during transport to the deep sea. Separation between shallow and deep traps is also caused by the location of the deep traps as they were moored below the lysocline or CCD (3000 - 3800 m), hence a carbonate matrix, which potentially protects labile organic compounds, is at least partially missing.

carbonates. Adsorbed AA decompose more slowly than dissolved ones (Henrichs, 1992) and can exert a strong affinity to clay minerals (Keil et al., 1994) such as chlorite (Boski et al., 1998) or kaolinite (Hedges and Hare, 1987). It is possible that acidic AA are occasionally decoupled from the carbonate content (Grutters et al., 2001), but it remains unresolved, though, why just solely Asp is being preferentially preserved in SCS deep-sea deposits.

6. Conclusions

Downward particle fluxes in the central SCS reveal a monsoon related seasonality with enhanced fluxes during the SW and NE monsoons. The variability of organic matter composition derived from amino acids and hexosamines is relatively low compared to other monsoon-influenced regions and detached from monsoon seasonality. As opposed to ENSO neutral conditions the reduction of productivity during ENSO warm periods leads to decreasing particle flux rates. Long-year trap investigations showed that organic matter reactivity seems to be reduced during ENSO warm conditions.

Particularly proteinogenic basic amino acids are susceptible to decomposition during El Niño years.

In the central SCS organic matter degradation deduced form amino acid compositions exhibits enhanced decomposition rates of labile components in the deep basin. Compared to other monsoon-influenced regions such as the Arabian Sea or Bay of Bengal, the SCS is characterised by highest organic matter degradation, especially in surface sediments, although similar particle flux rates have been recorded. The AA monomer His traces organic matter degradation, both in trap samples as well as in surface sediments and thus represents a good indicator for early diagenetic alteration in this region.

Station SCS-NE off Luzon does not show any monsoon related seasonality which could be due to special ENSO conditions as sampling was restricted to the El Niño warm phase. Particle fluxes at station SCS-SW off the Vietnamese coastline, on the other hand, are significantly elevated during the same sampling period with a very pronounced, ostensibly monsoon related seasonality. Particle composition, however, point to depletion of fresh organic material. This is also supported by amino acid spectra showing that organic matter during the sampling period is

more degraded compared to the other trap sites. At both stations close to the continental margins lateral advection and resuspension obviously play an important role. Our results therefore imply that seasonally enhanced particle fluxes rather reflect resuspension of surface sediments caused by strong coastal currents than upwelling-induced enhanced productivity.

Acknowledgements

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Publication 2:

Vertical distribution of mesozooplankton and its δ^{15}N signature at a deep-sea site
in the Levantine Sea (eastern Mediterranean) in April 1999

R. Koppelmann, H. Weikert, N. Lahajnar

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Vertical distribution of mesozooplankton and its $\delta^{15}N$ signature at a deep-sea site in the Levantine Sea (eastern Mediterranean) in April 1999

Rolf Koppelmann and Horst Weikert

Institute of Hydrobiology and Fishery Science, University of Hamburg, Hamburg, Germany

Niko Lahajnar

Institute for Biogeochemistry and Marine Chemistry, University of Hamburg, Hamburg, Germany

[1] Mesozooplankton samples were collected throughout the water column in the 4270 m deep Ierapetra basin, 30 nm SE off Crete, in April 1999. Information on trophic relationships within mesozooplankton size classes (<0.5, 0.5–1, 1–2, and 2–5 mm) and the sources of diet were obtained by measuring the composition of stable nitrogen isotopes of size-fractionated zooplankton and particles collected by sediment traps. Compared to data from the Arabian Sea, the $\delta^{15}N$ values of zooplankton were markedly lower in the Levantine Sea. Data from the upper 250 m (2–3‰) suggest that N_2 from the atmosphere was used by diazotroph cyanophycea as a nitrogen source for primary production. A loop system is hypothesized by which isotopically light NH_4^+ is recycled and used by phytoplankton. In the deep mesopelagic zone, an increase in $\delta^{15}N$ with increasing depth was observed. In the deep bathypelagic zone, the $\delta^{15}N$ values were more or less stable and indicate a trophic level of ~2.5. A first zooplankton analysis revealed that juveniles of the calanoid copepod *Lucicutia longiserrata,* one of the rare true deep-sea species in the Levantine basin, were predominant in this zone. The taxonomic composition as well as the vertical distribution of zooplankton in the large habitat zones resembled that in January 1987, before the onset of a hydrological shift in the eastern Mediterranean. We therefore suggest that the situation in April 1999 does not characterize the mode of nitrogen transfer during the EMT. *INDEX TERMS:* 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4815 Oceanography: Biological and Chemical: Ecosystems, structure and dynamics; 4855 Oceanography: Biological and Chemical: Plankton; 4870 Oceanography: Biological and Chemical: Stable isotopes; *KEYWORDS:* Mesozooplankton, trophic relationships, stable isotopes, eastern Mediterranean, Levantine Sea

1. Introduction

[2] The deep-sea ecosystem depends mostly on organic material from the epipelagic zone. The food is transferred into greater depth by the vertical migration of plankton and micronekton [see *Vinogradov*, 1968; *Vinogradov and Tseitlin*, 1983] in the form of gut contents and as a result of predation at depth [*Angel*, 1989; *Longhurst and Harrison*, 1989], but to a larger extent by sinking of particulate organic material [*Angel*, 1984; *Fowler and Knauer*, 1986]. Stable isotope tracing is becoming an increasingly important tool in studies of aquatic food webs in limnic as well as marine ecosystems [e.g., *Hobson et al.*, 1995; *Yoshii et al.*, 1999]. Since the $\delta^{15}N$ values of animals reflect their diets, the isotopic signature of an organism provides integrated information about its feeding habits

over longer time periods. This method allows some insight into the so far unknown functional mode of biomass transfer in the eastern Mediterranean from the surface down to great depths (>4000 m).

[3] The eastern Mediterranean is an oligotrophic semi-enclosed sea in an arid region. This basin has been described as the most impoverished one among the seas, in terms of dissolved nutrients [*Redfield et al.*, 1963] and phytoplankton production [*Dugdale and Wilkerson*, 1988, and references therein], though the estimates of annual production do not take into account short time processes that can locally stimulate new production [*Krom et al.*, 1991]. The hydrographic conditions indicate higher salinities and temperatures than in the open ocean, even in the deepest part (>4000 m) of the basin, with salinities around 38.65 PSU and temperatures around 13.6°C. In 1988/1989 a change in hydrography occurred [*Roether et al.*, 1996]: Owing to cold winters and reduced precipitation in summer [see *Theocharis et al.*, 1999], cold and salty water has
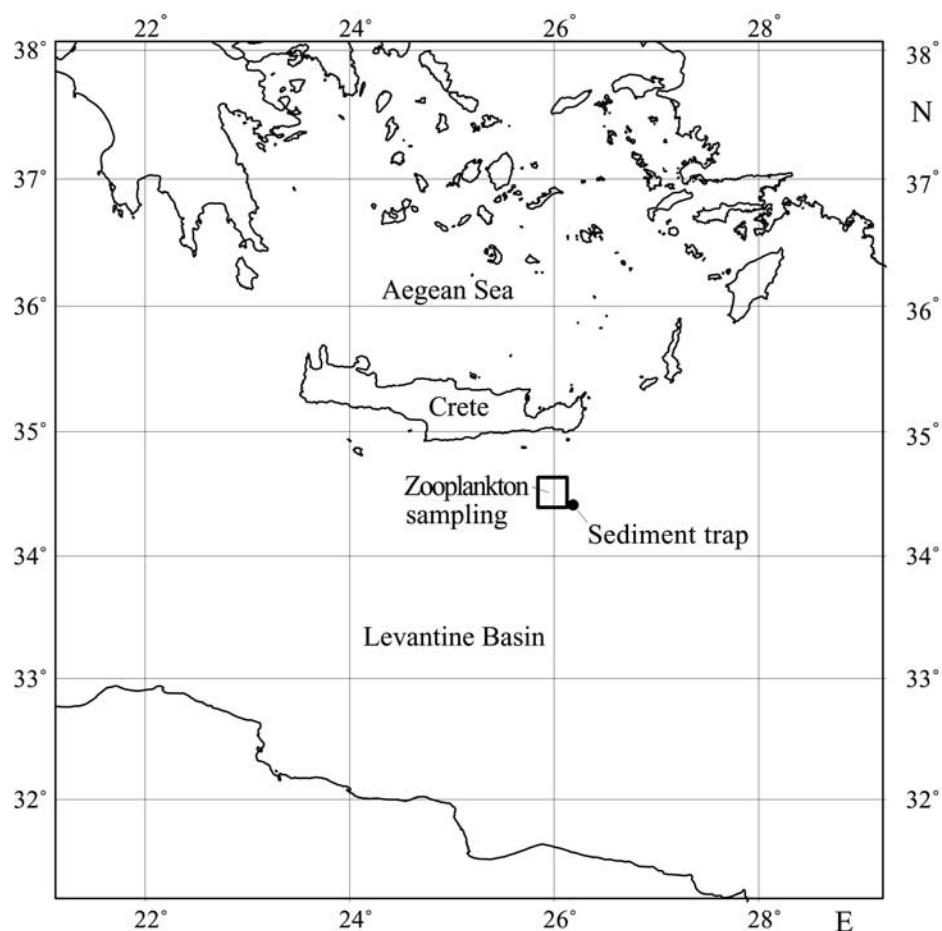
Figure 1.   The sites of zooplankton sampling and sediment trap deployment in the deep Levantine basin in April 1999.

developed in the area of the Aegean Sea. The outflow of the dense water into the Levantine basin with a rate of approximately 1 Sverdrup [*Theocharis et al.*, 1999] replaced the formerly Adriatic Water in the deep interior of the basin. As a result, the nutricline rose by about 100 m and is now found within the euphotic zone for large parts of the eastern Mediterranean [*Klein et al.*, 1999]. The change is called the Eastern Mediterranean Transient (EMT).

Table 1.   Zooplankton Sampling Data From the Iearapetra Basin (34°30′N, 26°00′E)[a]

Haul No.	Date	Local Time	Maximum Water Depth, m	Sampling Intervals, m
MOC 12-B	20 April 1999	1921–2318	4260	4100–4000–3750–3500–3250–3000–2750–2500–2250–2010–1850–1650–1450–1250–1050–900–750
MOC 15-B	26 April 1999	1904–2240	4260	4250–4000–3750–3500–3250–3000–2750–2500–2250–2041–1850–1650–1450
MOC 16-B	27 April 1999	0659–1005	4255	4250–4000–3750–3500–3250–3000–2750–2500–2250–2050–1850–1650–1450
MOC 17-B	27 April 1999	1339–1526	4045	1450–1250–1050–900–750–600–450–400–350–300–250–200–150–100–50–0
MOC 18-I	27 April 1999	2104–0033	4262	4250–3500–3000–2500–2000–1500–1000–500–250–0
MOC 19-B	28 April 1999	0628–0921	4258	4250–4000–3750–3500–3250–3000–2750–2500–2250–2050–1850–1650–1450
MOC 21-B	29 April 1999	0025–0203	4264	1450–1250–1050–900–750–600–450–400–350–300–250–200–150–100–50–0
MOC 22-B	29 April 1999	1039–1215	4041	1450–1250–1050–900–750–600–450–400–350–300–250–200–150–100–50–0
MOC 23-I	29 April 1999	1843–2157	4261	4250–3500–3000–2500–2000–1500–1000–500–250–0
MOC 24-B	1 May 1999	2242–0048	4261	1450–1250–1050–900–750–600–450–400–350–300–250–200–150–100–50–0

[a]B, biomass samples; I, stable isotope samples.

Table 2. Standing Stock of Zooplankton Groups in the Upper 250 m of the Levantine Basin During Night and Their Predominant Feeding Categories[a]

Taxon	<0.5 mm	0.5−1 mm	1−2 mm	2−5 mm
Herbivorous Zooplankton				
Cladocera	1.2	0.0	0.0	0.0
Gastropoda	75.7	5.6	4.6	0.1
Pteropoda	83.8	55.4	46.2	1.6
Appendicularia	4.1	4.4	1.9	0.2
Thaliacea	9.1	27.5	17.6	0.8
Calanus spp.	13.7	110.8	63.0	0.4
Spinocalanidae	3.5	14.7	1.0	0.0
Clausocalanus spp.	204.0	408.8	62.8	0.9
Calocalanus spp.	20.2	38.2	4.8	0.1
Omnivorous Zooplankton				
Ostracoda	564.9	367.9	50.9	1.0
Cypris-Larvae	1.0	0.0	0.0	0.1
Mysidacea	0.1	0.7	0.7	0.1
Euphausiacea	73.5	219.8	607.1	27.1
Corycaeus spp.	637.7	1482.9	294.8	14.4
Oncaeidae	149.0	70.2	17.2	0.7
Sapphirinidae	21.4	81.0	48.7	3.4
Pontoeciella abyssicola	8.7	0.5	3.0	0.0
Harpacticoida	1.5	1.8	0.9	0.2
Acartia spp.	10.9	15.7	2.7	0.3
Aetideidae	10.0	184.4	81.0	4.1
Haloptilus spp.	107.0	1111.0	1276.0	71.2
Centropages spp.	3.7	13.8	10.7	0.6
Calanidae	1.8	260.0	306.3	10.1
Eucalanus spp.	0.7	32.6	65.6	5.2
Lucicutia spp.	145.5	651.6	164.7	11.3
Mecynocera clausi	63.3	36.0	24.6	1.2
Pleuromamma spp.	48.5	459.0	429.4	62.1
Temora stylifera	117.3	321.5	92.6	1.2
Scolecithrichidae	219.5	452.4	55.3	0.6
Carnivorous Zooplankton				
Medusae	0.0	0.1	3.4	0.4
Polychaeta	26.9	71.6	84.6	4.8
Amphipoda	12.4	63.1	61.9	2.8
Decapoda	6.7	12.9	7.5	0.1
Heteropoda	1.8	5.8	5.3	0.5
Chaetognatha	12.4	101.8	99.8	9.0
Fish larvae	0.7	9.1	23.0	1.0
Oithona spp.	281.2	297.3	73.2	4.8
Euaugaptilus spp.	0.1	7.0	4.3	0.3
Heterorhabdus spp.	1.5	28.4	34.3	1.1
Candacia spp.	5.4	36.1	56.0	3.6
Euchaeta spp.	34.4	135.1	208.1	23.0
Pontellidae	0.1	1.2	1.0	0.0
Undetermined				
Larvae, div.	11.9	97.8	19.0	1.1
Calanoida, div.	117.7	120.7	43.8	2.2
Calanoida nauplii	1.6	0.9	0.0	0.1
Calanidae, juv.	30.2	125.6	45.2	1.5
Arietellus spp.	0.0	0.3	0.0	0.1
Augaptilidae, div.	0.0	1.5	1.7	0.1

[a]Units are in individuals m^{-2}.

[4] In 1993, *Weikert* [1995] found surprisingly high amounts of zooplankton in the deep-sea southeast off Crete. The spectacular increase in zooplankton abundance by a factor of 56 in the bathypelagic zone (>1000 m) as compared to samples taken in 1987 was caused by a mass development of two calanoid copepods, *Calanus helgolandicus* and *Eucalanus monachus* [*Weikert et al.*, 2001]. The former species was found for the first time in abundant numbers in the Levantine Sea. The authors supposed that this species, when expatriated by currents from the northern,

temperate parts of the eastern Mediterranean into the basin, found favorable conditions after the hydrographical change. The life cycle of these coarse filterers and related species is subject to the availability of food in tropical and subtropical seas, and maximum abundances are intimately linked with blooms of phytoplankton induced by eutrophication events [*Heinrich*, 1986; *Smith*, 1995, and references therein].

[5] In this paper, we will inform about the gross patterns of zooplankton biomass fractionated into size classes, and its faunal composition in the water column at the Cretan site approximately 12 years after the onset of the EMT. On the basis of this information and the depth-related δ^{15}N composition of the mesozooplankton, we try to give a first insight in the mode of nitrogen transfer in the local plankton community and the trophic pathways within the zooplankton assembly. An attempt is made to set the results in context to the EMT.

2. Material and Methods

[6] Mesozooplankton samples were taken by oblique hauls (towing speed: 2 knots) with the use of a 1m^2-Double MOCNESS (Multiple Opening and Closing Net and Environmental Sensing System [*Wiebe et al.*, 1985]) in the 4270 m deep Ierapetra basin, ~30 nm SE off Crete (34°30′N, 26°00′E; Figure 1) between 20 April and 1 May 1999 during cruise M44/4 of the R/V *Meteor* [*Weikert et al.*, 2000]. The MOCNESS was equipped with 18 nets of 333 μm mesh aperture and two nets of 100 μm mesh aperture. Results from the fine mesh sizes are not used in this paper.

[7] Sampling intervals for biomass determination were 50 m down to 450 m, 150 m down to 1050 m, 200 m down to 2250 m, and 250 m below this depth (Table 1). In total, four full depth profiles were obtained at the sampling site. Each profile consisted of two hauls with a total of 27 samples. In the upper 1050 m, two profiles were taken during the day and the night, each. In the bathypelagic zone, below 1050 m, no day/night discrimination was performed since diel vertical migrations of zooplankton are supposed to be of minor importance at these depths [*Angel et al.*, 1982]. Upon recovery of the MOCNESS, the nets were rinsed with seawater and the plankton was preserved immediately in a formaldehyde-seawater solution buffered with sodiumtetraborate [*Steedman*, 1976]. In the laboratory (~1 year later), the samples were sieved, and the fractions of <0.5 mm, 0.5−1 mm, 1−2 mm, 2−5 mm, and >5 mm wet weighed according to the method of *Tranter* [1962], including small amounts of foraminiferans. Instead of a more precise dry weight determination, this method was used to allow a taxonomic analysis of the entire sample, which is, especially in the deep-sea, too small to make

Table 3. Sediment Trap Sampling Data and δ^{15}N Values of POM[a]

Sample No.	Sample Depth, m	Time Interval	δ^{15}N, ‰
MID-S 1−4	700	9−13 Feb. 1999	1.15
MID-D 1−5	2700	30 Jan. to 16 Feb 1999	2.48
MID-D 6−9	2700	16 Feb. to 2 March 1999	2.36
MID-D 10−13	2700	2−16 March 1999	1.95
MID-D 14−17	2700	16−30 March 1999	2.32
MID-D 18−21	2700	30 March to 13 April 1999	1.74

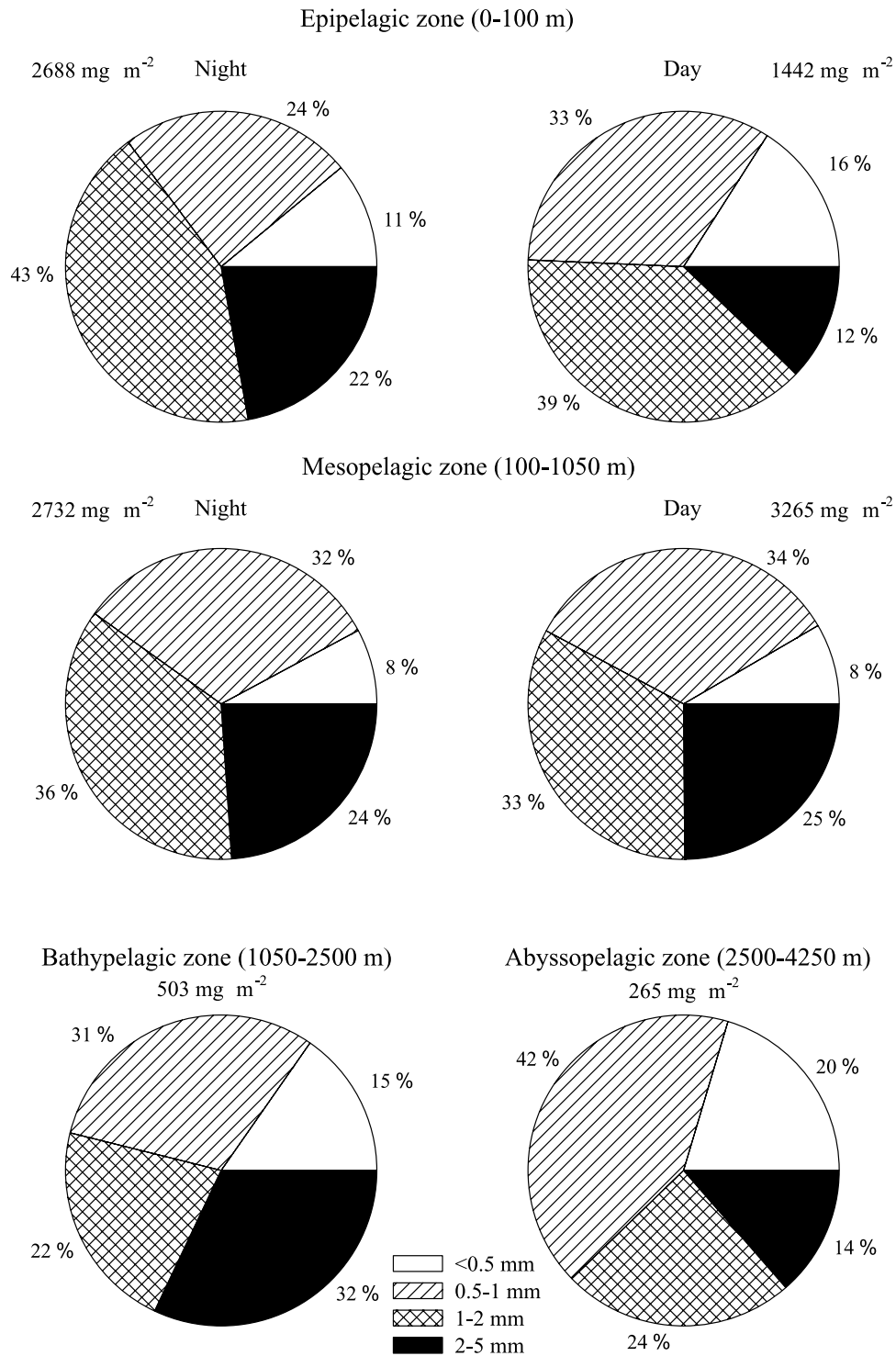[a]Position, 34°25.90′N, 26°10.75′E. Water depth, 3750 m.

Figure 2. Standing stock of zooplankton biomass (wet weight) and the percentage contributions of four size classes in the large habitat zones at the deep-sea site SE off Crete.

subsamples. In this paper, we only report on sizes <5 mm, termed mesozooplankton [*Weikert and Trinkaus*, 1990]. The fractionated metazoan zooplankton was sorted into its main groups. Carcasses, according to *Wheeler* [1967] and *Weikert* [1977], were counted separately. The copepods were identified at the family or genus level, abundant taxa of them at the species level. The zooplankton of the upper 250 m

(Table 2) was grouped into three classes of dietary preference (herbivores, omnivores, carnivores) and one undetermined class according to the relevant literature [*Turner*, 1984, 1986; *Longhurst*, 1985] and data compiled by *Mauchline* [1998].

[8] For the analysis of stable nitrogen isotopes, two additional night profiles, consisting of nine samples, each, were performed (Table 1). The material was rinsed with
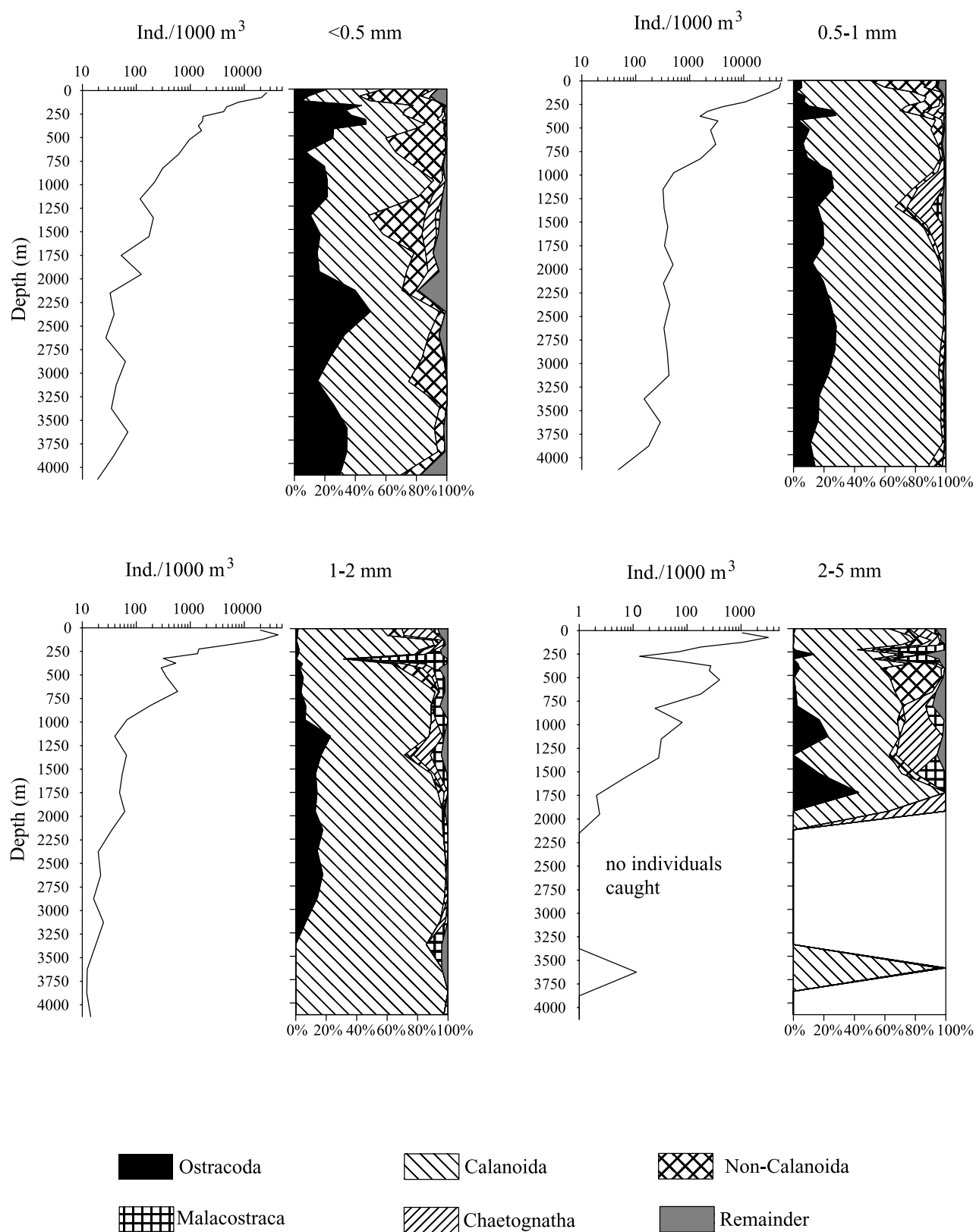
Figure 3. Vertical distribution of zooplankton individuals of different size classes (above 1050 m only night values) and the relative composition of the main groups.
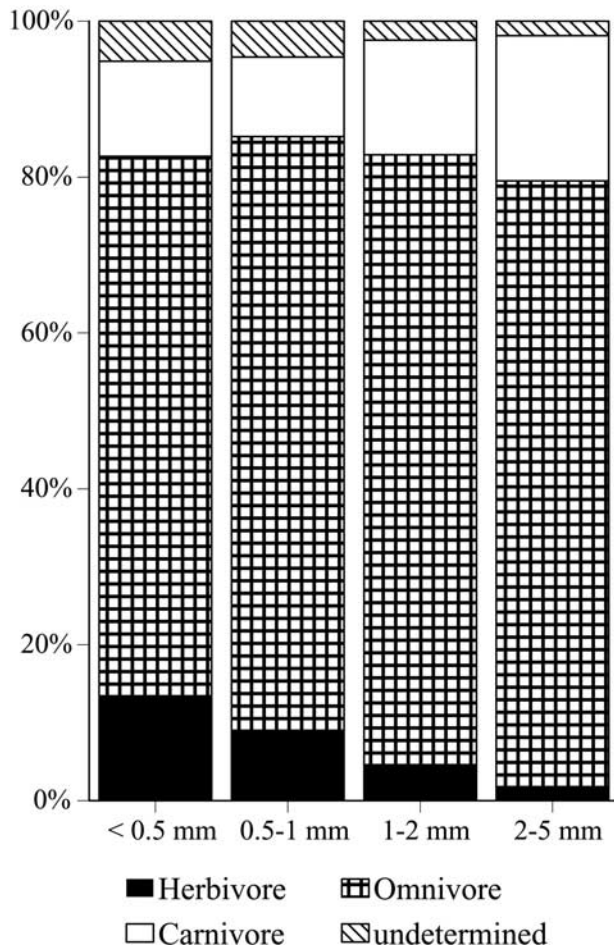
Figure 4. Trophic composition of different zooplankton size classes in the upper 250 m of the water column during night.

freshwater and fractionated according to the above mentioned method. The material was then dry-frozen at −40° C and pulverized using a pestle for further analyses. Measurements of nitrogen isotope ratios ($\delta^{15}N$) were prepared for combustion in a Carlo Erba NA-2500 Analyzer, from which the evolved N_2 was passed in a continuous flow of helium through a ConFlo II - Interface to a Finnigan MAT 252 isotope mass spectrometer. The analytical error of this method is ≤0.1 ‰. Stable isotope values are expressed in δ notations as parts per thousand (‰), where R is the ratio of $^{15}N/^{14}N$ and the standard is atmospheric nitrogen:

$$\delta^{15}N[‰] = ((R_{sample}/R_{standard}) - 1)*1000.$$

Sediment trap samples for stable isotope analysis were obtained using a time series sediment trap "Parflux Mark 7G-21" (see *Honjo and Doherty* [1988] for the description of a former version of the trap) moored on the 29 January 1999 during cruise 44/1 of R/V *Meteor* [*Jennerjahn and Cremer*, 2000] in the Ierapetra-Deep off Crete (34°25.90′N, 26°10.75′E, 3750 m water depth). The trap had an aperture area of 0.5 m², covered by baffles with 2.5 cm diameter cells with the aspect ratio of 2.5. The mooring was designed to collect settling particles at 700 and 2700 m water depth in

pre-programmed time intervals of 3.5 days between 30 January and 13 April 1999. Initial filling of the sampling cups was de-ionized water with 35 g L^{-1} NaCl and 3.3 g L^{-1} $HgCl_2$ added to avoid organic decomposition. The system was recovered on the 20 April 1999 [*Neumann and Schroll*, 2000] during the period of zooplankton collections. Owing to some malfunctions of the rotation unit, the shallow trap only covered the first time interval at the beginning. Since the vertical flux in the deep trap was very low, sampling material from the initial 3.5 days intervals were combined as shown in Table 3. To separate "swimmers" (organisms actively swimming into the sampling cups), which can increase and qualitatively alter particulate fluxes [e.g., *Karl and Knauer*, 1984; *Lee et al.*, 1988], the samples were carefully sieved into less than 1 mm and greater than 1 mm fractions. Only the fractions less than 1 mm were used for further analyses. The nitrogen stable isotope composition of the dried and gently ground samples was determined according to the method described above.

3. Results

3.1. Zooplankton Distribution and Composition

[9] In the epipelagic zone (0–100 m), highest biomass standing stocks (2688 mg m^{-2} wet weight) were found during the night, whereby the size fractions 1–2 and 2–5 mm made a share of 65% (Figure 2) within the mesozooplankton. During the day, these larger fractions comprised 51%, and the total standing stock was reduced to 1442 mg m^{-2}. In the mesopelagic zone (100–1050 m), day/night differences in the relative abundance of the size
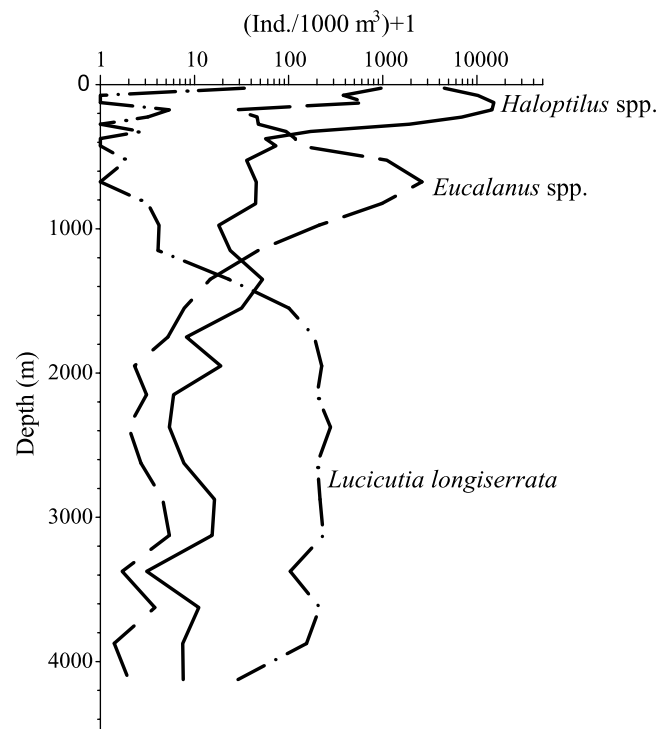

Figure 5. Numerical distribution (sum of the fractions <5 mm) of three prominent calanoid copepods (*Haloptilus* spp., *Eucalanus* spp., *Lucicutia longiserrata*) in the water column of the Levantine basin (above 1050 only night values).

fractions were not visible, but the total standing stock was larger during the day (3265 mg m^{-2}) than during the night (2732 mg m^{-2}). At greater depths, the standing stocks were markedly reduced to 503 mg m^{-2} in the bathypelagic zone (1050–2500 m) and 265 mg m^{-2} in the abyssopelagic zone (>2500 m). Between both habitat zones, there was a remarkable change in size group composition: the larger size fractions (>1 mm) comprised 54% in the bathypelagic zone, but in the abyssopelagic zone its relative portion was reduced to 38%. The 0.5–1 mm size fraction accounted for the largest portion (42%) of the mesozooplankton biomass.

[10] Figure 3 shows that the abundance of individuals is highest in the 0.5–1 mm size classes throughout the water column followed by the <0.5 mm and the 1–2 mm fractions. The abundance of the 2–5 mm size class was lowest. In the 0.5–1 and 1–2 mm size class calanoid copepods were the main contributors, whereas in the smallest size class (<0.5 mm) ostracods and noncalanoid copepods gained higher importance. In the 2–5 mm fraction malacostraceans showed an enhanced relative abundance.

[11] The trophic composition of the zooplankton was studied for the upper 250 m, which corresponds to the upper sampling interval for the stable isotopic composition. In this zone, where the primary production is modified into sinking particulate matter for the dietary requirements of the deep-sea fauna, omnivores were most important and showed a slight relative increase with increasing size classes from 69.4% to 78.4% (Figure 4). The importance of the herbivorous zooplankton decreased with increasing size from 13.2 to 1.5%. With regard to the total zooplankton, herbivorous animals like euthecosomatous Pteropoda and Tunicata, which are capable of ingesting picophytoplankton, made a share of 3.1% in the smallest size class (<0.5 mm), 1.2% in the 0.5–1 mm size class, 1.5% in the 1–2 mm size class, and 0.9% in the largest group (2–5 mm). Carnivores were most abundant in the 2–5 mm size group (18.7%).

[12] Figure 5 shows a vertical succession of numerically predominant calanoid copepod taxa: *Haloptilus* spp. was abundant in the upper 250 m, comprising 16.6% of the total zooplankton, *Eucalanus* spp. between 250 and 1050 m (27.3%), and *Lucicutia longiserrata,* one of the rare true deep-sea species in the Levantine basin, resided in depths below 1050 m (37.8%). This mode of distribution, which is characterized by the absence of *Calanus helgolandicus,* was already described for the Levantine basin by *Weikert and Trinkaus* [1990] and *Weikert and Koppelmann* [1993].

3.2. Stable Isotope Distribution

[13] The $\delta^{15}N$ values of the different mesozooplankton size classes were very similar in the upper 1000 m (Figure 6). A closer look at the $\delta^{15}N$ values of the mesozooplankton size classes in the upper 250 m of the eastern Mediterranean revealed that the difference between the smallest size class (<0.5 mm; 2.0 ‰) and the largest size class (2–5 mm; 3.1‰) was 1.1‰. Between 250 and 1000 m, the $\delta^{15}N$ values slightly increased to 4–6 ‰. At greater depths, the amount of material was to small to evaluate the full spectrum of size classes. Among the analyzed fractions, the 0.5–1 mm size class indicated the highest $\delta^{15}N$ values, which increased from approximately 6‰ at 1000 m to 11.5‰ at 2500 m. Below 2500 m, in the
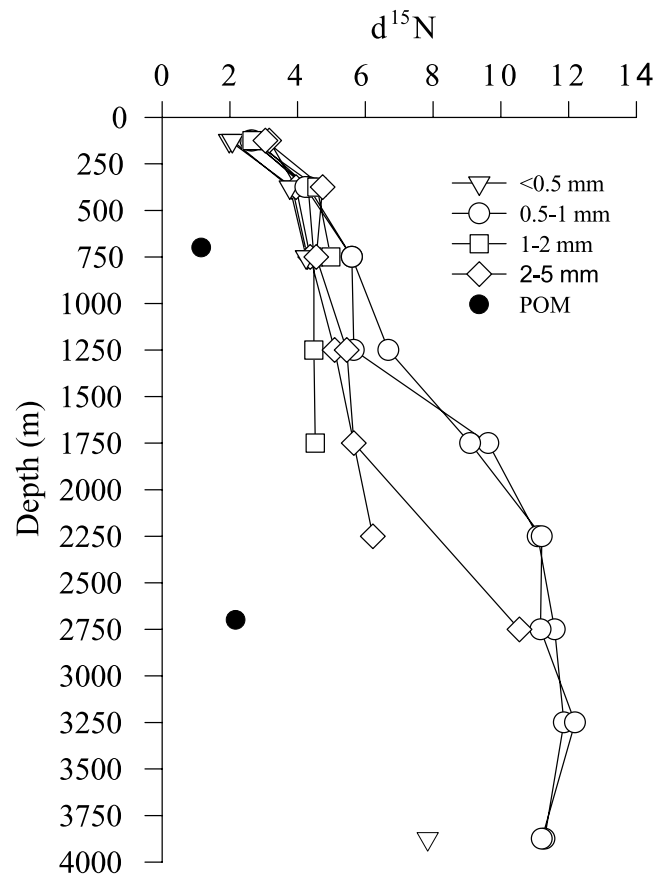

Figure 6. Vertical distribution of $\delta^{15}N$ values (night samples) for different mesozooplankton size classes and particulate organic matter (mean value) from sediment traps at the deep-sea site SE off Crete.

abyssopelagic zone, the values were more or less stable, ranging around 11‰.

[14] The $\delta^{15}N$ values of sinking particulate organic matter (POM) were 1.2‰ at 700 m but varied between 1.7 and 2.5‰ in the samples at 2700 m, without any significance of a temporal trend between January and April (Table 3).

4. Discussion
4.1. Trophic Interactions in the Upper Ocean

[15] Compared with $\delta^{15}N$ values of mesozooplankton obtained by identical methods in the Arabian Sea [*Koppelmann and Weikert,* 2000], the values from the Levantine basin were approximately 4–6‰ lower in all size classes and in all depths zones, but with two exceptions (Figure 7). In the central Arabian Sea (CAST), similarly low $\delta^{15}N$ values were found for the 1–2 mm and the 2–5 mm fractions between 250 and 500 m in April 1997. These findings can help to explain our data from the Levantine Sea.

[16] During April in the spring intermonsoon, filamentous diazotroph Cyanophycea (*Trichodesmium* spp.) are abundant in the Arabian Sea [*Veldhuis et al.,* 1997; *Capone et al.,* 1998] and probably lower the $\delta^{15}N$ baseline within the food web in the surface layer [*Montoya et al.,* 2002]. *Carpenter et al.* [1997] compiled stable nitrogen isotope
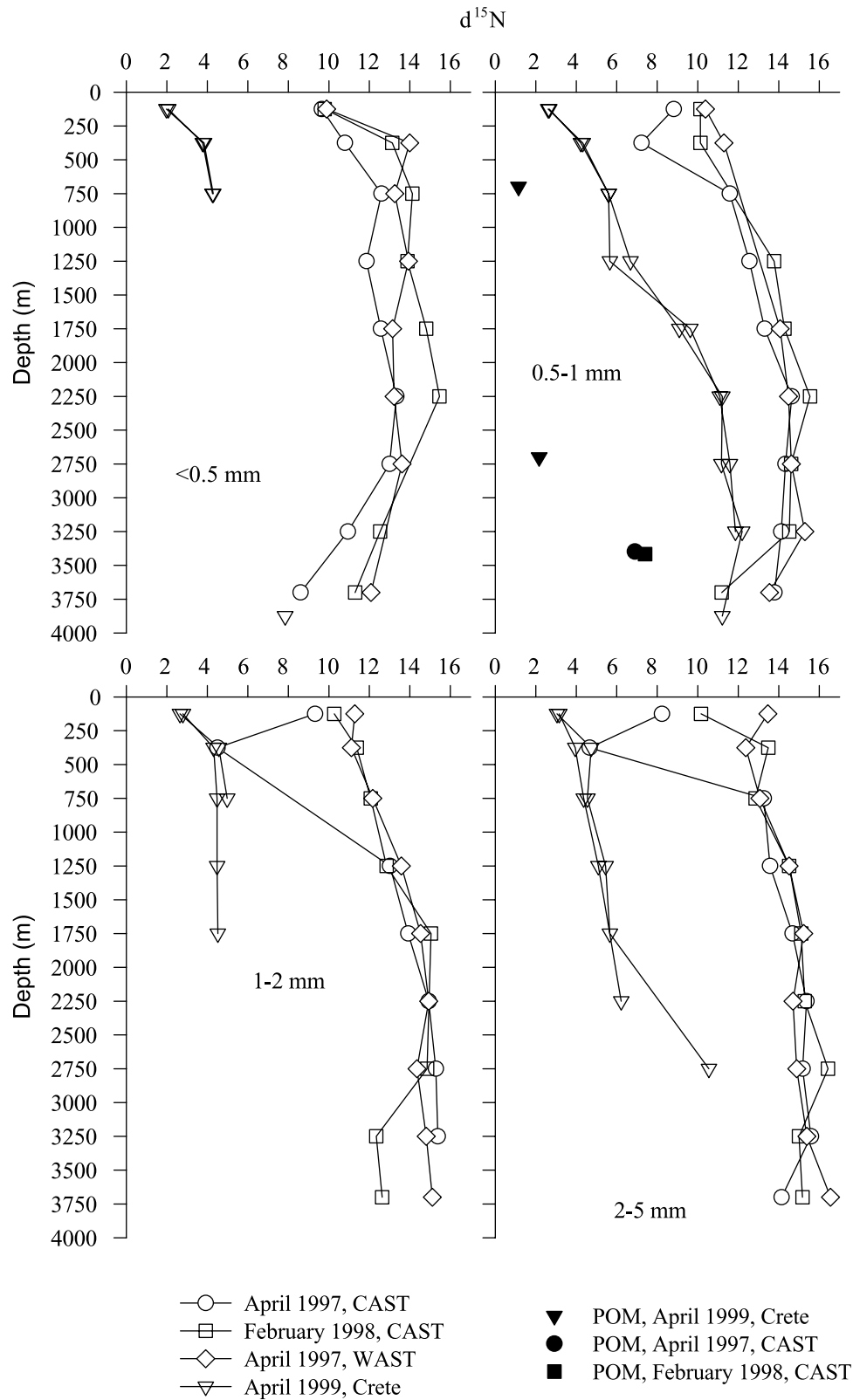
Figure 7. Vertical distribution of $\delta^{15}N$ values for different mesozooplankton size classes and particulate organic matter at the deep-sea site in the Levantine basin compared to the Arabian Sea (data from *Koppelmann and Weikert* [2000] and unpublished results). WAST, Western Arabian Sea Sediment Trap station; CAST, Central Arabian Sea Sediment Trap station.

data of zooplankton from different areas of the world oceans. The authors found values between 5.5 and 9.0‰ in "*Trichodesmium*-free" areas, but values between 2.1 and 5.9‰ in areas were *Trichodesmium* was present. Since atmospheric nitrogen is used as the standard for the calculation of the $\delta^{15}N$ values, N_2-fixing organisms normally range between 0 and 1‰ [*Mullin et al.*, 1984; *Carpenter et al.*, 1997]. If the larger, diel migrating zooplankton will feed at the surface at night on a diet with a low $\delta^{15}N$ signature, generated by the microbial loop, the migrators likely will transport the low $\delta^{15}N$ signal to the daytime residence depth in the mesopelagic zone.

[17] In April 1999, when our sampling took place, nutrients like phosphate, nitrate and nitrite were at very low concentrations in the surface layer of the Levantine Sea [*Kress*, 2000]. Generally, *Synechococcus* spp., small, coccoid nitrogen-fixing Cyanobacteria, were found to be prominent in the basin under oligotrophic conditions [*Li et al.*, 1993; *Detmer*, 1995]. *Zehr et al.* [2001] stated recently that these cyanobacteria are abundant enough to potentially have a significant role in N dynamics in the oligotrophic open Pacific Ocean. The very low $\delta^{15}N$ values in the surface (0−250 m) zooplankton of the Levantine Sea (Figure 6) fit the hypothesis that the $\delta^{15}N$ baseline in the food web is low due to the use of atmospheric nitrogen for primary production.

[18] The $\delta^{15}N$ value of the zooplankton diet can be calculated by subtracting 3.6‰ from the values of the zooplankton size classes, since 3.6‰ is the mean value of $\delta^{15}N$ increase from one trophic level to the next higher level [*Minagawa and Wada*, 1984; *Hobson and Welch*, 1992]. This results in a low $\delta^{15}N$ value of approximately −1.6 ‰ for the diet of the smaller zooplankton (<0.5 mm), which shows the highest portion of opportunistic picophytoplankton-feeders and herbivorous coarse filter feeders among the size classes (Figure 4). The higher $\delta^{15}N$ value of the 2−5 mm zooplankton size class results in a value of −0.5 ‰ for its diet. *Haloptilus* spp. and *Pleuromamma* spp. (Copepoda: Calanoida), which are considered to be omnivores [see *Hopkins*, 1985], are predominant in this size group. These yet low values, however, cannot be explained by the fixation of atmospheric nitrogen alone (see above). We therefore hypothesize that a loop system (Figure 8) seemed to be active in the Levantine Sea by which isotopically light NH_4^+ [*Checkley and Miller*, 1989] is recycled and used by pico- and nanophytoplankton, which are common in the Levantine basin [see *Li et al.*, 1993; *Detmer*, 1995]. It is known from the western Mediterranean Sea that excreted ammonia is able to supply up to 43% of the phytoplankton nitrogen demands [*Alcaraz et al.*, 1994]. Since in our study the standing stocks of tunicates and euthecosomatous pteropods, the only metazoan zooplankters which can directly feed on picophytoplankton [see *Turner*, 1984; *Deibel*, 1982], are small, protozoans would be the mediating link between the primary producers and metazoan zooplankton.

4.2. Deep-Ocean Processes

[19] The $\delta^{15}N$ baseline of the export flux is set at a low level in the epipelagic zone of the Levantine Sea, so that sinking particles contain more isotopically light nitrogen than particles in the Arabian Sea (Figure 6). *Kerhervé et al.* [2001] also found low $\delta^{15}N$ values (between 0.6 and −1.9‰) in sinking particles in the western Mediterranean
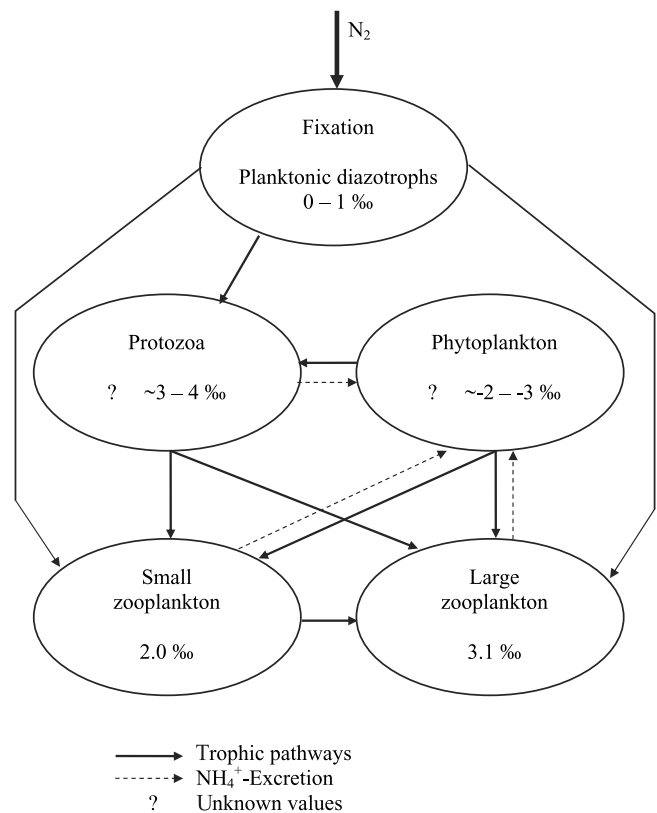
Figure 8. A hypothetical picture of pathways of different trophic levels in the surface layer at the deep-sea site in the Levantine basin.

Sea. These low values probably have caused relatively low $\delta^{15}N$ values in the zooplankton (Figure 7). Notwithstanding, a $\delta^{15}N$ increase in zooplankton with increasing depth could be detected in the deep mesopelagic zone and at bathypelagic depths in the Arabian Sea as well as in the Levantine Sea. Primary diet in the deep-sea [see *Angel*, 1990] is supposed to be provided largely by sinking particulate organic matter (POM) which will be decomposed and re-aggregated on the way through the water column by physico-chemical and biological activity [*Alldredge and Silver*, 1988; *Lampitt*, 1992; *Steinberg et al.*, 1998, and references therein].

[20] In the Levantine basin, the difference in $\delta^{15}N$ between POM and the zooplankton (0.5−1 mm) was 4.4‰ at 700 m depth and 9.1‰ at 2700 m depth (Figure 6), indicating that the length of the food chain increases with increasing depth. The trophic level (TL) of the zooplankton can be calculated by subtracting the $\delta^{15}N$ value of POM (TL = 0) from the $\delta^{15}N$ value of the zooplankton and dividing this result by 3.6, the mean value of trophic level increase [*Minagawa and Wada*, 1984; *Hobson and Welch*, 1992]. The TL of the zooplankton is around 1.2 at 700 m depth, suggesting a more or less direct feeding on POM, whereas at a depth of 2700 m, the 0.5−1 mm size group (not enough material is available from the other size classes for the analysis) lives at a TL of 2.5. The same size group from the Arabian Sea exhibited at a similar TL of 2.1. At depth in the Levantine Sea, the mesozooplankton was dominated by the calanoid copepod *Lucicutia longiserrata*. One may
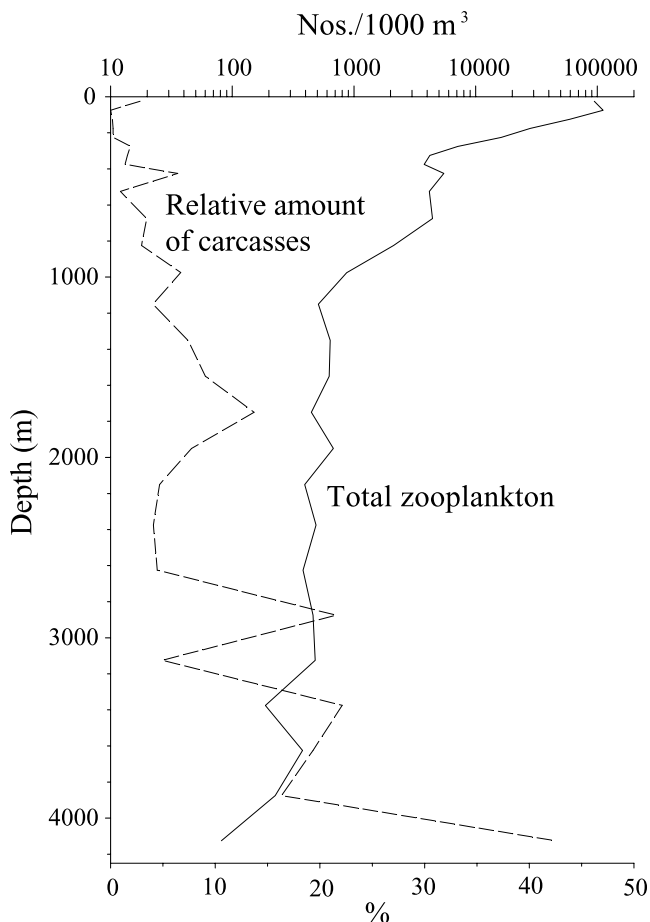
Figure 9. Vertical distribution of zooplankton numbers (sum of the fractions <5 mm) and the relative portion of carcasses to total zooplankton (above 1050 only night values).

suggest that these animals depend on small zooplankton or protozoans that fed on POM. Protozoans were found associated with aggregates in the deep Levantine Sea (H. Arndt, personal communication, 2002). On the other hand, selective feeding on carcasses cannot not be ruled out. *Roe* [1988] stated that copepod carcasses are potentially very important food sources for the deep sea. Our results also show a trend toward increased numbers of carcasses relative to living zooplankton with increasing depth (Figure 9), but *Yamaguchi et al.* [2002] found in the subarctic Pacific that copepod carcasses alone are not sufficient as a food source for detritivores. Probably different pathways for the nutrition of deep-sea plankton exist, including pulses of freshly organic particulate matter from the surface [*Koppelmann and Weikert*, 1999]. There is, however, no sound information available about trophic interactions in the deep sea of the oceans.

4.3. Summary Statement

[21] In April 1999, the zooplankton composition (Figures 3 and 5) and vertical distribution (Figure 9) in the Levantine Sea resembled that of January 1987 but both figures are very different from the situation found in June 1993 [*Weikert et al.*, 2001]. We therefore suggest that the results on trophic interactions in the Levantine Sea probably

do not reflect the situation that may have prevailed in 1993 when the Aegean outflow was strongest [*Theocharis et al.*, 2002] during the EMT, but likely describe the situation found in January 1987, before the onset of the event. Hydrographical data from the 1997 to 1999 period reveal a strong reduction of Aegean deepwater outflow into the eastern Levantine Sea [*Theocharis et al.*, 2002]. The outflowing Cretan Deep Water is no longer dense enough to reach the bottom of the adjacent basins, but ventilates layers between 1500 to 2500 m. In the epipelagic zone, a loop system seemed to exist in April 1999 by which atmospheric nitrogen and excreted isotopically light ammonium is used for primary production. This system generates an export flux of POM with a low $\delta^{15}N$ signature. In the deep-sea, the difference in $\delta^{15}N$ between POM and zooplankton increases, indicating an increase in the length of the food chain. Although the $\delta^{15}N$ values of zooplankton are still lower than in the open Arabian Sea, the length of the food chain does not indicate any differences, despite the fact that the deep Mediterranean Sea is impoverished in species diversity [see *Scotto di Carlo et al.*, 1984].

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R. Koppelmann and H. Weikert, Institute of Hydrobiology and Fishery Science, University of Hamburg, Zeiseweg 9, 22765 Hamburg, Germany. (koppelmann@uni-hamburg.de)

N. Lahajnar, Institute for Biogeochemistry and Marine Chemistry, University of Hamburg, Bundesstraße 55, 55, 20146 Hamburg, Germany.

Publication 3:

Stable nitrogen isotopic ratios of sinking particles and sediments from the northern Indian Ocean

B. Gaye, N. Lahajnar, K.-Ch. Emeis, D. Unger, T. Rixen, A. Suthhof,
V. Ramaswamy, H. Schulz, A.L. Parobkari, M.V.S. Guptha, V. Ittekkot

Stable nitrogen isotopic ratios of sinking particles and sediments from the northern Indian Ocean

B. Gaye-Haake[a],*, N. Lahajnar[a], K.-Ch. Emeis[a], D. Unger[b], T. Rixen[b], A. Suthhof[b,1], V. Ramaswamy[c], H. Schulz[d], A.L. Paropkari[c], M.V.S. Guptha[c], V. Ittekkot[b]

[a]*Institute of Biogeochemistry and Marine Chemistry, University of Hamburg, Bundesstraße 55, D-20146 Hamburg, Germany*
[b]*Center for Tropical Marine Ecology, Fahrenheitstraße 6, D-28359 Bremen, Germany*
[c]*National Institute of Oceanography, Dona Paula, 00403 Goa, India*
[d]*Institute of Geosciences, University of Tübingen, Sigwartstraße 10, D-72076 Tübingen, Germany*

Abstract

$\delta^{15}N$ values in modern sediments of the northern Indian Ocean range from <4‰ in the northern Bay of Bengal to >11‰ in the central Arabian Sea due to the strong spatial variability of processes influencing nitrogen cycling in the region. Suboxic conditions in Arabian Sea intermediate water lead to denitrification and accumulation of isotopically enriched nitrate in the water column. Upwelling of this enriched nitrate into the euphotic zone results in high $\delta^{15}N$ values in Arabian Sea particulate matter and surface sediments. $\delta^{15}N$ minima in the northern Bay of Bengal are caused by input of terrestrial organic matter as well as depleted nitrate from rivers. $\delta^{15}N$ is about 8‰ in the equatorial Indian Ocean as the influence of oxygen deficiency and river input ceases.

$\delta^{15}N$ of recent sediments correlates with the weighed mean $\delta^{15}N$ of sediment trap material caught 500–1000 m above the sea floor, but with an enrichment of 2–3‰ between deep traps and underlying sediments. Only at two locations characterised by high sedimentation rates, there is no significant offset of $\delta^{15}N$ values between traps and sediments. $\delta^{15}N$ of sediments and trap samples from the Arabian Sea are correlated to the Degradation Index (DI) [Dauwe, B., Middelburg, J.J., Hermann, P.M.J., Heip, C.H.R., 1999. Linking diagenetic alteration of amino acids and bulk organic matter reactivity. Limnology and Oceanography, 44, 1809–1814], an indicator of amino acid degradation intensity, confirming the sensitivity of the $\delta^{15}N$ to degradation.

These results have to be considered for the interpretation of the $\delta^{15}N$ record in sediment cores with large variations of diagenetic intensities.
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Keywords: Indian Ocean; Arabian Sea; Bay of Bengal; Sediments; Stable isotopes; Amino acids

* Corresponding author. Tel.: +49 40 42838 7088; fax: +49 40 42838 6347.
  E-mail address: haake@geowiss.uni-hamburg.de (B. Gaye-Haake).
[1] Present adress: Internationales Büro des BMBF beim DLR, Königswinterer Str. 522-524, 53227 Bonn, Germany.

1. Introduction

The $\delta^{15}N$ of particulate matter has been used to characterise the oceanic nitrogen cycle as it reflects nitrogen sources as well as transformation processes in the ocean that are associated with isotopic fractionation. Deep water nitrate seems to hold a relatively uniform $\delta^{15}N$ signal of $4.8 \pm 0.2‰$ (Sigman et al., 2000). Nitrate in intermediate waters is, however, often more enriched in ^{15}N, especially in regions with a suboxic water column and denitrification. The lighter isotope is preferentially released in N_2 with an isotopic effect of 20–30‰ so that residual nitrate can have $\delta^{15}N$ values above 20‰ (Altabet et al., 1999a; Naqvi et al., 1998; Voss et al., 2001). Mixing and upwelling enhance $\delta^{15}N$ values of nitrate in surface waters so that particulate matter of regions with a mid-water oxygen minimum can have $\delta^{15}N$ values far above 5‰. Denitrification leads to nitrate deficiency reflected in N/P ratios below the Redfield ratio of 16 (Naqvi et al., 1998). This is partly counteracted by nitrogen fixation, which regionally or seasonally introduces material with depleted $\delta^{15}N$, because atmospheric nitrogen has a $\delta^{15}N$ value of 0‰ and nitrogen fixation is associated with little isotopic fractionation (Carpenter et al., 1997). Isotopic fractionation during incomplete nitrogen uptake by phytoplankton can further reduce $\delta^{15}N$ values in particulate matter. Low $\delta^{15}N$ values in regions not affected by nitrogen fixation have been explained by allochthonous nitrogen sources, as well as by fractionation during nitrate uptake under phosphate limiting conditions (Struck et al., 2001). On an annual time scale, however, nitrate uptake in the euphotic zone can be considered as complete even in upwelling areas so that total annual $\delta^{15}N$ values of particulate matter should reflect the $\delta^{15}N$ of source nitrogen (Thunell et al., 2004).

Due to the short residence time of nitrogen in the ocean, the nitrogen cycle responds to perturbations on very short time-scales (Codispoti et al., 2001). Changes are reflected by $\delta^{15}N$ values of particulate matter, as well as of nitrate, due to isotopic fractionation in the various transformation processes and the different isotopic signals of the nitrogen sources (Brandes and Devol, 2002). Variations of $\delta^{15}N$ values in the late Quaternary have, therefore, been interpreted as signals of a response of the nitrogen cycle to climatic oscillations (Altabet et al., 2002; Ganeshram et al., 2002; Suthhof et al., 2001; Thunell and Kepple, 2004).

However, utility of sedimentary $\delta^{15}N$ values as a proxy for changes in the nitrogen cycle has been questioned: There is evidence that the diagenesis of sinking particulate matter and sediments is coupled to isotopic fractionation and that the isotopic effect may vary with the rates of sedimentation and early diagenetic conditions (Altabet et al., 1999a,b; Holmes et al., 2002; Lourey et al., 2003; Smith et al., 2002). Experimental results have produced both enrichment and depletion of $\delta^{15}N$ during early diagenesis, and have emphasised the important role of redox conditions (Altabet et al., 1999b; Freudenthal et al., 2001; Lehmann et al., 2002). Altabet et al. (1999a) and Francois et al. (1997) have estimated a diagenetic effect on $\delta^{15}N$ values of 3–5‰ in deep sea sediments in areas of low sedimentation rates, whereas there may be no effect on sediments in areas of moderate to high sedimentation rates.

In this work, we have compiled the flux-weighed averages of $\delta^{15}N$ values from nine sediment trap systems moored in the northern Indian Ocean and compared them to the $\delta^{15}N$ signals in the underlying sediments as an empirical means to estimate the effects of early diagenesis on $\delta^{15}N$ values of sediments. We have also inspected the composition of total hydrolysable amino acids–the main carrier of nitrogen–and their relation to changes in $\delta^{15}N$ during degradation of organic matter.

2. Materials and methods

2.1. Study area

Due to high primary productivity and a reduced ventilation, the northern Indian Ocean has suboxic conditions in mid-water with intensive denitrification in the Arabian Sea. Lowest oxygen concentrations are present in the northeastern Arabian Sea (Sen Gupta and Naqvi, 1984); oxygen concentrations increase south of $10°N$. Together with the eastern Pacific, the Arabian Sea is the major nitrogen sink of the ocean (Bange et al., 2000, 2001; Ganeshram et al., 2002; Gruber and Sar-

miento, 1997). Denitrification leads to the accumulation of isotopically enriched nitrate in Arabian Sea subsurface water. Due to monsoonal upwelling, mixing and diffusion of enriched nitrate into the euphotic zone, $\delta^{15}N$ values in particulate matter and sediments are high (Altabet et al., 1999a; Schäfer and Ittekkot, 1993). Although the Bay of Bengal also has an oxygen minimum in subsurface waters, denitrification has not been reported (Howell et al., 1997; Rao et al., 1994). The enormous river input from Ganges-Brahmaputra and the south Indian rivers, part of which can enter the distal fan area through a channel system, make lateral transport at depth an important mechanism influencing the quality and isotopic composition of sinking particulate matter (Ittekkot et al., 1991, 1992; Schäfer and Ittekkot, 1995).

2.2. Sampling and data source

Sediment trap samples were taken at nine locations in the Arabian Sea, equatorial Indian Ocean and Bay of Bengal (Table 1, Fig. 1). Results of the trap study, which was initiated in 1986, as well as details of deployments and sampling have been published elsewhere (Haake et al., 1993; Ittekkot et al., 1991; Nair et al., 1989; Ramaswamy et al., 1991; Rixen et al., 2000; Unger et al., 2003). $\delta^{15}N$ results of the first 3 or, respectively, 5 years of the trap investigations have been published by Schäfer and Ittekkot (1993, 1995). The basic monsoon related seasonality of $\delta^{15}N$ values which has been described by these authors has been found also in all subsequent data sets and will not be discussed here. For the comparison of $\delta^{15}N$ values of sinking particles with those of surface sediments, we have utilised all trap results available at each location (Table 1). Mean values, standard deviations of mean values as well as nitrogen flux-weighed mean values were calculated for all samples listed in Table 1. Some samples, mostly from the shallow traps, with large swimmers such as fish or crabs in them and $\delta^{15}N$ values above 10‰ were assumed to be biased by swimmers and therefore discarded.

Surface sediment samples have been taken during cruises Meteor 5, 32/2 as well as Sonne 42, 51, 54, 72, 90 and 93 to the northern Indian Ocean. They cover the intervals 0–1 cm or 0–2 cm obtained from box grabs, gravity cores or multicorers.

2.3. Methods

2.3.1. Carbon and nitrogen

Total carbon and nitrogen were measured by a Carlo Erba Nitrogen Analyser 1500 (Milan, Italy). The precision of this method is 0.05% for carbon and 0.005% for nitrogen. Carbonate percentages were determined by a Wösthoff Carmhograph 6 (Bochum, Germany). The relative error of carbonate analyses is 1%. Organic carbon was calculated as the difference between total and carbonate carbon.

2.3.2. Amino acids

Total hydrolysable amino acids (AA) were analysed with a Pharmacia LKB Alpha Plus 4151 Amino Acid Analyser (Freiburg, Germany) after hydrolysis of 2–4 mg for trap samples and of 30–40 mg for sediments with 6 N HCl for 22 h at of 110 °C. After separation with a cation exchange resin, the individual monomers were detected fluorometrically. Duplicate analysis according to this method results in a relative error of 4% for total AA. Further analytical details are given in Jennerjahn and Ittekkot (1999).

The molar percentages of the 14 protein amino acids have been used to calculate the Dauwe Degradation Index (DI) developed by Dauwe and Middelburg (1998) and Dauwe et al. (1999). This index assesses the diagenetic alteration of a sample by comparing it to a set of 28 samples of different degradational states and environments. Molar percentages of individual AA are standardised by the mean and standard deviations of the 28-sample data set. The DI then integrates the AA weighed by the factor coefficients for the first axis of the principal component analyses (PCA) of Dauwe et al. (1999) according to the formula:

$$DI = \sum_i \left[\frac{var_i - AVGvar_i}{STDvar_i} \right] \cdot fac.coef._i$$

where var_i is the original mole percentage of each AA_i, $AVGvar_i$ and $STDvar_i$ are the mean and standard deviations, respectively, and $fac.coef._i$ is the factor coefficient of the first axis of the PCA of Dauwe et al. (1999). The DI thus represents the cumulative deviation with respect to an assumed average molar composition with negative values indicating more and positive values less degradation than the average.

Table 1

Trap locations, trap depths, water depths, deployment periods and number of samples, mean $\delta^{15}N$ values, weighed mean $\delta^{15}N$ values of trap and standard deviations of mean values

Station	Position		Trap depth (m)			Water depth (m)	Deployment period (no. of samples)			$\delta^{15}N$ (‰) mean			$\delta^{15}N$ (‰) weighed mean			Standard deviation		
	Lat.	Long.	Shallow	Middle	Deep		Shallow	Middle	Deep	Shallow	Middle	Deep	Shallow	Middle	Deep	Shallow	Middle	Deep
EPT	24°45.5	65°49.3			~590	1100			93–96 (29)			7.79			7.68			0.67
WAST	16°20	60°30	1080	2080	~3020	4020	86–88, 90–95 (68)	90; 99 (22)	86–88, 90–95 (125)	7.45	7.17	7.19	7.32	6.75	7.06	0.87	1.01	0.68
CAST	14°31	64°46	730–1570		~2900	3900	86–95, 99 (69)		86–94, 97–99 (87)	7.67		7.11	7.75		7.17	0.73		0.60
EAST	15°31	68°43	1200–1690		~2800	3770	86–93 (46)		86–93 (71)	6.12		5.84	6.16		5.80	0.72		0.71
SAST	13°09	67°08	1090		3090	4075	92–93 (13)		92–93 (13	6.48		6.42	6.37		6.35	0.49		0.35
EIOT	3°33	77°48	930–1370		~2400	3400	95–97 (40)		95–97 (41)	5.91		4.86	5.68		4.80	0.96		0.58
SBBT	04°28–05°24	86°45–87°19	885–1071	1518–1919	2952–3024	~4020	87/88, 90/91, 93 96/97 (69)	92, 93–95 (25)	87/88, 90–97 (98)	5.28	5.14	4.86	5.50	5.40	5.13	1.03	1.12	0.81
CBBT all									87–93 (91)			4.14			4.26			0.90
CBBT no 06	13°08	84°20	893–988		2227–2327	~3270	88–91, 93 (67)	93–95 (13)	87–91, 93 (78)	4.30	3.93	4.16	4.26	4.51	4.29	0.80	0.87	0.95
CBBT 06	11°02	84°26		1588	2527	3462		92 (13)	92 (13)		4.03	4.04		3.96	4.01		0.63	0.45
NBBT N+S							87–92, 94/95 (103)		87–92, 94/95 (102)	3.58		3.51	3.57		3.62	0.61		0.44
NBBT-N	17°27	89°36	684–967		1714–2029	~2250	87–89; 94/95 (51)		87–89, 94/95 (52)	3.58		3.49	3.54		3.43	0.76		0.48
NBBT-S	15°30	89°10	731–1156		1666–2146	~2700	90–92, 94/95 (52)		90–92, 94/95 (50)	3.58		3.53	3.61		3.62	0.43		0.39

As station CBBT 06 has been situated 2° south of the other CBBT locations and NBBT-S about 2° south of NBBT-N values are given separately and as means for the total CBBT and NBBT locations.
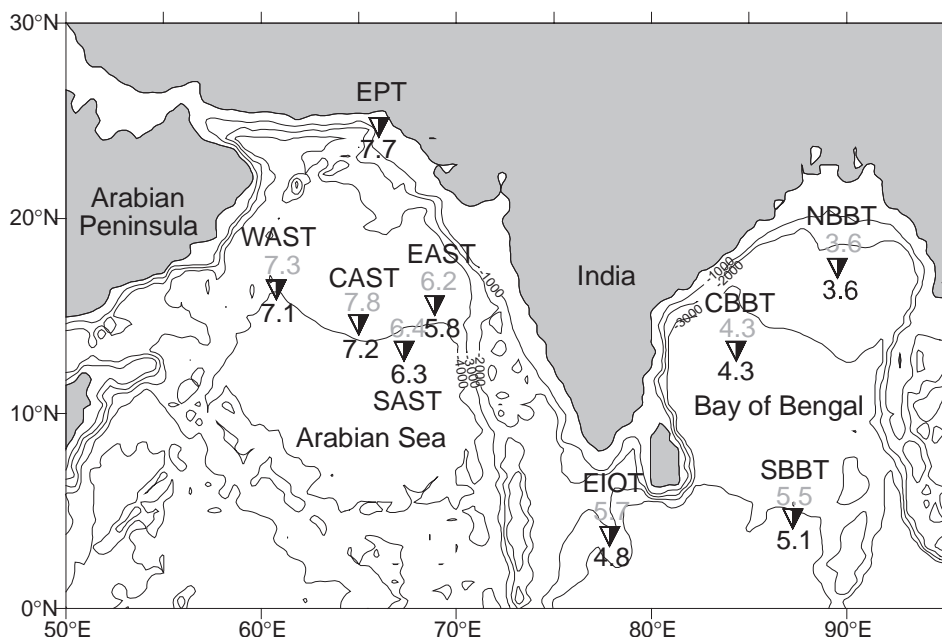
Fig. 1. Study area in the northern Indian Ocean with bathymetry and trap locations (triangles). Abbreviations of trap locations used in the text (EPT WAST, CAST, EAST, SAST, EIOT, SBBT, CBBT, NBBT), and weighed long-term average $\delta^{15}N$ values of shallow traps (light grey figures above triangles) and deep traps (black figures below triangles) are indicated.

2.3.3. Stable isotopes

$\delta^{15}N$ values were determined using a Finnigan MAT 252 isotope ratio mass spectrometer after high-temperature flash combustion in a Carlo Erba NA-2500 elemental analyzer at 1100 °C. Pure tank N_2 calibrated against the reference standards IAEA-N-1 and IAEA-N-2 of the International Atomic Energy Agency was used as a working standard. $\delta^{15}N$ is given as the per mil deviation from the N-isotope composition of atmospheric N_2. Analytical precision was better than 0.1‰ based on replicate measurements of a reference standard. Duplicate measurements of samples resulted in a mean deviation of 0.2‰.

3. Results

3.1. Distribution of $\delta^{15}N$, percentage of total nitrogen (N %) and DI values in surface sediments

Based on $\delta^{15}N$ measurements of surface sediments from 122 locations, we have plotted contours of the $\delta^{15}N$ distribution in the northern Indian Ocean by ordinary kriging (Fig. 2). Highest $\delta^{15}N$ values of >11‰ occur in the central part of the Arabian Sea, whereas surface sediments of the northern Bay of Bengal have lowest $\delta^{15}N$ values of <4‰. $\delta^{15}N$ contours in the northern Arabian Sea appear to partly follow the morphology with values around 8‰ on shelf, slope and ridges, and maxima of >11‰ in the central deep Arabian Sea. Towards the central Indian Ocean $\delta^{15}N$ values decrease to 7–8‰. Low $\delta^{15}N$ values of 5‰ to 7‰ occur in the southeastern Arabian Sea and on the Indian continental shelf and slope. The Bay of Bengal has an increase of $\delta^{15}N$ values from <4‰ in the north to values of 7–8‰ in the equatorial Indian Ocean. Due to the much higher sampling density in the central and northern Arabian Sea, the contours are, probably, much more realistic than in other parts of the study area (Fig. 2). Contours are preliminary due to a lack of surface sediment samples from the equatorial Indian Ocean and the Bay of Bengal. Whereas $\delta^{15}N$ values may be relatively uniform in the equatorial Indian Ocean, spatial variability in the Bay of Bengal may not be appropriately resolved due to its complicated channel and levee structures
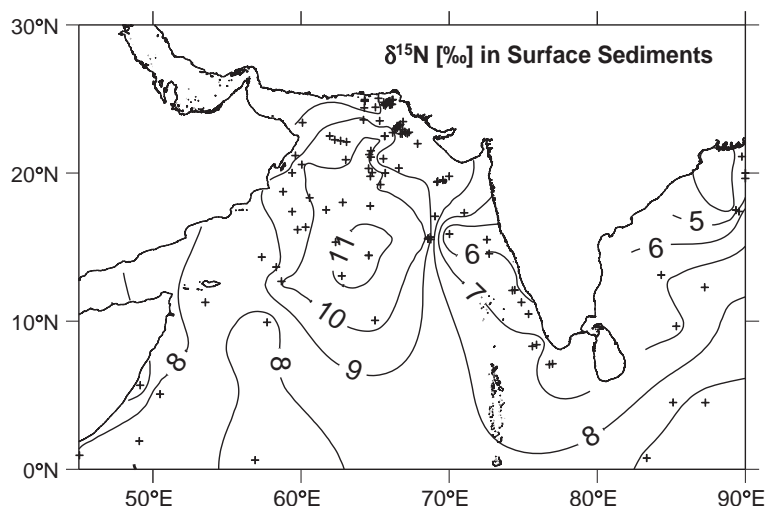
Fig. 2. Contours of $\delta^{15}N$ distributions in surface sediments in the northern Indian Ocean obtained by ordinary kriging based on results from 122 surface sediment samples. Small crosses indicate sampling locations.

in addition to local cross shelf transport (Schwenk et al., 2003; Kudrass et al., 1998).

Organic carbon and carbonate contour plots for the Arabian Sea have been published by several authors based on larger data sets than ours (Kolla et al., 1976; Slater and Kroopnick, 1984; Paropkari et al., 1992). We have, therefore, plotted only total N (%), which show a similar general pattern as organic carbon with high values on the shelves and slopes and low values in offshore areas (Fig. 3). Nitrogen as well as organic

carbon percentages in Bay of Bengal surface sediments are much lower compared to the Arabian Sea, probably due to the stronger dilution with terrigenous mineral matter in addition to lower primary productivity (Unger et al., 2003).

The DI calculated for 62 surface sediment samples from the Arabian Sea range from minima of less than -1.4 in the central Arabian Sea to DI >1.0 on the shelves, and again contours appear to follow the morphology (Fig. 4).
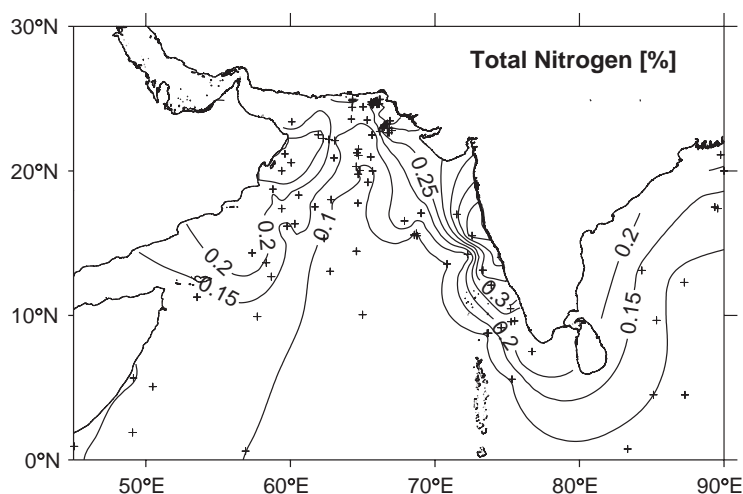

Fig. 3. Contours of total nitrogen (%) in surface sediments in the northern Indian Ocean obtained by ordinary kriging. Small crosses indicate sampling locations.
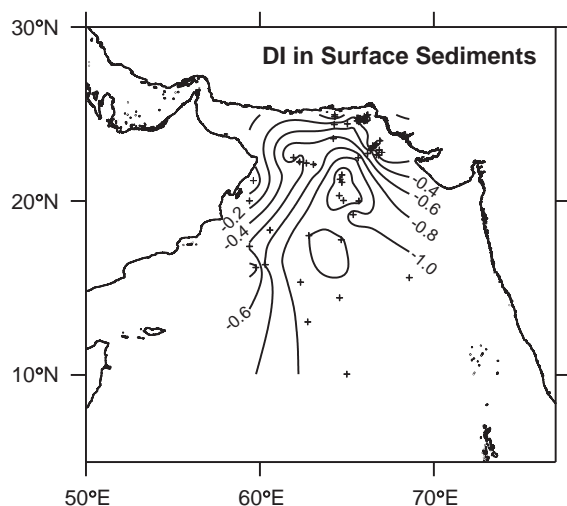
Fig. 4. Contours of the Degradation Index (DI; calculated after Dauwe et al., 1999) in a subset of 62 surface samples from the Arabian Sea. Small crosses indicate sampling locations.

3.2. Distribution of $\delta^{15}N$ values in sinking particles

Flux-weighed means of $\delta^{15}N$ values are between 3.6‰ and 7.8‰ in the shallow and between 3.6‰ and 7.2‰ in the deep traps (Fig. 1, Table 1). At four of the locations, $\delta^{15}N$ values decrease by 0.4‰ to 0.9‰ between shallow and deep traps. The general pattern of $\delta^{15}N$ values in sinking particles follows the trend of surface sediments with higher values in the Arabian Sea, intermediate values in the equatorial Indian Ocean and decreasing values from the southern to the northern Bay of Bengal. $\delta^{15}N$ values in the bathypelagic sediment traps are approximately 2–3‰ lower than $\delta^{15}N$ values of the underlying sediments. No significant differences between trap mean value and surface sediments are observable at the locations EPT and NBBT (Fig. 5).

4. Discussion

4.1. Spatial distribution of $\delta^{15}N$ in the northern Indian Ocean

$\delta^{15}N$ in the Arabian Sea trap samples and sediments are significantly enriched compared to the average ocean (Figs. 1 and 2). This is mainly due to the upwelling of enriched nitrate from subsurface water into the euphotic zone (Altabet et al., 1999a; Schäfer and Ittekkot, 1993), as is reflected in higher $\delta^{15}N$ values in the western Arabian Sea samples close to upwelling centres off Oman (Fig. 2). $\delta^{15}N$ of nitrate ($\delta^{15}NO_3^-$) in vertical profiles have revealed $\delta^{15}N$ maxima of ~15–18‰ in the oxygen minimum zone (OMZ) at about 300 m in the northeastern Arabian Sea, whereas OMZ maxima in the western and central Arabian Sea are ~12‰ (Naqvi et al., 1998; Altabet et al., 1999a). The $\delta^{15}NO_3^-$ just below the euphotic zone does, however, not suggest any geographical trend and is about 7.5‰ (Altabet et al., 1999a). This is identical to the $\delta^{15}N$ of plankton tow samples from the euphotic zone in the northern Arabian Sea and close to the weighed mean values in the traps at EPT, WAST and CAST locations (Table 1). In the eastern Arabian Sea trap $\delta^{15}N$ are more depleted, although the oxygen minimum is more intense (Sen Gupta and Naqvi, 1984). This may be due to nitrogen fixation in the eastern part of the basin, which may be caused by nitrogen deficiency over phosphate (Brandes et al., 1998; Naqvi et al., 1998).
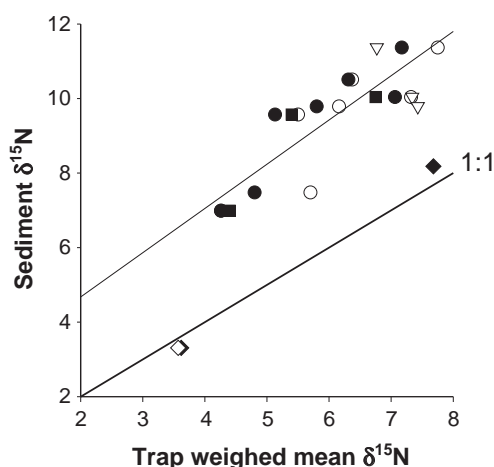

Fig. 5. Long-term weighed mean $\delta^{15}N$ values of shallow (open circle), middle (filled square) and deep traps (filled circle) from the northern Indian Ocean (except EPT and NBBT) plotted against the $\delta^{15}N$ values of underlying sediments. Open triangles indicate $\delta^{15}N$ values of near bottom short-term deployments at locations WAST, CAST and EAST. Long-term trap data correlate with sediment data ($R^2 = 0.75$, $n = 16$) with a y-offset of 0.23‰. Weighed means of shallow (open diamond) and deep (filled diamond) at EPT and NBBT locations have no offset to sediment values (see line of 1:1 correlation).

Lower $\delta^{15}N$ in the equatorial Indian Ocean and Southern Bay of Bengal traps (EIOT, SBBT) are close to mean oceanic values (Table 1). However, the $\delta^{15}N$ in the northern Bay of Bengal are relatively depleted, which could be due to the enormous river input. Suspension distributed offshore with the river plume and river-derived sediments being transported into the deep Bay of Bengal via active channels lead to high content of terrestrial material in sinking particles and sediments (Unger et al., in press, 2003). River suspension can have quite variable $\delta^{15}N$ values (Maksymowska et al., 2000). Generally, one would expect them to be lower than oceanic values (Brandes and Devol, 2002). Variations seem to be indicators of environmental conditions and may reflect anthropogenic disturbance (Bratton et al., 2003; Struck et al., 2000). River-derived suspended matter collected off the mouth of Ganges-Brahmaputra during November/December 1997 had $\delta^{15}N$ values of 3.7–3.8 (Unger et al., in press), which is in the range of other tropical rivers (Jennerjahn and Ittekkot, 2002; Jennerjahn et al., 2004). The $\delta^{15}N$ values of 3–4‰ in the northern Bay of Bengal sediments and sinking particulates (Figs. 1 and 2) could thus result from the input of river suspension as well as biological assimilation of isotopically depleted riverine dissolved organic and inorganic nitrogen.

Although total nitrogen percentages in surface sediments (Fig. 3) follow the same general trend in the Arabian Sea, they are not correlated with $\delta^{15}N$. Some of the differences may result from dilution by mineral matter in the northern Arabian Sea leading to lower N % as well as lower $\delta^{15}N$ values in the eastern Arabian Sea due to an additional atmospheric N source (see above).

4.2. Decrease of $\delta^{15}N$ in the water column between shallow and deep sediment traps

A decrease of $\delta^{15}N$ between shallow and deep sediment traps (Table 1, Fig. 1) is unexpected as decomposition of organic matter taking place during the sinking of particulate matter are believed to increase $\delta^{15}N$ values. With each trophic level $\delta^{15}N$ values increase by approximately 3–4‰ (Montoya et al., 1991). Our findings are, however, in accordance with the results of other trap experiments (Altabet et al., 1991; Saino and Hattori, 1987; Thunell et al.,

2004; Voß, 1991). This counter-intuitive decrease between the meso- and bathypelagic ocean has been explained by an increase of bacterial biomass on sinking particles, the preferential preservation of isotopically depleted and organic constituents of possibly terrestrial origin, or the preferential preservation of diatoms, which are isotopically depleted compared to other plankton as they fractionate much more during nitrate uptake (Altabet, 1996). We can exclude the latter explanation as we have found no higher biogenic opal contents in deep compared to shallow trap samples. The amount of lithogenic matter is also not related to the $\delta^{15}N$ values, which does, however, not exclude a relationship between the terrigenous fraction of organic matter and $\delta^{15}N$. Amino acid as well as N fluxes decrease by 30% to 50% from shallow to deep traps, while less than 20% of total fluxes are lost. Degradation during sinking in the water column is further indicated by a decrease of the DI by about 0.3 between shallow and deep traps. As the preferential loss of amino acids should increase the $\delta^{15}N$ of the residual, the mechanism which leads to decreases in the $\delta^{15}N$ may be more efficient than the measured $\delta^{15}N$ values suggest.

A different explanation for lower $\delta^{15}N$ values in deeper traps could come from an unresolved methodological problem of trap experiments—the "swimmer problem" (Lee et al., 1992). The traps at 1000 m depths collect considerable amounts of swimmers, whereas the deep traps collect only very small amounts. Large swimmers have been removed by hand-picking and small by sieving with a 1 mm mesh-size sieve. Some of the samples, which had fish or large zooplankters in them, have very high $\delta^{15}N$ values and have, therefore, not been included in the calculations of average $\delta^{15}N$ values. However, in the other samples, not all small individuals may have been removed, others may have been disrupted and may have increased $\delta^{15}N$ values of the samples. The shallow traps may thus be more biased by swimmers than deep traps.

4.3. Effect of early diagenesis on $\delta^{15}N$ values

Weighed mean $\delta^{15}N$ values of deep sediment traps and the $\delta^{15}N$ values of underlying sediments are correlated with an offset of about 2–3‰ between sinking particles and sediments ($R^2 = 0.75$, $n = 16$) if

all weighed averages of long-term trap deployments except EPT and NBBT are used (Fig. 5). The stations EPT on the slope off Pakistan and NBBT in the northern Bay of Bengal were not included in this correlation, as they have no offset between trap and sediment $\delta^{15}N$ values. Both traps are situated only about 500 m above the seafloor. However, short-term traps deployed 500 m above the sea floor at locations WAST, CAST and EAST in the Arabian Sea have revealed $\delta^{15}N$ values in the same range as the traps 1000 m above ground (Fig. 5; N. Lahajnar, unpublished data). Together with the dependence of sedimentary $\delta^{15}N$ values on water depth, we hypothesize that relatively depleted $\delta^{15}N$ values are due to reduced diagenesis in surface sediments in regions of higher rates of sedimentation such as shelves and slopes as well as the northern Bengal Fan with its enormous river input. The increase of $\delta^{15}N$ values by about 2–3‰ between sinking matter and sediments seems to be typical only for the deep sea with its relatively low rates of sedimentation. The observed increase in $\delta^{15}N$ may be due to degradation processes at the sediment water interface where 95% of the incoming amino acids–the main carriers of nitrogen in the water column–are decomposed (Haake et al., 1992). Kinetic fractionation during their hydrolysis as well as uptake by microorganisms can increase the $\delta^{15}N$ values of the residual amino acids (Macko et al., 1987; Silfer et al., 1992).

4.4. Amino acid degradation and change in $\delta^{15}N$

Biogeochemical indicators derived from amino acids confirm that there is a relationship between the degradational state of nitrogenous organic matter and its $\delta^{15}N$. In fresh marine organic matter amino acids contribute almost 100% of total nitrogen. As they are the major nitrogen source for heterotrophic organisms and bacteria, less than 1% of the amino acids produced in surface waters escape degradation and are buried in sediments (Haake et al., 1992; Lee et al., 2000). In surface sediments, the proportion of total nitrogen present as acid hydrolysable amino acids is reduced to 25–60% on the shelf (Dauwe et al., 1999) and to around 20% in the deep sea (Haake et al., 1992; Lee et al., 1998, 2000; Whelan and Emeis, 1992). The unidentified portion of total nitrogen may be sorbed ammonia or nitrogen fixed in humic substances, which are, however, also mostly products of amino

acid degradation and polymerisation (Francois, 1990; Lee, 1988; Müller, 1977). During the degradation of amino acids, characteristic changes in the monomeric distribution of the residue occur. The enrichment of non-protein amino acids due to enzymatic formation from their proteinaceous precursors has often been used to estimate degradation intensity (Cowie and Hedges, 1994; Ittekkot et al., 1984a,b; Lee and Cronin, 1982, 1984). More recently, the Reactivity Index (RI; Jennerjahn and Ittekkot, 1997) or the Degradation Index (DI; Dauwe and Middelburg, 1998) have been applied (Ingalls et al., 2003; Pantoja and Lee, 2003) of which the RI is more applicable for fresher organic matter from the water column, whereas the DI allows a finer resolution of sedimentary diagenesis (Unger et al., 2005).

We have measured amino acids and calculated the DI of a subset of 68 surface sediments and the trap samples from the central, northern and western Arabian Sea (Fig. 4) and find that the DI correlates negatively with $\delta^{15}N$ (Fig. 6). The decrease of the DI from 0.5 in trap samples to -1.5 in the most degraded sediments from the central Arabian Sea is accompanied by an increase of $\delta^{15}N$ by about 3‰, which is in a similar range as the offset between sediment traps and deep sea surface sediments (Fig. 5). The samples with DI and $\delta^{15}N$ values between these two extremes are surface sediments from the continental slopes, the Murray and Owen Ridges and the highly productive upwelling area in the western Arabian Sea. This
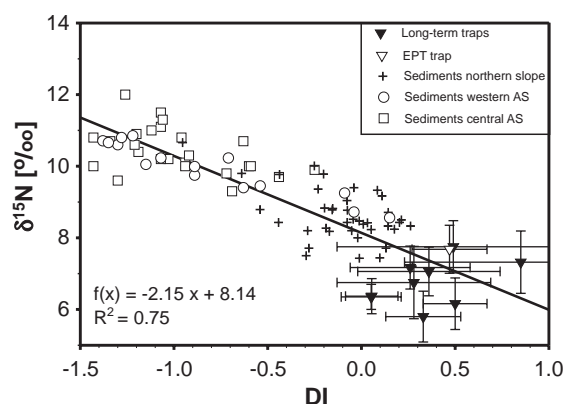

Fig. 6. Correlation of the Degradation Index (DI) and the $\delta^{15}N$ values of trap and sediment samples from the Arabian Sea ($R^2 = 0.75$, $f(x) = -2.15 \times +8.14$). Standard deviations of DI and $\delta^{15}N$ values are indicated by error bars.

suggests that early diagenesis has an important influence on sedimentary $\delta^{15}N$ values and that the observed pattern of $\delta^{15}N$ values in Arabian Sea surface sediments is partly related to the intensity of early diagenesis. Despite a similar general pattern (see Figs. 2, 3 and 4) nitrogen contents of surface sediments did neither correlate with $\delta^{15}N$ nor with the DI of the subset of 68 samples from the western, northern and central Arabian Sea. Nitrogen contents of sediments may be influenced by primary productivity, dilution with mineral matter and biogenic frustules as well as by early diagenesis. $\delta^{15}N$ and DI variations in an area with roughly the same $\delta^{15}N$ source value may be mainly related to the intensity of degradation.

It may be important to consider these findings for an interpretation of the $\delta^{15}N$ record of areas in which the rate of sedimentation has varied considerably. This has, however, not been the case in the recent geological history of the Arabian Sea and there are further indications that diagenesis has not changed the interpretation of this $\delta^{15}N$ record. Trap and modern core top $\delta^{15}N$ values correspond to each other on the continental margins so that we do not have to assume a diagenetic effect (Altabet et al., 2002; Suthhof et al., 2001). In the geological record high $\delta^{15}N$ values have, generally, occurred during the warmer periods, i.e. the Holocene and interstadials, when organic carbon and nitrogen contents are high. This has been related to higher productivity and to a stronger OMZ with more intense denitrification (Altabet et al., 2002; Suthhof et al., 2001). By about 5‰ lower $\delta^{15}N$ values have been found in the stadials, especially the Younger Dryas and Heinrich events. This indicates less or absent denitrification, probably due to reduced productivity and increased ventilation of mid-water. One would expect diagenesis to be stronger during such lower productive periods, so that if modifications of the $\delta^{15}N$ record of the Arabian Sea have taken place they would have dampened the actual $\delta^{15}N$ fluctuations.

5. Conclusions

1. The $\delta^{15}N$ in surface sediments from the northern Indian Ocean show a very wide range reflecting differences in nitrogen cycling and sources. Denitrification in the Arabian Sea leads to a significant enrichment of ^{15}N, whereas input from large rivers depletes ^{15}N in the northern Bay of Bengal. Towards the central Indian Ocean oceanic average $\delta^{15}N$ values are attained.

2. The weighed mean $\delta^{15}N$ of samples from long-term sediment trap deployments show a similar spatial variation of $\delta^{15}N$ as the underlying sediments with trap samples from about 3000 m being 2–3‰ lower than sedimentary $\delta^{15}N$. This isotopic enrichment of residual nitrogenous organic matter during diagenesis seems to be typical only for areas with low rates of sedimentation and was not observed in regions of higher sedimentation rates such as shelves and slopes and the northern Bengal Fan.

3. The Degradation Index (DI) significantly correlates with $\delta^{15}N$ of sediment trap and sediment samples from different water depths in the Arabian Sea suggesting a close relationship of degradation intensity and the enhancement of $\delta^{15}N$.

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Publication 4:

Dissolved organic carbon (DOC) fluxes of deep-sea sediments
from the Arabian Sea and NE Atlantic

N. Lahajnar, T. Rixen, B. Gaye-Haake, P. Schäfer, V. Ittekkot

Dissolved organic carbon (DOC) fluxes of deep-sea sediments from the Arabian Sea and NE Atlantic

Niko Lahajnar[a,*], Tim Rixen[b], Birgit Gaye-Haake[a],
Petra Schäfer[a], Venugopalan Ittekkot[b]

[a]*Institut für Biogeochemie und Meereschemie, Universität Hamburg, Bundesstrasse 55, D-20146 Hamburg, Germany*
[b]*Zentrum für Marine Tropenökologie, Fahrenheitstrasse 6, D-28359 Bremen, Germany*

Abstract

Diffusive flux of dissolved organic carbon (DOC) from deep-sea sediments is a poorly constrained component of the global marine carbon cycle, but may play an important role for DOC concentrations in the oceans. During six cruises between the years 1995 and 2000 we measured DOC concentrations in pore-waters of surface sediments and the ambient bottom waters at five stations in the deep Arabian Sea (water depths: 3190–4420 m) and at two sites in the NE Atlantic (4500–4800 m). Pore-water DOC concentrations were usually one order of magnitude greater than in bottom waters, with maximum DOC contents between 509 and 1526 μmol/L in the uppermost sediment interval (0–0.5 cm). DOC values generally decrease towards ∼3 cm core depth with slightly increasing concentrations in deeper layers under sub-oxic to anoxic conditions.

Calculated benthic DOC effluxes into the bottom water caused by concentration gradients ranged between 59.8 and 223.9 μmol m^{-2} d^{-1} in the Arabian Sea and 47.2 and 121.2 μmol m^{-2} d^{-1} in the NE Atlantic. DOC efflux rates were highly correlated with the annual vertical particle flux rates at the sites and thus appear to be a function of the regional productivity. Taking an average global oceanic DOC efflux rate between 50.5 and 78.1 μmol m^{-2} d^{-1}, we calculated that the DOC release is in the order of 70–103 × 10^{12} g C yr^{-1} from sediments below 2000 m water depth. Thus, deep-sea sediments have the potential to represent a significant source of DOC in the oceans.

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1. Introduction

Dissolved organic carbon (DOC) is by far the largest organic carbon pool in the oceans (0.6 × 10^{18} g DOC). It holds almost as much carbon as the atmosphere (0.75 × 10^{18} g) and even more than the terrestrial biosphere (0.56 × 10^{18} g)

*Corresponding author. Tel.: +49 40 42838 7087;
fax: +49 40 42838 6347.

E-mail address: lahajnar@geowiss.uni-hamburg.de
(N. Lahajnar).

(Williams and Druffel, 1987; Emerson and Hedges, 1988; Hedges and Keil, 1995; Amon and Benner, 1996). Sources, cycling as well as decomposition of marine DOC are still poorly constrained (Hedges, 1992; Amon and Benner, 1994; Bauer et al., 1995; Hedges et al., 1997; Hansell and Carlson, 1998; Burdige et al., 1999). The overall nature of DOC in the ocean appears to be refractory and nutrient-poor with a mean age of several thousand years (Williams and Druffel, 1987; Bauer et al., 1992; Benner et al., 1992; Guo et al., 1995). Because of its significance in the global carbon budgets, marine DOC (or in a broader sense: dissolved organic matter—DOM) has been the subject of numerous research projects during the past two decades (Hansell and Carlson, 2002).

One major aspect of the global carbon cycle comprises the burial of organic matter in marine sediments, since it is the main carbon sink over geologic time (Berner, 1982, 1989). Extent, mechanisms and regional variability of organic carbon preservation in open-ocean sediments, however, are still a matter of debate (Emerson and Hedges, 1988; Henrichs, 1992; Canfield, 1994; Jahnke, 1996). Almost all of the particulate organic matter (POM) reaching the seafloor is derived from the photic zone where inorganic CO_2 is converted via photosynthesis to organic matter. The majority of POC produced in the surface ocean is rapidly remineralized and recycled; only a minor fraction is exported by the *biological pump* to the deep sea where it is incorporated into the underlying sediments (Suess, 1980; Broecker, 1982; Berger et al., 1989).

The formation of DOC during the decomposition of POC within the sediments increases the DOC concentration in the pore-water compared to the ambient overlying bottom water and leads to a gradient-controlled efflux of DOC across the sediment–water interface (Krom and Sholkovitz, 1977; Orem et al., 1986; Burdige and Homstead, 1994; Alperin et al., 1999; Holcombe et al., 2001). From coastal (water depth 0–200 m) and continental margin sediments (water depth 200–2000 m) the global DOC flux into the overlying water has been estimated to be 88 and 89 tera gram (1 Tg = 10^{12} g) carbon per year, respectively

(Burdige et al., 1999; Burdige, 2002). In contrast, DOC flux rates are not very well-constrained for open-ocean regions with water depths > 2000 m (Heggie et al., 1986; Bauer et al., 1995; Hulth et al., 1997; Otto and Balzer, 1998; Burdige et al., 1999).

This study was dedicated to investigate the factors controlling the DOC formation in sediments at water depths greater than 2000 m and to quantify the DOC flux across the sediment–water interface. Therefore, six cruises in the Arabian Sea and NE Atlantic, respectively, between 1995 and 2000 have been conducted within the framework of the German research project BIGSET (Biogeochemical transports of energy and matter in the deep sea).

2. Study sites

Comprehensive information on the BIGSET program in the Arabian Sea is provided by Pfannkuche and Lochte (2000). Briefly, sampling of the northern (NAST), central (CAST), western (WAST), eastern (EAST), and southern (SAST) (Table 1 and Fig. 1A) have been chosen in accordance with sampling sites occupied during JGOFS Arabian Sea and the Indo-German sediment trap projects (Nair et al., 1989; Rixen et al., 1996, 2000a, b).

The stations BENGAL and BIOTRANS are situated in the West-European Basin of the NE Atlantic Ocean (Table 1 and Fig. 1B). Station term BENGAL was adopted from the BENGAL program (High-resolution temporal and spatial study of the BENthic biology and Geochemistry of a north-eastern Atlantic abyssal Locality; see Billett and Rice (2001)). The study site is located in the middle of the Porcupine Abyssal Plain (∼4.850 m depth), which appears as a relatively flat area. It is remote from both the continental slope to the east and the mid-ocean ridge to the west and thus represents a deep-sea environment unaffected by lateral input. Station BIOTRANS (BIOlogical vertical TRANSport and energetics in the benthic boundary layer of the deep sea; see, e.g., Lochte (1992), Lochte et al. (1993), and Thiel et al. (1989)) is located about 350 km to the southwest of station BENGAL at ∼4500 m water depth. The seafloor

Table 1
Stations sampled during the BIGSET program: station codes, positions, mean bathymetric depth, cruise codes, and time periods

Station	Latitude	Longitude	Depth (m)	Cruises	Dates
NE Atlantic					
BENGAL	48°55.40′N	16°35.00′W	4800	*METEOR 36/6*	09 Oct.–04 Nov. 1996
BIOTRANS	47°08.00′N	19°40.30′W	4500	*METEOR 42/2*	23 Jul.–22 Aug. 1998
				POSEIDON 260	25 Apr.–23 Jun. 2000
Arabian Sea					
WAST	16°13.00″N	60°16.02′E	4050	*METEOR 33/1*	19 Sep.–31 Oct. 1995
CAST	14°25.00′N	64°34.00′E	3950	*SONNE 118*	31 Mar.–11 May 1997
NAST	20°00.00′N	65°35.00′E	3190	*SONNE 129*	31 Jan.–08 Mar. 1998
EAST	15°35.00′N	68°34.00′E	3850		
SAST	10°02.00′N	65°00.00′E	4420		

of station BIOTRANS is more spatially variable due to topographic undulations. This station is situated in the area of the JGOFS North Atlantic Bloom Experiment (NABE) at 48°N 20°W (Ducklow and Harris, 1993; Honjo and Manganini, 1993; Newton et al., 1994).

3. Methods

3.1. Sample collection

In the Arabian Sea, cruise *M 33/1* (German RV *Meteor*) took place during the late SW-monsoon and early fall inter-monsoon in 1995 (Lochte et al., 1996). Cruise *SO 118* (German RV *Sonne*) was carried out during the spring inter-monsoon in 1997 (Pfannkuche and Utecht, 1998). Cruise *SO 129* was dedicated to the study during the NE-monsoon in 1998 (Pfannkuche and Utecht, 1999).

In the Atlantic Ocean, cruise *M 36/6* was carried out during autumn 1996 (Mienert et al., 1998), cruise *M 42/2* during summer 1998 (Pfannkuche et al., 2000). Expedition *POS 260* (German RV *Poseidon*) covered only study site BENGAL (Pfannkuche and Utecht, 2001). It took place at the beginning of the North Atlantic spring bloom (April–June 2000).

High-quality 10 cm-diameter cores with a maximum length of approximately 30 cm were taken by the use of a multiple corer (MC) according to Barnett et al. (1984). After recovery, MC samples were immediately transferred to a refrigerated laboratory maintained at 2 °C for further processing (except for *POS 260*, where no cold room was available; therefore, cores were stored in a refrigerator at 2 °C and processed in a ship's laboratory at ~20°C).

The sediment cores were extruded and cut into defined layers (0–0.5, 0.5–1, 1–1.5, 1.5–2, 2–2.5, 2.5–3, 3–4, 4–5, 6.5–7.5, 9–10 cm; only during *M 33/1* sediments were sectioned into 1 cm intervals down to 10 cm). The wet sediment slices were centrifuged at 2 °C and 2000 rpm for 20 min. Subsequently, the extracted pore-waters were filtered through glass fiber filters (*Whatman* GF/F, pre-combusted overnight in a muffle furnace at 450 °C) in order to remove the particulate fraction, and sealed in 10 mL glass ampoules (pre-combusted at 550 °C overnight) with a Bunsen burner under a pure nitrogen atmosphere. The samples were immediately stored at −20 °C for preservation until further processing. Storage time before analysis usually did not exceed two months. Prior to the sediment sampling, bottom water samples were taken from each core with a pipette at about 2 cm above sediment surface. Only cores with clear bottom water were taken. Bottom water samples were treated in the same manner as sediment samples.

3.2. Analytical methods

DOC was determined by a high-temperature catalytic oxidation (HTCO) method (Sugimura and Suzuki, 1988; Suzuki et al., 1992; Chen and
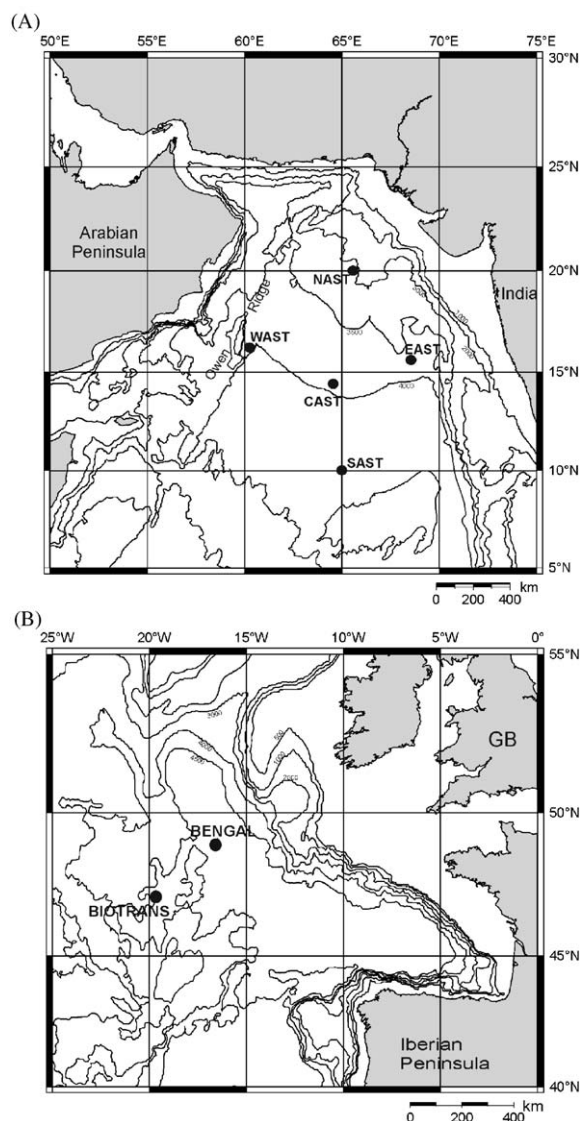
(A)

(B)

Fig. 1. Locations of the two study areas, showing the geographical positions of the five sites in the Arabian Sea (A) and the two sites in the NE Atlantic (B). Bottom contours are in meters.

Wangersky, 1993; Martin and McCorkle, 1993; Sharp et al., 1993; Wangersky, 1993; Cauwet, 1994; Peltzer et al., 1996) using a slightly modified DIMA-TOC 100 instrument (DIMATECH, Essen, Germany). Before the samples were analyzed for DOC, inorganic carbon had been removed by adding 50 μL phosphoric acid (50%) and then purging the samples

at pH < 2 for 5 min with pure nitrogen. The DOC samples (100 μL each) were combusted at 850 °C using a platinum catalyst on an aluminum-support (3% Pt on Al_2O_3). Scientific pure synthetic air (*Messer* 5.0) was used as carrier gas. The evolved CO_2 was determined by IR detection.

Standard solutions of potassium hydrogen phthalate ($C_8H_5O_4K$) were used for calibration (0, 0.5, 1, 3, 5, 7.5, 10, 15, 20 mg C L^{-1}) as it is sufficiently bacteriostatic (Chen and Wangersky, 1993) and could be stored for several days. Standard determinations were performed at the beginning and at the end of each analytical run. Only linear regressions with a correlation coefficient (CC) of > 0.999 were accepted for further processing. Each sample and blank was injected four times. Certified reference material (CRM) from D. Hansell (Rosenstiel School of Marine and Atmospheric Science, University of Miami) was used to determine the precision of our HTCO. The deviation from the deep Sargasso Sea water (44–45 μmol/L DOC) was 6% (± 2.5 μmol/L) or better.

According to Peltzer et al. (1996), distilled and deionized *Millipore* Milli-Q_{plus} water was filled into a pre-combusted (550 °C) *Schott* Duran bottle. Subsequently, 1 mL of 30% H_2O_2 was added to 1 L water. The bottle was sealed and set in direct daylight for one day. This process was repeated three times, exposing the bottle during the last step for two days to daylight in order to decompose any residual H_2O_2. Assuming that the blank was carbon-free, we were able to determine the instrument's blank, which was about 20 μmol/L. This was also confirmed by the use of CRM low-carbon water.

At the beginning of each analytical cycle up to ten blank samples were analyzed to ensure stable conditions during the measurement. After every second DOC sample a blank was inserted to avoid memory effects and to detect a potential short-term variability of the instrument (Cauwet, 1994). Furthermore, samples with presumably lowest DOC contents (bottom water samples) were analyzed separately or at the beginning of the analytical run, pore-water samples from the sediment surface with high DOC concentrations at the end.

3.3. DOC flux calculations

Diffusive flux rates were calculated by applying Fick's First Law

$$J_0 = -\varphi^m D_{sw} \frac{dC}{dz_0}, \qquad (1)$$

where φ^m is the porosity of the surficial sediment with m considering the tortuosity (Ullman and Aller, 1982). D_{sw} is the molecular diffusion coefficient for DOC, and dC/dz_0 is the DOC concentration gradient (dC) between pore-water and bottom water over the applied distance dz_0. Several assumptions have to be made in order to obtain reliable results:

1. Porosity data in Table 3 were taken from Grandel et al. (2000) and Luff et al. (2000) for the Arabian Sea and from Pfannkuche et al. (unpubl. data) for NE Atlantic sediments. Porosities > 0.7 result in $m = 3$ (Ullman and Aller, 1982).
2. The DOC concentration gradient dC/dz_0 is approximated by $\Delta C/\Delta z$, where ΔC is the difference between the DOC concentration from 1.5 to 2 cm interval (1–2 cm interval for sediments from the *M 33/1* cruise) of each core and the corresponding bottom water. Accordingly, Δz is the distance between the midpoint of our sampling interval and the bottom water (i.e., $\Delta z = 1.75$ cm for 1.5–2 cm sediment sample).
3. Values for D_{sw} were calculated for in situ conditions with the Stokes–Einstein relation (e.g., Ullman and Aller, 1982; Boudreau, 1997) by using the fresh water coefficient at $25\,^\circ C$ given in Burdige et al. (1992 and references therein):

$$\log D_{0(25\,^\circ C)} = 1.72 - 0.39 \log MW, \qquad (2)$$

where MW is the average molecular weight of DOC. In shallow marine and continental slope sediments an average DOC weight distribution of 1–50 kDa has been assumed for benthic flux calculations (Burdige et al., 1992, 1999; Alperin et al., 1994; Otto and Balzer, 1998). Recently, it has been found that during the transformation of solid organic matter into dissolved constituents,

reactively high molecular weight DOC is produced and released (Burdige et al., 2000; Burdige, 2001). Thus, for our deep-sea regions we adopted the approach of Otto and Balzer (1998) who assumed a 50/50 mixture of fixed molecular weights of 3 and 100 kDa for all of our study sites, leading to $D_{0(25\,^\circ C)} = 1.45 \times 10^{-6}\,cm^2\,s^{-1}$. More details are provided in Table 3.

4. Results and discussion

4.1. DOC in deep-sea sediments

Total pore-water DOC concentrations, in general, decreased rapidly with increasing sediment depth (Fig. 2) with pronounced DOC maxima in the uppermost centimeter where DOC concentrations between 509 and 1526 µmol/L occurred (Table 2). At all stations pore-water DOC concentrations were significantly elevated in comparison to bottom water concentrations. DOC in the bottom water varied between 47 and 104 µmol/L for the Arabian sea with an average value of 75.5 µmol/L (Table 2). In the NE Atlantic, bottom water DOC concentrations had a range from 59 to 122 µmol/L, giving a similar average concentration of 77.6 µmol/L DOC. Both temporal (inter-annual or seasonal) and (small-scale) spatial variability occurred in our cores.

Bottom water DOC concentrations at our study sites are elevated in comparison to mean deep-water values of 42.8 and 45.1 µmol/L in the Arabian Sea and North Atlantic, respectively (Hansell and Carlson, 1998). A potential contamination with pore-water DOC during core recovery cannot be completely ruled out. On the other hand, in situ samples from the NE Atlantic taken with a bottom water sampler at 30–55 cm above sea floor (Lahajnar and Springer, unpubl. data) show similar DOC concentrations (45–75 µmol/L) as our mean values taken from the overlying MC water.

Differences in the DOC concentrations among study sites can be related to rates of sedimentation and redox-conditions. Stations CAST, EAST, NAST and especially WAST from the Arabian Sea are representatives for ocean regions with
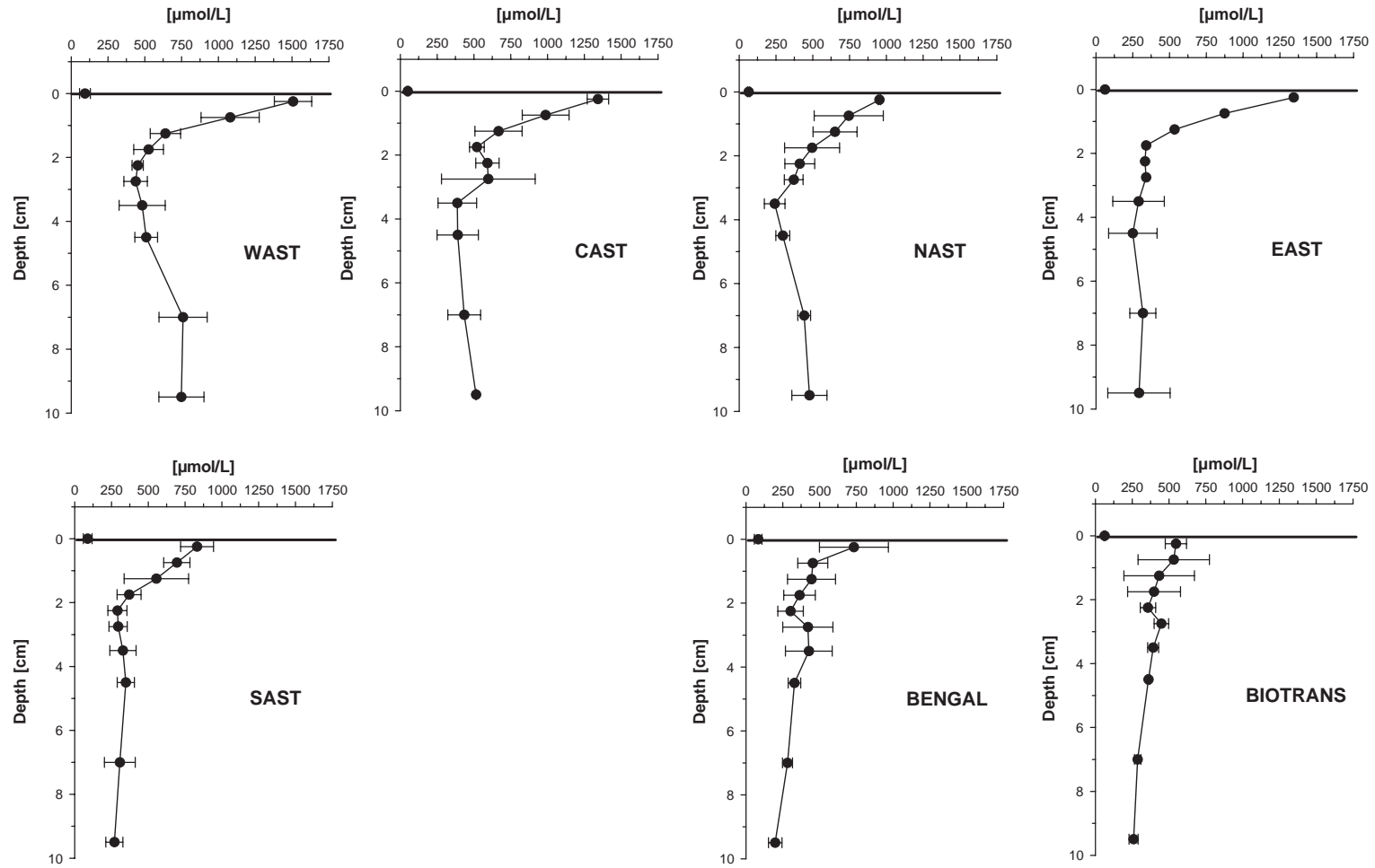
Fig. 2. Mean pore-water DOC concentration profiles from the Arabian Sea and the NE Atlantic. Number of independent MC hauls per station are listed in Table 2. Cruise information is listed in Table 1. The horizontal solid lines represent the sediment surface and the symbols at zero centimeters denote bottom water concentrations. Error bars indicate the variability (1σ) of the different cruises at a given site. At all sites pore-water DOC is significantly elevated over corresponding bottom water concentrations with highest amounts occurring in the uppermost sampling interval. Note that during *M 33/1* different sampling intervals were applied (1 cm instead of 0.5 cm steps). From *M 33/1* NAST the first centimeter is missing; *SO 118* EAST and *POS 260* BIOTRANS were not sampled.

Table 2
Mean DOC concentrations in surface sediments and the corresponding overlying bottom waters (values in μmol/L)

Cruise	M 33/1 Oct. 1995					SO 118 Aug. 1997				SO 129 Feb. 1998				
Station	WAST	CAST	NAST	EAST	SAST	WAST	CAST	NAST	SAST	WAST	CAST	NAST	EAST	SAST
Arabian sea														
No. of MC depth (cm)	1	1	1	1	1	5	2	1	2	2	1	1	1	1
BW	91	68	81	70	98	107	47	71	81	62	56	59	62	104
0–0.5	918	869	—	832	672	1526	1315	959	788	1460	1397	946	1343	917
0.5–1						1168	1063	911	714	859	835	579	873	654
1–1.5	814	675	605	636	362	683	715	757	617	533	571	546	534	431
1.5–2						548	525	628	364	470	510	364	340	381
2–2.5	456	349	222	391	269	455	608	483	255	443	559	340	333	362
2.5–3						455	585	415	271	394	621	326	341	344
3–4	504	224	162	166	289	470	421	269	358	500	481	294	413	307
4–5	487	576	244	134	319	487	281	310	345	578	422	336	367	382
5–6	419	437	385	130	162	—	—	—	—	—	—	—	—	—
6–7	511	254	485	308	188	—	—	—	—	—	—	—	—	—
6.5–7.5	—	—	—	—	—	784	455	485	380	858	543	441	381	308
7–8	370	314	312	205	129	—	—	—	—	—	—	—	—	—
8–9	468	422	401	182	342	—	—	—	—	—	—	—	—	—
9–10	443	—	345	143	241	799	514	576	307	775	517	511	442	224

Cruise station	M 36/6 Oct. 1996		M 42/2 Aug. 1998		POS 260 May 2000
	BENGAL	BIOTRANS	BENGAL	BIOTRANS	BENGAL
NE Atlantic					
No. of MC depth (cm)	1	1	2	2	1
BW	67	68	72	59	122
0–0.5	1038	624	550	509	795
0.5–1	562	809	369	394	515
1–1.5	653	709	316	296	497
1.5–2	406	603	279	297	492
2–2.5	288	400	248	336	429
2.5–3	575	499	274	423	561
3–4	303	367	452	405	503
4–5	375	353	303	365	337
6.5–7.5	324	313	257	275	291
9–10	244	295	172	242	208

Note: During M 33/1 different sampling intervals were applied (1 cm instead of 0.5 cm steps).
All DOC samples were retrieved from two to three tubes per MC haul. Number of MC indicates the number of MC hauls per station from where DOC samples were taken. DOC concentrations in case of multiple MC hauls represent average values from all samples.

enhanced primary production (Haake et al., 1993). This is also reflected by the sedimentary input with POC accumulation rates up to $600 \, \text{mg m}^{-2} \, \text{yr}^{-1}$ (Gaye and Breul, unpubl. data). Consequently, oxygen is depleted 2–5 cm below the sediment surface (Grandel et al., 2000; Luff et al., 2000). Highest DOC values in these sequences indicate that under sub-oxic conditions DOC is preferentially accumulated in deep-sea sediments. Sub-oxic to anoxic DOC accumulation also has been observed in shelf and continental margin sediments (Henrichs and Farrington, 1984; Martin and McCorkle, 1993; Burdige and Homstead, 1994; Otto and Balzer, 1998; Alperin et al., 1999; Holcombe et al., 2001). Station WAST, though, is unique among the other deep-sea environments covered by our study because of its adjacency to the Owen Ridge. A turbidite layer originating from the Owen Ridge has been detected between 6 and 85 cm core depth (Schnetger et al., 2000). It is characterized by 5–20-fold higher TOC, higher sulfur and phosphate contents due to enhanced sulfate reduction (Boetius et al., 2000; Böttcher et al., 2000; Grandel et al., 2000; Schnetger et al., 2000) and explains the significant increase of DOC concentrations below 6 cm core depth.

In contrast to the northern Arabian Sea, the open-ocean station SAST and the stations from the NE Atlantic are characterized by low to moderate rates of sedimentation (Honjo and Manganini, 1993; Newton et al., 1994; Rixen et al., 2000b) with POC accumulation between 30 and $84 \, \text{mg m}^{-2} \, \text{yr}^{-1}$ (Lee et al., 1998) at SAST and $\sim 130 \, \text{mg}$ in the NE Atlantic (Ståhl et al., 2004). Here, oxygen is not depleted within the first 10 cm (Grandel et al., 2000 and Grandel, unpublished data; Luff et al., 2000). Under these conditions DOC in the upper 2 cm is much lower than at the highly productive sites in the Arabian Sea and decreases slightly towards deeper core sections.

4.2. DOC effluxes in the deep sea

Significantly elevated DOC concentrations occur at the top of our sediment cores. These very striking increases of interstitial DOC towards the sediment surface in almost all of our sampled cores have to be treated with caution since pore-water

results from shelf and continental margin regions ($<2000 \, \text{m}$) usually do not show such elevations (Krom and Sholkovitz, 1977; Burdige and Homstead, 1994; Alperin et al., 1999; Mucci et al., 2000; Holcombe et al., 2001; Burdige, 2002; Papadimitriou et al., 2002). Highly elevated concentrations within deep-sea sediment surfaces are suspicious and have been considered as sampling artifacts due to pressure drop and increasing warming of the sediment cores during the transit through the water column and on-deck processing. These physical changes can cause biological cells to rupture, which then release intra-organismal organic and inorganic substances to the ambient pore-water (Jahnke et al., 1982; Martin and McCorkle, 1993; Glud et al., 1994; Balzer et al., 1998; Lohse et al., 1998). In our case, organic carbon contents from the uppermost core sections, where the microbial biomass reaches maximum values (Boetius et al., 2000), would be mainly influenced by cell-lysis during DOC extraction (Chin and Gschwend, 1991; Martin and McCorkle, 1993; Holcombe et al., 2001). Thus, for the following calculation and interpretation of our data we use the rather conservative but common flux estimates calculated from the 1.5–2 cm core intervals to the bottom water (e.g., Otto and Balzer, 1998). According to this approach mean DOC effluxes range between 62 and $224 \, \mu\text{mol m}^{-2} \, \text{d}^{-1}$ in the Arabian Sea and between 47 and $121 \, \mu\text{mol m}^{-2} \, \text{d}^{-1}$ in the NE Atlantic (Fig. 3 and Table 3). These effluxes are almost equal to those calculated by Otto and Balzer (1998) for deep-sea sediments in the NE Atlantic. Moreover, Burdige et al. (1999) have obtained similar efflux rates by in situ DOC measurements in sediments $>2000 \, \text{m}$ off the coast of California (see also Table 4). These similarities underline the feasibility of calculating DOC flux rates from 1.5 to 2 cm core depth although we cannot completely rule out that the DOC content in deeper core sections was altered by sampling artefacts as well. On the other hand potential DOC flux calculations from the uppermost core sections would lead to efflux rates that were many times greater than the accumulating POC flux based on sediment trap studies (Haake et al., 1993; Newton et al., 1994; Rixen et al., 2000a). Although intensively debated
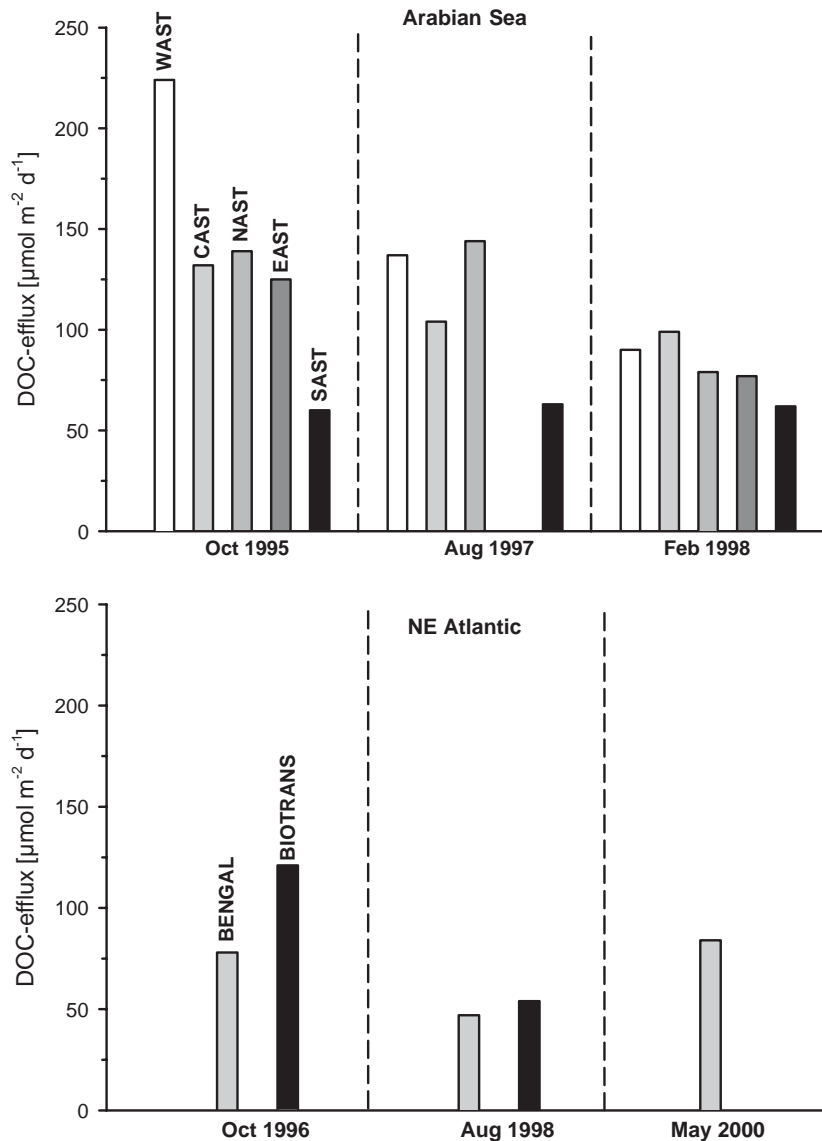
Fig. 3. DOC efflux rates in the Arabian Sea and NE Atlantic (positive efflux values = negative flux values from the calculation). Fluxes were calculated with $D_0 = 1.45 \times 10^{-6}\,\text{cm}^2\,\text{s}^{-1}$ from the respective 1.5–2 cm core interval (1–2 cm for *M 33/1*). All stations are characterized by DOC fluxes out of the sediments into the overlying bottom waters. In the Arabian Sea highest variability was found for station WAST, whereas station SAST showed no differences between the three cruises. In the NE Atlantic, stations BENGAL and BIOTRANS showed significant differences of DOC efflux rates in October 1996; both stations revealed lower values in August 1998. BIOTRANS was not sampled in May 2000.

elsewhere, sediment traps in the Arabian Sea as well in the NE Atlantic seem to measure the vertical particle flux correctly (Scholten et al., 2001; Yu et al., 2001). As a consequence calculated DOC efflux rates from the uppermost horizon would be much too high if compared to the downward particle flux.

For all approaches of calculating DOC fluxes from deep-sea sediments their limitations should be kept in mind since it is not clear how much of

Table 3
Porosity, salinity, temperature, and $D_{sw}(T)$ data for DOC benthic flux calculations

Station	Porosity[a]	Salinity[a] (‰)	Temp[a] (°C)	$D_{sw}(T)$ $(10^{-6}\,cm^2\,s^{-1})$	Benthic flux $J_{(DOC)}$ ($\mu mol\,m^{-2}\,d^{-1}$)		
					M 33/1	*SO 118*	*SO 129*
WAST	0.95	34.75	2.0	0.296	−223.9	−136.2	−90.3
CAST	0.85	34.70	1.5	0.291	−131.8	−103.9	−98.8
NAST	0.90	34.84	2.0	0.291	−139.4	−143.7	−78.6
EAST	0.85	34.86	2.0	0.296	−125.0	—	−76.6
SAST	0.85	35.00	2.0	0.299	−59.8	−63.2	−61.6
					M 36/6	*M 42/2*	*POS 260*
BENGAL	0.85	35.25	2.5	0.305	−77.8	−47.2	−83.7
BIOTRANS	0.85	35.25	2.5	0.304	−121.2	−53.8	—

Negative values indicate DOC fluxes out of the sediments (= effluxes).

[a]Porosity, salinity, and temperature data for the Arabian Sea from Luff et al. (2000); porosity for the NE Atlantic from Pfannkuche (unpubl.), salinity and temperature from Pfannkuche et al. (2000).

Table 4
Mean benthic DOC fluxes from our study sites in comparison with other deep-sea areas

Region	Depth (m)	Average benthic flux ($\mu mol\,DOC\,m^{-2}\,d^{-1}$)	
Arabian Sea			
WAST	4050	−150	Our study
CAST	3950	−112	Our study
NAST	3190	−121	Our study
EAST	3850	−101	Our study
SAST	4420	−62	Our study
NE Atlantic			
BENGAL	4800	−70	Our study
BIOTRANS	4500	−88	Our study
Other study sites			
NE Atlantic, St. IOS	4805	−100	Otto and Balzer (1998)
NE Pacific, St. N	4100	−2920 (−130)	Bauer et al. (1995)[a]
E Pacific, Site M	3100	−102	Heggie et al. (1986)[b]
Wedell Sea St. 3	2514	−577	Hulth et al. (1997)[c]
NE Pacific, St. 3	3,595	−720	Direct measurements during benthic lander incubations
NE Pacific, St. 4	2144	−140	Burdige et al. (1999)
NE Pacific, St. PE	3733	−100	

Benthic DOC fluxes in the NE Pacific (Burdige et al., 1999) were directly measured and calculated during short-term benthic lander deployments.

[a]Benthic flux (in parenthesis) recalculated with average DOC concentration from 1 to 2.5 cm core depth.

[b]MANOP Site M at the East Pacific Rise; porosity (estimated): 0.90, core depth: 1–2 cm.

[c]Core depth 0–1 cm.

the DOC is remineralized by, e.g. microbial activity. Second, a linear flux gradient can only be the best estimate of the true gradients at the sediment–water-interface. Last, lateral input of POC is not considered in this study but may affect some stations in the Arabian Sea. These uncertainties can only be reduced or eliminated by in situ measurements of DOC fluxes (benthic lander

deployments, see e.g., Burdige et al., 1999), and is therefore a major goal for future DOC flux studies in the deep sea.

4.3. Factors controlling the DOC efflux in the deep sea

To investigate the reason for spatial variations of our DOC fluxes, annual DOC efflux rates were calculated by using the average value from each study site. These averages were compared to the annual particle flux data of the Arabian Sea taken from Haake et al. (1993) and Rixen et al. (2000b) for stations WAST, CAST and EAST (sediment trap deployed at ~1000 m above bottom), and by Lee et al. (1998) for station SAST (sediment trap 500 m a.b.). For NAST, no long-term particle flux studies are available yet. Therefore, we used the particle flux measurements from short-term deployments (500 m a.b.) carried out during the BIGSET program and extrapolated these fluxes to an annual record. For the NE Atlantic Scholten et al. (2001) recalculated annual POC fluxes from Schulz-Bull (unpubl.) at our study site by using Thorium isotopes (^{230}Th) for trapping efficiency estimation. Since our deep traps (>2500 m) in the Arabian Sea measure the particle flux with a trapping efficiency close to 100% (Yu et al., 2001) it is feasible to use uncorrected sediment trap data from the deep Arabian Sea and corrected data from the Atlantic Ocean to compare them with our DOC fluxes. Since the decomposition of POC is low we refrain from applying a depth correction for the trap data.

The DOC effluxes in the deep sea are strongly positively correlated ($r^2 = 0.98$) to annually averages of POC flux rates (Fig. 4). Hence, the particle flux and consequently even the amount of primary production in the photic zone determine DOC efflux rates from deep-sea sediments. This relationship is valid ($r^2 > 0.91$) for all efflux calculations with concentrations from any core depths between 0 and 2 cm. These correlations, however, seem to be feasible only for deep-sea regions remote from continental margins. At the NW European continental margin, for example, DOC effluxes (Otto and Balzer, 1998) and vertical POC fluxes (Antia et al., 1999, 2001) do not
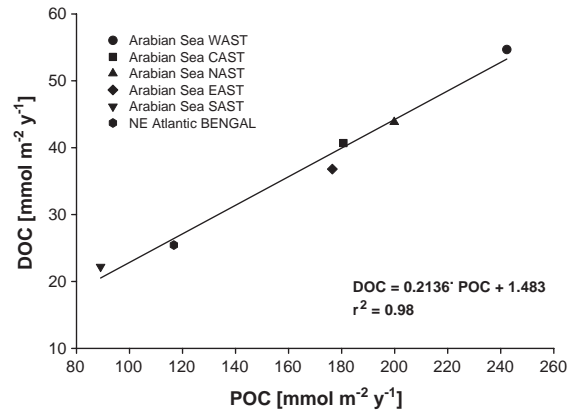

Fig. 4. Particulate organic carbon flux in the deep sea vs. DOC efflux rates in deep-sea sediments. Long-term POC fluxes were taken from Haake et al. (1993), Lee et al. (1998), Rixen et al. (2000a, b), and Scholten et al. (2001), DOC effluxes represent the annual mean based on our study. Dissolved organic carbon efflux rates correlate with POC fluxes in the water column and their sedimentation on the sediment surface. If the correlation is valid for the entire open ocean then DOC efflux rates from deep-sea sediments can be deduced from a given POC export ratio.

correlate, probably due to lateral inputs of (resuspended) marine and terrestrial sediments. Similarly, a relationship between the organic carbon content and accumulation rate could not have been established in various oxygen-depleted continental margin sediments (Stein, 1986; Henrichs, 1992; Davidson et al., 1995).

4.4. Fate of organic carbon in deep sea

A small fraction of vertically settling POC becomes buried in the sediments and is stored there over a geological time span. Another portion of this POC is decomposed to DOC by biological or geochemical processes, but the vast majority of POC is consumed as an energy and nutrition source by the benthic community and is released as inorganic carbon (CO_2) (Degens and Mopper, 1976; Bender and Heggie, 1984; Emerson et al., 1985; Hedges, 1992; Henrichs, 1992). Assuming that the benthic biomass, CO_2, and DOC pore-water concentrations remain constant, the incoming POC must be balanced by the organic carbon burial and the release of DOC and CO_2.

Accumulation rates for the Arabian Sea were calculated from bulk sediment accumulation data (Haake et al., 1993; Gaye-Haake and Breul, unpubl.) and the average POC-content in our MC samples from the BIGSET program for stations WAST, CAST, EAST, NAST and from Lee et al. (1998) for station SAST. For the NE Atlantic a bulk accumulation rate of $27 \, \mathrm{g \, m^{-2} \, yr^{-1}}$ (Cremer et al., 1992) was assigned for our study site, which then was used for the calculation of POC accumulation rates derived from POC contents in our sediment samples. Finally, the fraction of remineralized carbon was calculated by the subtraction of organic carbon accumulation rates and the diffusive DOC efflux rates from the vertical POC flux. Our calculations show that approximately 21% (station EAST) to 25% (station SAST) of the incoming POC is converted into DOC and subsequently released by benthic diffusive fluxes. Hence, about 72–75% of the sedimenting POC is respired and finally converted to CO_2 (Fig. 5), except for station WAST where $\sim$57% is released as CO_2 (Fig. 5). The latter station is governed by significantly higher vertical POC flux
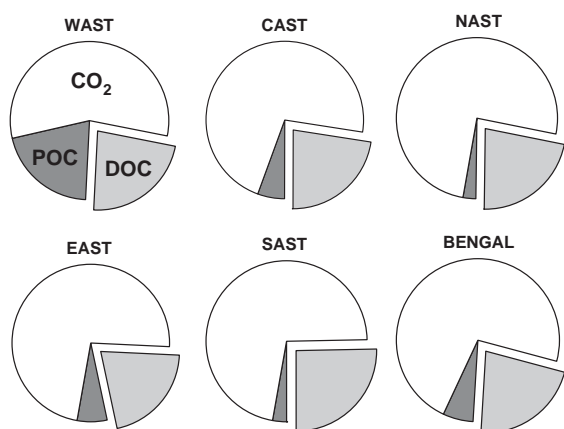

Fig. 5. Fate of POC in deep-sea sediments assuming that the annual vertical POC flux represents 100% of the sedimenting material and that the fraction, which is not buried as POC or released as DOC, is converted to inorganic CO_2. The vast majority (72–75%) of the incoming POC is respired to CO_2 or released as DOC (21–25%) Concurrently, only a minor part (2.5–6%) becomes eventually buried in deep-sea sediments. Station WAST exhibits an exceptional situation with 21% of buried POC and only 57% of released CO_2. The fraction of released DOC at station WAST is about 22%.

rates than common open-ocean regions and is influenced by elevated lateral transport from the adjacent Owen Ridge (Schnetger et al., 2000). For deep-sea sediments in the NE Atlantic, Ståhl et al. (2004) have calculated a POC burial efficiency of $\sim$6%, which exactly matches our results.

The further fate of the released DOC (DOM) depends on the reactivity of the organic compounds. If deep-sea sediments released labile and reactive DOM, it would be rapidly remineralized and not be significant for the oceanic DOC inventory (Bauer et al., 1995). However, recent investigations have revealed that at least a considerable portion of DOC in marine sediments is released as refractory organic compounds (Guo and Santschi, 2000; Burdige, 2001, 2002). Thus, deep-sea sediments at open-ocean regions, where the organic matter is more degraded (Hedges et al., 1999), may play an important role for the oceanic organic carbon budget.

4.5. Global estimates

Our study as well as other deep-sea investigations from the NE Atlantic (Otto and Balzer, 1998; Papadimitriou et al., 2002), NE Pacific (Bauer et al., 1995; Burdige et al., 1999), E Pacific (Heggie et al., 1986), SE Pacific (Henrichs and Farrington, 1984), and the Southern Ocean (Hulth et al., 1997) strongly suggest that an efflux of DOC takes place all over the deep sea (Table 4). Calculated DOC efflux values, however, differ significantly between these sampling sites. For example, Otto and Balzer (1998) reported a DOC flux of $100 \, \mu\mathrm{mol \, m^{-2} \, d^{-1}}$ at 4800 m water depth in the NE Atlantic, which agrees with our calculations. Hulth et al. (1997) calculated benthic DOC efflux rates in the Weddell Sea (2514 m) of $577 \, \mu\mathrm{mol \, m^{-2} \, d^{-1}}$, which would be more than twice as much as the DOC efflux of the eutrophic station WAST in the Arabian Sea (Table 4). In contrast, Bauer et al. (1995) calculated average DOC efflux rates of $2920 \, \mu\mathrm{mol \, m^{-2} \, d^{-1}}$ for the eastern Pacific station off California (4100 m).

The main reason for this dramatic variability of diffusive flux rates is mainly derived from differences in calculating benthic DOC fluxes. Taking different core intervals would change the DOC concentration *and* the diffusion length. If we

recompute the DOC efflux rate from Bauer et al. (1995) using the same diffusion length than in our calculations we obtain similar results ($130\,\mu mol\,m^{-2}\,d^{-1}$) to our deep-sea sites (Table 4). Efflux rates from the deep Weddell Sea (Hulth et al., 1997) are higher than those at our sites as DOC concentrations from 0 to 1 cm instead of 1–2 cm core depth were used. As a consequence we need standardized calculations in order to compare efflux rates in the deep sea. With this standardized (yet not fully optimized) calculation we conclude that the deep sea can be described by generally uniform DOC efflux rates between ~50 and $200\,\mu mol\,m^{-2}\,d^{-1}$ (Table 4). Flux rates are further reduced at deep-sea regions remote from continental margins. These calculated values correspond fairly well with directly measured DOC fluxes from the eastern Pacific (Burdige et al., 1999), where at Station PE (3733 m) and Station 4 (2144 m) effluxes range between 100 and $140\,\mu mol\,DOC\,m^{-2}\,d^{-1}$, respectively.

Our results in concert with the above-mentioned DOC efflux rates indicate that deep-sea sediments potentially release $184\,\mu mol\,DOC\,m^{-2}\,d^{-1}$ (average benthic efflux rates of all stations from Table 4 with recalculated flux rate at Station N). Given an open-ocean area of $302 \times 10^{12}\,m^2$, a first estimate suggests a total efflux rate of about $243\,Tg\,DOC\,yr^{-1}$ from deep-sea sediments below 2000 m water depth. This high mean efflux rate would be distinctly reduced to $106\,\mu mol\,m^{-2}\,d^{-1}$ if Station 3 from the NE Pacific (Burdige et al., 1999) with its high efflux rate and Station 3 from the Weddell Sea (Hulth et al., 1997) were omitted. This would lead to a lower estimate of about $141\,Tg\,DOC$ annually released from deep-sea sediments.

Taken into account that the DOC efflux depends on the quantity of the organic matter transported from the surface ocean to the deep sea as well as the fact that the available data do not cover low productivity zones, we have calculated potential DOC efflux rates based on global POC flux rates. Our results have been derived from POC fluxes at 2000 m water depth calculated from primary production rates by a *Suess-type* equation (Suess, 1980; Rixen et al., 2002). These POC flux rates are then used to calculate DOC efflux rates

(Table 5) according to the regression equation in Fig. 4 (Antoine et al., 1996; Behrenfeld and Falkowski, 1997; Rixen et al., 2002). From this perspective global DOC efflux rates range between 50.5 and $78.1\,\mu mol\,m^{-2}\,d^{-1}$ or between 66.9 and $103.4\,Tg\,C\,yr^{-1}$, covering the complete open ocean with the entire range of low- to high-productivity areas.

Alperin et al. (1999) estimated benthic DOC efflux to be $40\,Tg\,C\,yr^{-1}$ for marine sediments $\leqslant 2000\,m$. Burdige et al. (1999) calculated benthic DOC fluxes in coastal (0–200 m) and continental margin (200–2000 m) sediments of 88 and $89\,Tg\,C\,yr^{-1}$, respectively. Hence, deep-sea sediments contribute to at least one-third of the DOC released from marine sediments, although the sediments $> 2000\,m$ water depth account for 82.7% of the area covered by the ocean (Kennish, 2001). This apparent imbalance can be explained by enhanced sedimentation and carbon burial rates in coastal environments (Müller and Suess, 1979; Bender and Heggie, 1984; Hedges and Keil, 1995; Soetaert et al., 1996; Middelburg et al., 1997). On the other hand, only 18% of the settling flux of labile organic carbon and 5% of organic matter burial take place below 2000 m water depth (Middelburg et al., 1997). Thus, the efficiency of DOC released from settling and sedimenting POC is several times greater in the deep sea than in coastal and continental margin regions and can be explained by the higher efficiency of POM decomposition in oxic deep-sea sediments (Henrichs, 1992; Hedges et al., 1999). Altogether, marine sediments release about $262\,Tg\,C\,yr^{-1}$ and thus even exceed the global mean riverine DOC input of 210–$215\,Tg\,C\,yr^{-1}$ (Meybeck, 1982; Ludwig et al., 1996), which suggests that marine sediments act as an important source of DOC in the oceans.

5. Conclusions

1. Highest DOC concentrations within deep-sea sediments from the Arabian Sea and NE Atlantic occur in the uppermost core sections with a sharp decrease towards ~3 cm core depth. Under sub-oxic to anoxic conditions DOC concentrations increase with increasing

Table 5
Global mean DOC efflux rates from deep-sea sediments (> 2000 m water depth) calculated from POC flux rates (Rixen et al., 2002) and regression equation derived from Fig. 4

Primary production (PP) (10^{12} g C yr^{-1})	POC Export$_{2000}$ (10^{12} g C yr^{-1})	DOC efflux[e] (µmol m^{-2} d^{-1})	DOC efflux[f] (Tg yr^{-1})
29,925[a]	288[c]	50.5	66.9
34,485[b]	459[d]	78.1	103.4

Water depths taken from the ETOPO 5 data set with a $1° \times 1°$ resolution (http://ingrid.ldgo.columbia.edu/SOURCES/WORLDBATH).

[a]Primary Production derived from Antoine et al. (1996).

[b]Primary Production derived from Behrenfeld and Falkowski (1997).

[c]POC export rates at 2000 m water depth calculated with POC(ER$_{2000}$) = $0.01PP^2/z^{0.628}$ (z = water depth) with an $1° \times 1°$ resolution for open ocean regions (Rixen et al., 2002).

[d]POC export rates at 2000 m water depth calculated with POC(ER$_{2000}$) = $3.523PP/z^{0.734}$ (z = water depth) with an $1° \times 1°$ resolution for open ocean regions (Rixen et al., 2002).

[e]DOC efflux rates derived from POC export rates and calculated with regression equation Fig. 4.

[f]Annual DOC efflux from marine sediments (water depth > 2000 m; area: 302×10^{12} m^2).

core depth whereas at open-ocean sites with well-oxygenated sediments (SAST, BIO-TRANS, BENGAL) DOC values tend to slightly decrease in deeper core segments.

2. The high DOC concentrations within approximately the first centimeter are problematic because sampling artifacts (e.g., cell lysis) cannot be completely ruled out. DOC concentrations from deeper core intervals are also significantly elevated over bottom water DOC, leading to the assumption that a DOC efflux takes place at all of our sampling sites. Potential conservative efflux rates calculated from 1 to 2 cm core depth to the ambient bottom water range from ~60 to 224 and 47 to 121 µmol m^{-2} d^{-1} in the Arabian Sea and NE Atlantic, respectively.

3. In deep-sea sediments, about 21–25% of the sedimenting POC flux is decomposed to DOC and subsequently released from the sediments. Incoming POC fluxes and diffusive DOC effluxes are strongly positively correlated in open-ocean regions. Thus, DOC efflux rates are governed by the quantity of accumulating POC and therefore even depend on the regional productivity in the corresponding photic zone. This relationship enables us to calculate the world-wide DOC efflux from deep-sea sediments below 2000 m water depth, ranging between 50.5 and 78.1 µmol m^{-2} d^{-1}. Following

this approach, deep-sea sediments release a mean of ~85 Tg DOC yr^{-1} and thus make an important contribution to the oceanic organic carbon pool.

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6. Concluding remarks

All presented publications elucidate processes and pathways of organic matter alteration, decomposition and cycling in deep-sea environments. They have focused on quantitative fluxes but particularly on qualitative changes of organic matter in sinking particles from the water column and in surface sediments by using amino acid concentrations and spectra as well as stable isotopic ratios of bulk nitrogen. Furthermore, processes of organic matter degradation and dissolved organic carbon release in surface sediments have been related to the amount and degradational state of organic matter reaching the sediment-water-interface.

The study of particulate organic matter fluxes in the South China Sea exemplarily shows that the magnitude of vertical organic matter transport within deeper water masses and its qualitative composition are closely coupled to climatic and oceanographic conditions at the sea surface. Both, steady monsoon oscillations as well as temporarily occurring global climatic events such as the El Niño phenomenon directly affect the biogeochemistry of particulate organic matter in the deep sea. Particularly El Niño conditions in the SCS lead to a change in primarily produced material at the sea surface, reduced seasonality of particle fluxes as well as enhanced organic matter degradation as discerned by amino acid spectra. In this context basic proteinogenic amino acids, all above histidine, seem to trace organic matter alteration in the deep SCS. Overall, the extent of early diagenesis increases from the mid-water column to surface sediments. In general, the SCS stands for an oligotrophic regime with similar flux rates compared to other monsoon-influenced regions but depicts highest organic matter degradation rates of all studied oceanic regions.

The influence of sea-surface processes on particulate organic matter in the deep ocean has also been documented in the eastern Mediterranean Sea where changing circulation patterns potentially favour primary production by N_2-fixing diazotrophs. Consequently, the $\delta^{15}N$ signals in particulate organic matter range between 1.2 and 2.5 ‰, values close to the atmospheric N_2 standard. Isotopic nitrogen ratios from particulate organic matter provide valuable information on food chains in the deep Mediterranean Sea. Moreover, the $\delta^{15}N$ signature increases with increasing water depth, indicating a preferential uptake and remineralisation of light nitrogen and thus reveals early diagenetic pathways. Enrichment of residual $\delta^{15}N$ not only takes place in the water column, but to a high degree also at the sediment-water-interface as shown in the northern Indian Ocean. In the open ocean, unaffected from continental margins, $\delta^{15}N$ is

generally 2-3 ‰ higher in surface sediments compared to the respective sediment trap samples from 500 m above ground. Based on amino acid composition (Degradation Index) the relationship between the diagenetic effect on organic matter and the isotopic signature has been circumstantiated. This has to be taken into account for paleoceanographic and paleoclimatological reconstructions and are important for their interpretation.

The paper on DOC release from deep-sea sediments stresses the association between qualitative and quantitative studies of organic matter. The quality of organic matter not only has an effect on the particulate residue in the deep sea but also triggers, in combination with flux magnitudes, the degree of organic matter regeneration, i.e. the transformation from particulate to dissolved organic or inorganic constituents. It has been corroborated that the vast majority (> 70 %) of sedimenting organic matter at the seafloor is respired and remineralised to CO_2 (and other inorganic substances). Most of the residual organic substances within the sediments are converted to dissolved organic matter and are concentrated in the upper sediment horizon, leading to a significant efflux to the deep water where it can undergo further recycling. It is well demonstrated that the amount of DOC released is significantly correlated with the incoming organic matter flux. Furthermore, this study presents the first calculation of DOC efflux rates for the entire deep sea (> 2000 m water depth) with an estimate of global DOC release of approximately 85 Tg DOC y^{-1} for deep-sea sediments and about 260 Tg DOC y^{-1} for all marine sediments including shelves and continental margins. This implies that the deep-sea floor acts as an important potential DOC source that matches riverine input.

These new insights acquired by the presented studies also point to important topics for future investigations. It is crucial to understand the transfer and interactions between inorganic and organic matter. For instance, more data on isotopic signatures of nutrients such as nitrate is required to improve our understanding of nitrogen sources and cycling in the water column. Isotopic ratios ($\delta^{13}C$, $\delta^{15}N$) from bulk amino acids or even compound specific stable isotope analyses would significantly improve our knowledge of organic matter cycling in detail. In addition, dissolved organic matter (DOC, DON) needs to be characterised, both chemically and isotopically, in order to elucidate sources and potential sinks and to get more information on their reactivity and thus "bioavailability". Undoubtedly, sediment trap studies have been an invaluable aid for the understanding of marine biogeochemistry. Particularly our knowledge of particle fluxes and organic matter cycling in the deep sea have benefited from

these long-year field investigations. But it also became obvious that we need more information, solid and comprehensive data, from various, insufficiently studied oceanic areas.

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