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Evidence for terrigenous dissolved organic nitrogen in the Arctic deep sea

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Abstract

To trace the fate of terrigenous dissolved organic nitrogen (DON) in the Arctic Ocean, principal-components analyses (PCA) was used on a data set of 13 amino acids released via hydrolyses from a total of 110 water samples from Russian rivers, adjacent near-shore locations, and the Laptev Sea. The first component of the PCA distinguished significantly between terrigenous DON from the rivers (1.2 ± 0.1) and marine-derived DON in the deep central Arctic Ocean (−1.1 ± 0.2). The significance of this distinction was validated with amino acid data from seawater and river samples from other regions. The second PCA component correlated significantly with the proportion of D-alanine, a tracer for microbial degradation. The percentage of terrigenous DON in the Arctic Ocean was assessed from the first PCA component. The model was calibrated using data from the rivers (100% terrigenous) and the deep central Arctic Ocean (~0% terrigenous) as end members. Terrigenous DON accounted for 28 ± 13% of the total DON on the Laptev Sea shelf, which is in good agreement with independent, lignin-based estimates. High proportions of terrigenous DON (up to 100%) were calculated for the continental slope down to 2,000 m depth and are probably due to downward convection of brine-enriched shelf waters. The model presented here provides the first direct evidence of terrigenous DON in the deep sea. The model may be directly applied to trace the fate of terrigenous DON in other terrestrially dominated marine environments.

Fluvial inputs of dissolved organic matter are an important source of bioavailable nitrogen to the oceans (Cornell et al. 1995 and references therein). Because it is the availability of nitrogen that often limits phytoplankton growth in the euphotic zone, terrigenous dissolved organic nitrogen (DON) plays a major role in marine element cycles. Organically bound nitrogen, however, is only available to most primary producers after mineralization. Its resistance to microbial or abiotic degradation determines the scale on which continental fluxes of organic nitrogen affect marine ecosystems. Labile compounds enhance primary production on an estuarine and inshore scale. Refractory compounds, on the other hand, are transported further offshore and there may affect marine production. Continental fluxes of inorganic and organic nutrients to the ocean have strongly increased as a result of human activity (e.g., Cornell et al. 1995). Any assessment of human effects on global element cycles requires a detailed knowledge of the cycling and fate of terrigenous organic compounds in the ocean. However, the biogeochemistry of dissolved organic compounds in the ocean is not well understood. In particular, the fate of terrigenous DON is still a conundrum in contemporary marine sciences.

For tracing the fate of terrigenous dissolved organic matter in the ocean, thus far lignin is the only unambiguous molecular tracer that has been successfully applied (Meyers-Schulte and Hedges 1986; Opsahl and Benner 1997; Lobbes et al. 2000; Dittmar et al. 2001*b*). Spectroscopic properties have also been used to identify the source of dissolved organic matter in coastal zones (e.g., Moran et al. 1991). For organic nitrogen, however, the usefulness of lignin or general spectroscopic information as tracers is limited, because DON may cycle uncoupled from organic carbon or bulk organic matter (e.g., Kattner and Becker 1991). A molecule that would unambiguously trace terrigenous organic nitrogen in the ocean is not yet known.

Amino acids, the principal building blocks of DON, can be identified at the molecular level. In Arctic rivers, ~40% of DON (primarily refractory and terrigenous) is composed of hydrolyzable amino acids, whereas, in the Arctic Ocean, they make up only ~10% of DON (Dittmar et al. 2001*a*). Other world rivers and ocean basins have similar values (Hedges et al. 1994, 2000; Hubberten et al. 1995; Lara et al. 1998). The amino acid composition of the ultimate source is almost invariant over a wide range of different organisms compared with alterations that occur on degradation (Cowie and Hedges 1992; Dauwe and Middelburg 1998). During diagenesis in marine sediments, the proportions of the individual amino acids change in a characteristic way and can therefore be used as diagenetic tracers (Dauwe et al. 1999). Amino acids also serve as tracers for the early diagenesis of dissolved compounds (Amon et al. 2001). The environment in which degradation takes place influences the amino acid signature of DON. Highly degraded, refractory DON of marine and terrestrial origin exhibits significantly different amino acid patterns, which reflects the contrasting environmental conditions (Dittmar et al. 2001*a*). In soils, gram-positive

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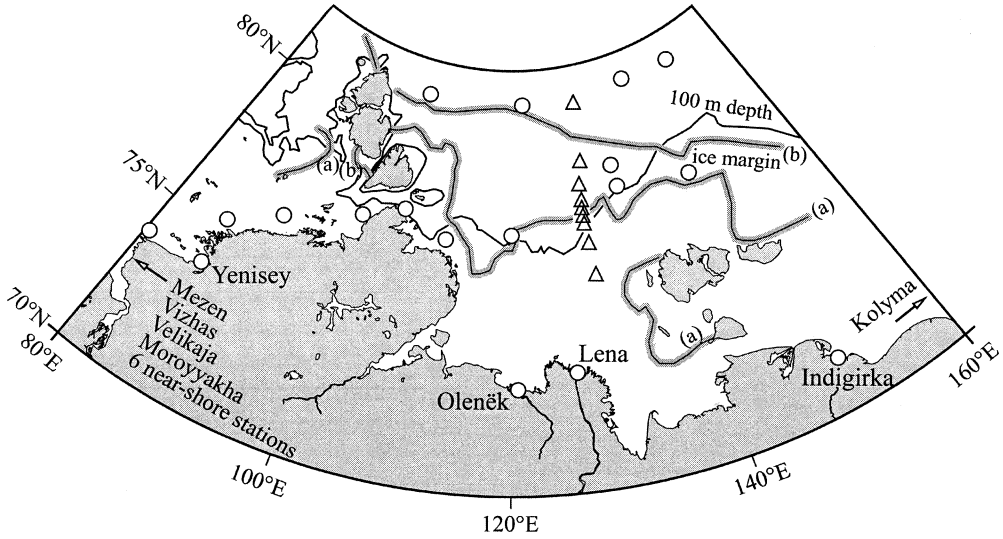

Fig. 1. Map of the sampling stations along the Siberian coast, in the Laptev Sea and in Amundsen Basin (Kattner et al. 1999; Dittmar et al. 2001*a*). The ice margin in the Laptev Sea at the beginning of sampling, (a) 7 July 1995, and the end of sampling, (b) 20 September 1995. Samples were taken at the surface (circles) and from depth profiles from water surface to bottom (triangles).

bacteria and strong particle-solute interactions dominate diagenesis. Marine-derived dissolved organic matter, on the other hand, is mainly the product of gram-negative bacteria and photodegradation.

Because of the high terrestrial input in terms of freshwater and organic matter, the Arctic Ocean is one of the best-suited regions for studying the fate of terrigenous compounds in the ocean. The concentration of terrigenous dissolved compounds in the Arctic Ocean is an order of magnitude higher than that in the Pacific or Atlantic (Opsahl et al. 1999). It is stably stratified, with a distinctive surface layer of reduced salinity throughout the year, and the transport of riverine freshwater to the outer shelf and advective mixing of surface with halocline waters lasts several years (e.g., Schlosser et al. 1995).

For the rivers, shelves, and open ocean in the eastern Arctic, an extensive data set on amino acids exists (Kattner et al. 1999; Dittmar et al. 2001*a*). In the present study, these amino acid data were used for multivariate statistics to differentiate between terrigenous and marine-derived DON. The aim was to quantitatively trace terrigenous DON in the ocean by exploiting the differences in the amino acid signature of refractory marine-derived and terrigenous DON and to introduce a quantitative approach for determining the fate of DON in the ocean.

Materials and methods

Sampling and chemical analyses—Individual amino acid data from riverine and marine sampling sites (Fig. 1) were used for statistical analyses. Detailed information on data, chemical analyses, and expeditions are presented by Kattner et al. (1999) and Dittmar et al. (2001*a*). In brief, the Arctic rivers exhibit a pronounced seasonal cycle, becoming free of ice during early summer and discharging >90% of the annual water delivery to the Arctic Ocean from May to July. Samples were obtained by freshet in 1994 and 1995. Surface water samples were collected from nine estuaries (salinity ~0) and along the coast (salinity 25–34) over an east-west distance of ~4,000 km of coastline (Dittmar et al. 2001*a*; Fig. 1). The rivers studied account for approximately one third of the riverine dissolved organic carbon (DOC) discharge to the Arctic Ocean (Lobbes et al. 2000). Additionally, samples were obtained from the Laptev Sea at vertical profiles (water surface to bottom) along a 550-km transect and from several surface water stations (Kattner et al. 1999; Dittmar et al. 2001*a*). A total of 110 water samples were taken for amino acid analyses.

The samples were filtered on board through precombusted Whatman GF/F filters (nominal pore size ~0.7 μm) with the application of a gentle vacuum, to prevent cells from breaking. Filters and filtrates were kept frozen (−30°C) in precombusted sealed glass ampoules. DON was determined by wet oxidation with potassium persulfate (Koroleff 1983). Total dissolved and particulate amino acids (TDAA and PAA) were quantified after hydrolysis (in 16% HCl at 110°C for 24 h in the presence of 55 μmol L^{-1} ascorbic acid; Fitznar et al. 1999). The concentrations of glycine and the D- and L-enantiomers of the individual amino acids aspartic acid, glutamic acid, serine, threonine, arginine, alanine, γ-amino butyric acid, tyrosine, valine, phenylalanine, isoleucine, and leucine were determined in the hydrolysates by high-performance liquid chromatography/fluorescence-detection after precolumn derivatization with *o*-phthaldialdehyde and *N*-isobutyrylcysteine. Each sample was analyzed in duplicate with two derivatizing agents (*N*-isobutyryl-L-cysteine and *N*-isobutyryl-D-cysteine). Only amino acid concentrations that were reproducibly quantified after derivatization with both reagents and only those D-enantiomers that were significantly different from the racemization blank are reported. The coefficients of variation between the duplicates were 1–

8%, and the relative standard deviation for the individual amino acids and each run was ≤3.5%.

Statistical analyses—The amino acid data were statistically analyzed by principal-components analysis (PCA). PCA is a variable-reduction procedure that can be defined as a linear combination of optimally weighted variables, in our case the mole percentages of the individual amino acids. The weights are optimal in the sense that they produce a set of components or orthogonal axes that are more successful in accounting for variance in the observed variables than any other set of weights. The optimal weights are created by the principle of least squares, similar to linear regression. The maximum variance in the data is described by the first component, the maximum of the remaining variance by the second, and so forth. The PCA components (factors) may each represent and describe quantitatively the sources of or the processes that influence the amino acid signature—for example, the proportion of terrigenous versus marine-derived DON or the degree of degradation. The underlying forces causing the variations in the data are not necessarily separated by PCA, and it needs to be proved that the PCA factors are each related to a suggested underlying cause.

PCA was done with data from 13 amino acids (variables) for 110 TDAA and 42 PAA samples (cases). The mole percentages of the individual amino acids were tested for normal distribution (Shapiro Wilks' *W*-test) and used for PCA without further transformation. For the PCA, the amino acid percentages were standardized by subtracting the mean and dividing by the standard deviation. PCA was done with StatSoft Statistica for Windows (1999 edition; StatSoft). The meaning of the derived principal components or PCA factors was assessed and validated with independent data—amino acid data from other rivers or oceans and D–amino acid proportions, which are tracers for microbial degradation. For comparing two independent parameters (e.g., PCA factors and D–amino acid proportions) a geometric mean regression using Ricker's (1973) method was done. The significance of Pearson's correlation coefficients was tested by Student's *t*-test. Variances of average values are expressed as confidence intervals ($P = 0.05$).

Results and discussion

The amino acid concentrations were highest in the rivers (3.2 μmol L^{-1} TDAA and 5.0 μmol L^{-1} PAA, on average) and decreased near shore and in surface waters of the Laptev Sea to 520 nmol L^{-1} for TDAA and 170 nmol L^{-1} for PAA (Dittmar et al. 2001*a*). In the estuaries and on the shelf, the TDAA concentration decreased approximately conservatively, whereas PAA were efficiently removed from the water column. TDAA concentrations further decreased with water depth to values <200 nmol L^{-1} in the deep sea (Fig. 2a). Exceptions to these general patterns were present in deep-sea samples close to the shelf slope, where concentrations >300 nmol L^{-1} were found. PAA exhibited much lower concentrations in the central Arctic Ocean (29 nmol L^{-1} on average at >30 m depth) than TDAA (Fig. 2b).

The first component of the PCA (PCA factor 1) accounted for 26% and 41%, and the second component (PCA factor 2) for an additional 18% and 17%, of the variability of the TDAA and PAA composition, respectively. PCA factor 1 followed a pattern similar to that of the amino acid concentrations (Fig. 2c). River and deep-sea samples exhibited significantly different values (Fig. 3; Table 1). In the rivers, PCA factor 1 for TDAA was 1.2 ± 0.1, and, in the deep central Arctic Ocean (>100 m depth), it was −1.1 ± 0.2 on average. Rotation of the orthogonal axis of the PCA did not enhance this difference, which shows that the maximum amount of source-related variations (terrigenous vs. marine) is incorporated within PCA factor 1. On the shelf, PCA factor 1 was higher than in the deep central Arctic Ocean (Table 1). The PCA factor 1 for PAA and TDAA exhibited a similar pattern (Fig. 4). At the continental slope down to water depths of 2,000 m, extraordinarily high values (1.3 ± 0.2), identical to those of the rivers, were found for TDAA. A local maximum of TDAA concentration was present north of these high PCA factor 1 values at the continental slope. No information is available for PAA in that region.

The results from the PCA suggest that PCA factor 1 can be used as a measure for terrigenous DON. This hypothesis was tested with independent data. Using the factor coefficients, average values, and standard deviations of the individual amino acid proportions of the Arctic Ocean data set (Table 2), the PCA factors for other river and seawater samples were calculated according to Eq. 1 (*see Table 2*). The amino acid signature of the Amazon River, its tributaries (Hedges et al. 2000), and the Lena River (Lara et al. 1998) resulted in PCA factor 1 values consistently >1.4 (Fig. 3). Antarctic and Greenland seawater (Hubberten et al. 1995; Lara et al. 1998) exhibited values of −0.5 or below. The similarity of the independent data from different regions or climate zones supports the hypothesis that PCA factor 1 is indicative of the amount of terrigenous versus marine DON in the Arctic Ocean. Freshwater inputs to the Eurasian shelves produce a characteristic radium isotope signature (Rutgers van der Loeff et al. 2003). For our Laptev Sea samples, the $^{228}Ra:^{226}Ra$ ratios (Hanfland unpubl. data) correlated highly significantly with PCA factor 1 of TDAA ($r = 0.71$, $P < 0.001$, $n = 22$). This correlation further confirms the significance of PCA factor 1 as a terrestrial source indicator.

In environments with a major contribution of fresh algal-derived DON, on the other hand, the variability of the amino acid signature is in the first place because of early diagenesis (Amon et al. 2001; Yamashita and Tanoue 2003). The application of Eq. 1 to labile algal-derived DON from sea ice (Amon et al. 2001) or from coastal waters in Japan (Yamashita and Tanoue 2003) provided PCA factor 1 values that were out of the range of the model. Care should therefore be taken in applying the model to environments with high amounts of diagenetically fresh DON. In the Arctic Ocean, however, DON is a final product of terrestrial and marine diagenesis, which reflects an integrated signal of strongly contrasting degradation processes. The amino acid composition can largely be explained by conservative mixing of refractory compounds, and significant modifications of these patterns due to degradation are unlikely during the timescale of mixing in the Arctic Ocean (Dittmar et al. 2001*a*). Neither in the rivers nor in the deep sea does the amino acid com-

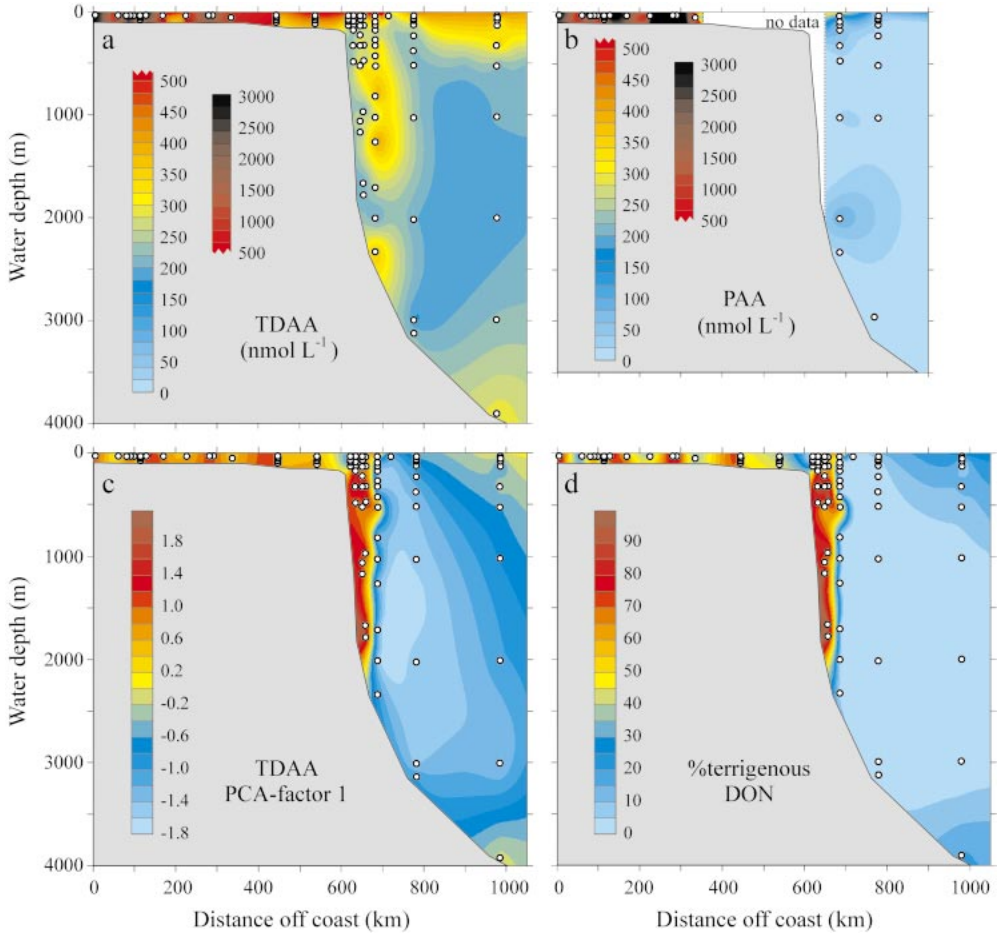

Fig. 2. Amino acids in the eastern Arctic Ocean. Data from all sampling stations are plotted vs. the distance off the coast and water depth; the sampling stations in the estuaries (''rivers'') are located at 0 km. Presented are (a) concentrations of TDAA, (b) concentrations of PAA, (c) values of PCA factor 1, and (d) the ratio of terrigenous DON to total DON, estimated from PCA factor 1.

position resemble the ultimate sources—vascular plants and phytoplankton. Cell-wall constituents (e.g., glycine), nonprotein amino acids (e.g., γ-amino butyric acid), and microbial-derived D-enantiomers were highly enriched in all samples compared with vascular plant tissue or phytoplankton, which indicates that DON has repeatedly passed through the microbial loop (Dittmar et al. 2001*a*). The different amino acid pattern of deep-sea and riverine DON cannot be explained by different levels of degradation. For instance, the proportion of threonine (a cell-wall constituent) in riverine TDAA was roughly twice the proportion of deep-sea TDAA, which indicates a higher degree of degradation. Glycine and alanine, on the other hand, indicated the contrary, being significantly lower in riverine than in deep-sea TDAA. A significant correlation between lignin and amino acid concentrations in the Siberian rivers indicates an association of amino acids with soil humic substances (Dittmar et al. 2001*a*). Also, the D–amino acid pattern found in riverine TDAA is characteristic of soil humic substances and differs from deep-sea TDAA. Because dissimilar degradation mechanisms in soils and the ocean are the likely cause of characteristic amino acid patterns, it is reasonable that those amino acids in particular which are most affected by degradation and are not necessarily dominant in vascular plants or phytoplankton exhibit the highest PCA factor score coefficients (Table 2). Even though PAA and TDAA are derived from the same ultimate sources (vascular plants and phytoplankton), their amino acid compositions and PCA factor score coefficients were highly different. Different compositional patterns of dissolved and suspended humics are commonly observed (e.g., Dittmar and Lara 2001) because of different pathways of release, degradation, and transport to the water column.

In the Arctic Ocean, the amino acid composition of TDAA fulfills all criteria of a source tracer (source specificity and conservative behavior in the timescale considered), and the percentage of terrigenous DON in the Arctic Ocean could be assessed from PCA factor 1. For this purpose, a nonlinear function between PCA factor 1 and the percentage of terrigenous DON was established (Fig. 5). The model was calibrated using the average amino acid composition of the Russian rivers (~100% terrigenous; Dittmar and Kattner 2003*a*) and the deep central Arctic Ocean, where DON was assumed to be of pure marine origin (~0% terrigenous). With the

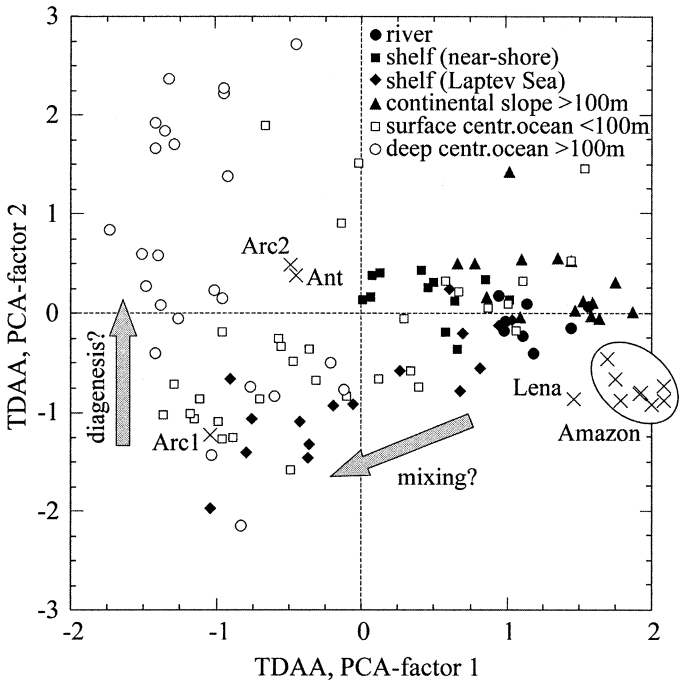

Fig. 3. PCA of TDAA. Values of PCA factor 1 vs. values of PCA factor 2 for the different sampling sites in the eastern Arctic Ocean are shown. Values for the Amazon and its tributaries (Amazon; Hedges et al. 2000), the Lena River and Fram Strait (Lena and Arc2; Lara et al. 1998), and the Greenland Sea and the Antarctic Atlantic (Arc1 and Ant; Hubberten et al. 1995) were calculated according to Eq. 1.

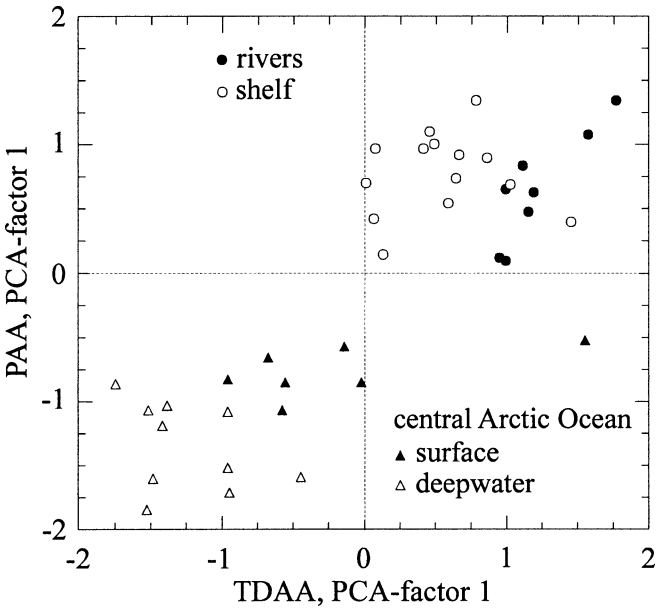

Fig. 4. Values of PCA factor 1 are shown. Values of PAA are plotted vs. values of TDAA.

Antarctic sample as a marine end member, where terrigenous influence can be almost excluded, similar results were achieved. The results of the calculations are given in Fig. 2d and Table 1. Terrigenous DON accounted for 28 ± 13% of the total DON on the Laptev Sea shelf. Kattner et al. (1999) calculated a terrigenous DON contribution of 20–30% for the Laptev Sea shelf, on the basis of lignin data and the assumption that terrigenous DOC and DON behave in a similar fashion in this area. The consistency of the two independent approaches confirms the usefulness of PCA factor 1 as a quantitative measure for terrigenous DON. On the shelf, local algae blooms are probably responsible for the patchy pattern of proportions of marine versus terrigenous DON (Fig. 2d). These blooms generally occur along the receding ice edge. This algal-derived marine DON had already passed the first stages of degradation at the time of sampling, as indicated by high D–amino acid proportions and the overall amino acid composition (Dittmar et al. 2001*a*), but is probably less refractory than riverine DON. Therefore, the relative proportion of terrigenous DON probably increases again after algae growth due to microbial degradation of the less-stable algae component.

Along the entire continental slope down to 2,000 m depth, the percentage of terrigenous DON was consistently higher than that on the shelf, reaching values of up to 100% (Fig. 2d). Further north of this maximum, the proportion of terrigenous DON in the surface waters was low to negligible throughout the whole water column. Local maxima of TDAA concentrations (Fig. 2a) were dominated by marine-derived DON and may have been caused by the release of TDAA from decaying phytoplankton and sinking detritus. The high proportion of terrigenous DON on the continental slope, on the other hand, was obviously uncoupled from the actual situation in the surface waters. What are the reasons for the dominance of terrigenous DON in the deep-sea of the conti-

Table 1. PCA of TDAA and PAA. PCA factors and percentages of dissolved organic nitrogen that is terrigenous (terr. DON: estimated from PCA factor 1). Average values with confidence ($P = 0.05$) and number of samples (n) for the different sampling areas.

	TDAA				PAA		
Location	PCA factor 1	PCA factor 2	terr. DON (%)	n	PCA factor 1	PCA factor 2	n
Rivers	1.21 ± 0.15	−0.09 ± 0.13	100*	9	0.73 ± 0.43	0.91 ± 1.09	8
Shelf (near-shore)	0.45 ± 0.19	0.18 ± 0.14	38 ± 10	12	0.70 ± 0.13	−0.54 ± 0.21	16
Shelf (Laptev Sea)	0.01 ± 0.35	−0.81 ± 0.29	28 ± 13	16	—	—	0
Continental slope (>100 m)	1.32 ± 0.19	0.31 ± 0.19	88 ± 10	15	—	—	0
Central ocean (surface; <100 m)	−0.23 ± 0.28	−0.33 ± 0.29	23 ± 10	32	−0.77 ± 0.14	−0.38 ± 0.33	7
Central ocean (deepwater; >100 m)	−1.09 ± 0.16	0.70 ± 0.56	0*	27	−1.36 ± 0.21	0.43 ± 0.40	10

* Rivers and the deep central Arctic Ocean are, per definition, 100% and 0% terrigenous, respectively.

Table 2. Principal components analysis (PCA) of the mole percentages of 13 amino acids from water samples of the eastern Arctic Ocean (Kattner et al. 1999, Dittmar et al. 2001a).

	TDAA (n=10)				PAA (n=42)			
	Factor score coefficients		Mol % of individual amino acids (% of TDAA)		Factor score coefficients		Mol % of individual amino acids (% of PAA)	
Amino acid	PCA factor 1	PCA factor 2	Average	SD	PCA factor 1	PCA factor 2	Average	SD
Asp	−0.05	−0.21	10.9	4.4	0.02	−0.35	9.2	1.1
Glu	0.11	−0.25	7.8	2.0	0.03	−0.32	12.3	1.7
Ser	0.17	0.06	8.5	2.6	−0.16	0.00	10.0	2.1
Thr	0.20	−0.01	6.3	2.7	0.13	−0.08	7.7	2.0
Gly	−0.15	−0.08	24.7	4.9	−0.12	−0.07	13.0	2.4
Arg	0.17	0.23	2.7	1.7	−0.13	0.12	6.5	2.7
Ala	−0.11	0.06	21.4	5.3	0.05	−0.16	13.3	1.7
GABA	0.20	0.07	0.8	1.1	−0.03	0.24	0.3	0.3
Tyr	0.24	−0.02	1.4	1.1	0.15	−0.09	2.0	1.1
Val	0.17	−0.12	4.8	2.0	−0.13	0.15	10.1	3.0
Phe	−0.01	−0.27	2.3	1.2	0.14	0.23	3.6	1.1
Ile	−0.05	−0.22	3.0	2.0	0.15	0.17	4.6	1.2
Leu	−0.12	0.32	5.3	6.0	0.17	0.12	7.6	2.5

TDAA: total dissolved amino acids, PAA: particulate amino acids, AA_i: individual amino acid i, FSC1: factor score coefficient for PCA factor 1, Gly: glycine, Asp: aspartic acid, Glu: glutamic acid, Ser: serine, Thr: threonine, Arg: arginine, Ala: alanine, GABA: γ-amino butyric acid, Tyr: tyrosine, Val: valine, Phe: phenylalanine, Iso: isoleucine, Leu: leucine, FSC: factor score coefficient. The first component of the PCA is:

$$\text{PCA factor 1} = \sum_i \left(\frac{\%\text{AA}_i - \text{avg}_{\%\text{AA}_i}}{\text{stdev}_{\%\text{AA}_i}} \times \text{FSCI}_{\%\text{AA}_i} \right) \quad (1)$$

nental slope? Two possible scenarios are put forward and discussed (1) The release of DON from terrigenous compounds in the sediment may be a major source of DON, because sedimentary organic matter on the shelf and continental slope consists of a major fraction of terrigenous organic matter (Boucsein and Stein 2000). (2) The selective freezing out of salts and other solutes during ice formation and the subsequent downward convection of highly saline water may transport terrigenous compounds into the deep sea.

The first scenario is supported by similar spatial trends of the PCA factors of TDAA and PAA in the different marine environments (Fig. 4). However, this coupling does not necessarily indicate any biogeochemical transformation of PAA into TDAA but may have a simple hydrographic explanation (i.e., the mixing of river water and seawater on the shelf). Most suspended terrigenous organic matter settles out in the estuaries, and only a small proportion escapes the shelf (Cauwet and Sidorov 1996; Moreira-Turcq and Martin 1998). Phase transitions may occur primarily in the salinity gradient of the estuaries. However, TDAA concentrations in the estuaries did not systematically exceed conservative mixing concentrations, which indicates that TDAA are not released from PAA in considerable amounts. Even though this first scenario cannot completely be ruled out on the basis of the available data, it seems unlikely that TDAA on the continental slope are derived primarily from terrigenous sedimentary compounds.

The second scenario postulates the downward transport of terrigenous dissolved organic matter. Convection down the continental slope due to ice formation, with brine rejection and dense water formation on the shelves, has been described for the Arctic Ocean by several authors (e.g., Anderson et al. 1999; Rudels et al. 2000). The water at the Laptev Sea slope that is rich in terrigenous DON is located within the boundary current north of the Siberian shelves. Cold and less saline riverine waters reach >1,000 m and contribute to this boundary current along the continental slopes of the Barents, Kara, and Laptev Seas (Schauer et al. 1997; Rudels et al. 2000). The presence of the Severnaya Zemlya islands located at the shelf break between the Kara and Laptev Seas favors the creation of lee polynyas, which leads to large ice formation and strong brine rejection (Rudels et al. 2000). These are favorable conditions for the deep, penetrative slope convection of brine-enriched shelf waters (Rudels et al. 2000), which are rich in terrigenous, refractory dissolved organic matter. The terrigenous DON present at the slope of the Laptev Sea shelf may therefore be derived from Kara or Barents Sea waters and is probably not from the Laptev Sea itself.

An enrichment of terrigenous DON in the downward transported water may result from the selective rejection of solutes during ice formation. In a recent study, Belzile et al. (2002) demonstrated that the exclusion factor for natural organic matter from Canadian lakes is typically greater than twice the exclusion factor for inorganic solutes. Only less-complex, low-molecular-weight molecules were retained in the ice. If this model is applied to conditions in the Arctic Ocean, complex terrigenous humic substances are probably efficiently rejected during ice formation, whereas marine-derived organic matter, which exhibits low aromaticity and low molecular weight (Benner et al. 1997; Dittmar and Kattner 2003*b*), may be partly retained in the ice. Therefore, terrigenous compounds can become enriched in the brine, adding to the increased proportion of terrigenous DON at the continental slope.

Another parameter that influences the proportion of ma-

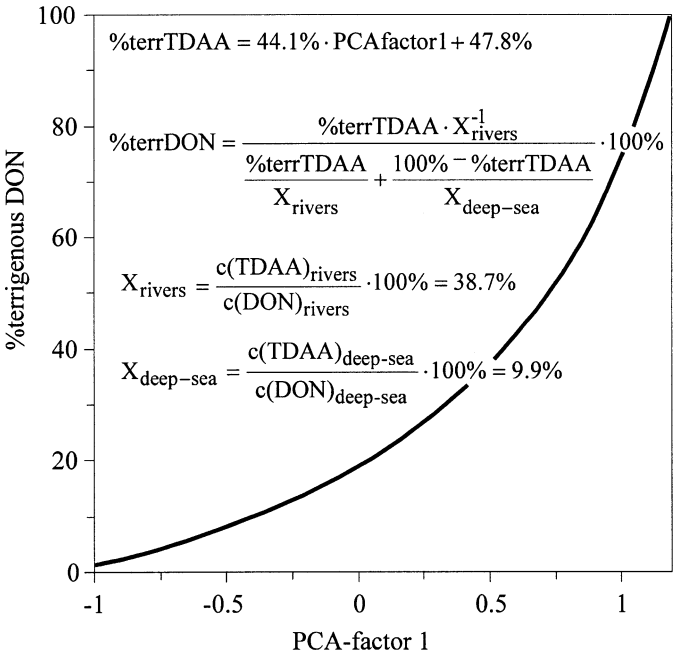

Fig. 5. Equations and diagram of a quantitative model to estimate the percentage of terrigenous DON in the Arctic Ocean, based on PCA factor 1. The model was calibrated using the average amino acid composition of the Russian rivers (100% terrigenous) and the deep central Arctic Ocean (~0% terrigenous). PCA factor 1 was calculated for both end members and any mixture. The percentage of terrigenous TDAA (%terrTDAA) is a linear function of PCA factor 1. Considering the average amino acid content of terrigenous and marine DON (X_{rivers} and $X_{deep\text{-}sea}$), a nonlinear function between PCA factor 1 and percent terrigenous DON (%terrDON) was established.

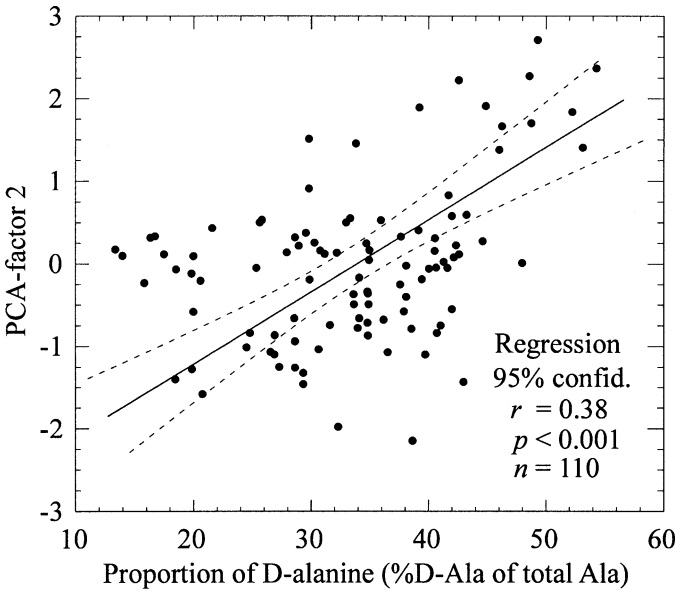

Fig. 6. Values of PCA factor 2 plotted vs. the ratio of D-alanine to total alanine, which is a tracer for microbial degradation (Dittmar et al. 2001*a*).

rine versus terrigenous DON is the stability against microbial degradation, which leads to an accumulation of more refractory compounds. D–amino acids are unambiguous tracers for microbial degradation. Bacterial biomass is rich in D–amino acids, in particular D-alanine, whereas phytoplankton and other primary producers contain almost exclusively L-enantiomers (e.g., Jørgensen et al. 1999). The percentage of D-alanine to total alanine was, on average, 12% (±4%) in the rivers, 30% (±2%) in surface waters of the Laptev Sea, and increased with depth to 46% (±3%) in the deep Arctic Ocean (Dittmar et al. 2001*a*). At the continental slope, the D-alanine proportion was 37% (±3%), on average, which is significantly higher than at the surface ($P < 0.01$), which reflects considerable degradation by marine microorganisms.

Diagenetic alterations of the TDAA composition are not the dominant influence for PCA factor 1, because it was shown that this factor is indicative of the primary source of TDAA. Although PCA factor 2 was consistently close to zero for the Russian rivers, it ranged widely for the marine samples and is therefore not a source indicator for TDAA (Fig. 3; Table 1). However, PCA factor 2 did correlate significantly with the D-alanine proportion (Fig. 6) and may therefore be a measure for diagenesis. Some variance is introduced into the correlation by the fact that during marine diagenesis more D-alanine is produced than during terrestrial diagenesis in soils (Dittmar et al. 2001*a*). To reduce this variance, the correlation was repeated under exclusion of the river and near-shore data, which had no influence on the significance of the correlation.

The first direct evidence of terrigenous DON in the deep sea was provided by its amino acid signature and multivariate statistical analyses. The model developed for the Arctic Ocean was validated with amino acid data from seawater and river samples from other regions and with lignin-based estimates for the Laptev Sea. The similarity between the trends of the first PCA components of suspended and dissolved amino acids indicates that the source of PAA may also be assessed on the basis of its amino acid composition and PCA. To reliably assign the quantitative model to suspended organic nitrogen, however, the database for PAA should be broadened. The particular conditions on the Arctic shelf edge caused extraordinarily high proportions of terrigenous DON in the deep sea at the continental slope. The huge amount of terrigenous DON that flows from the Siberian rivers into the Arctic Ocean is efficiently removed from the photic layer and is transported into the deep ocean. On the scale of the whole Arctic Ocean, however, it is controversial how efficiently deep-water formation transports terrigenous dissolved organic matter into the deep ocean. According to Opsahl et al. (1999), a major proportion of terrigenous dissolved organic matter leaves the Arctic Ocean via surface currents and is not incorporated into deep waters.

The model presented here may be directly applied to trace the fate of terrigenous DON in other terrestrially dominated marine environments. Restrictions apply for environments with a dominance of diagenetically fresh, algal-derived DON. An unambiguous tool to verify the diagenetic degree of DON is the D–amino acid proportion. This proportion was high in all Arctic samples, which indicates strong microbial decay. In ocean basins with low proportions of terrigenous compounds, terrigenous DON may reliably be assessed after

the precise definition of the marine end member. For the present estimates, DON in the deep sea of the central Arctic Ocean was, by definition, 100% marine derived. For marine environments with sharp gradients from terrestrial to marine-dominated regions, like the Arctic Ocean, this simplification introduces only a negligible error. Bottom water formed on the Antarctic shelf receives very low amounts of terrigenous compounds but contains diagenetically altered marine-derived DON. A detailed knowledge of the amino acid composition of this water mass would enable us to define more exactly the marine end member and to assess the proportion of terrigenous DON in the deep sea of the world oceans.

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