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The use of amino acid analyses in (palaeo-) limnological investigations: A comparative study of four Indian lakes in different climate regimes

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Abstract

In the present study, we report the results of comprehensive amino acid (AA) analyses of four Indian lakes from different climate regimes. We focus on the investigation of sediment cores retrieved from the lakes but data of modern sediment as well as vascular plant, soil, and suspended particulate matter samples from individual lakes are also presented. Commonly used degradation and organic matter source indices are tested for their applicability to the lake sediments, and we discuss potential reasons for possible limitations. A principal component analysis including the monomeric AA composition of organic matter of all analysed samples indicates that differences in organic matter sources and the environmental properties of the individual lakes are responsible for the major variability in monomeric AA distribution of the different samples. However, the PCA also gives a factor that most probably separates the samples according to their state of organic matter degradation. Using the factor loadings of the individual AA monomers, we calculate a lake sediment degradation index (LI) that might be applicable to other palaeo-lake investigations.

1. INTRODUCTION

Amino acid (AA) analyses yield reliable information about the state of organic matter degradation and organic matter sources in modern as well as in palaeo-sediments especially from the marine environment (Lee, 1988; Cowie and Hedges, 1994; Wakeham et al., 1997; Dauwe et al., 1999; Keil et al., 2000). This is due to the fact that specific AAs accumulate as a consequence of their production during degradation processes (e.g. microbial built-up) or their resistance to degradation processes (Lee and Cronin, 1984; Lee, 1988). They may, furthermore, be protected from degradation by incorporation into shell material or

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by sorption to mineral surfaces (Hecky et al., 1973; King, 1977; Müller and Suess, 1977; Carter and Mitterer, 1978; Hedges and Hare, 1987; Henrichs and Sugai, 1993). AA composition in marine samples is very similar in different regions, and variations depend mostly on the degradation state of organic matter. In contrast, the variations in AA composition are much larger in terrestrial influenced systems where sources of organic matter have a stronger imprint on AA spectra potentially complicating their interpretation (Meckler et al., 2004; Gaye et al., 2007; Unger et al., 2013).

Many attempts were made to summarise the degradation or source information that can be obtained by AA analyses in terms of individual indices that have universal applicability. Early information about the state of organic matter degradation gathered from AA analyses was based on the diminished concentration of AA in marine sediments with progressing sediment depth and the reduced percentage of nitrogen associated with AA (Emery et al., 1964; Kemp and Mudrochova, 1973; Whelan, 1977; Rosenfeld, 1979). Later, ratios between proteinogenic AAs and their respective degradation products or intermediates were used to assess the state of organic matter degradation (Henrichs et al., 1984; Ittekkot et al., 1984a). Also, the sensitivity of AA-based proxies to different stages of organic matter decomposition (Cowie and Hedges, 1994; Unger et al., 2005; Davis et al., 2009) and to different environmental conditions (Cowie et al., 1995; Nguyen and Harvey, 1997; Keil et al., 2000) was investigated. Based on the previous works, more complex degradation indices were invented as for example ratios of the sums of different protein and non-protein AAs (Jennerjahn and Ittekkot, 1997; Gupta and Kawahata, 2007) or the combination of the differences in molar percentage of individual AAs between samples and a reference data set, weighted on the basis of a principal component analysis (Dauwe and Middelburg, 1998; Dauwe et al., 1999). In a next step, AA-based indices were also applied to terrestrial systems (Das, 2002; Verma and Subramanian, 2002; Jennerjahn et al., 2004), and the adopted indices were tested and adapted to the different environments (Meckler et al., 2004; Ingalls et al., 2006; Menzel et al., 2013).

Early source information gathered from AA analyses was based on the preferential association of individual AAs with specific organisms, as for example bacteria (Schleifer and Kandler, 1972; Lee and Bada, 1977; Kandler, 1979), or biologically produced substances, such as chitinaceous (Degens and Mopper, 1975; Müller et al., 1986), calcareous (King, 1977; Müller and Suess, 1977; Carter and Mitterer, 1978; Ittekkot et al., 1984b), and siliceous (Hecky et al., 1973; King, 1977) matter. Ratios and sums of individual AAs were invented to characterise the dominant origin of organic matter in marine sinking particles and sediments (Ittekkot et al., 1984a; Müller et al., 1986; Lomstein et al., 2006).

Source indicators may be even better applicable in lakes than in the marine realm as terrestrial and aquatic organic matter has specific compositions (Degens and Mopper, 1975; Cowie and Hedges, 1992). Furthermore, organic matter sources can vary considerably between individual lakes due to the limited catchment areas and specific plankton assemblages related to environmental conditions (Menzel et al., 2013). However, AA analyses were only rarely applied to limnic and fluvial systems (Kemp and Mudrochova, 1973; Gupta et al., 1997; Meckler et al., 2004; Unger et al., 2005; Das et al., 2010). This is partly due to the fact that most AA-based degradation and source proxies were developed on the basis of marine samples and might not be suitable in terrestrial aquatic environments. Thus, their applicability to lake sediments needs further elaboration and potential adjustment. Therefore, we analysed the AA assemblages of sediment cores of four Indian lakes from different climatic regimes as well as samples from the vicinities of two of the investigated lakes and tested the different AA-based degradation and organic matter source indices. We identified degradation and organic matter source indices that probably show universal applicability and that are transferred to deeper sediments. Moreover, we detected factors that potentially bias the use of individual indices in lake systems, and we calculated an AA-based degradation proxy on the basis of the investigated lake sediments which should also be suitable to other (palaeo-) limnological investigations.

2. STUDY SITES

Four Indian lakes were investigated during this study (Fig. 1): The Tso Moriri in Leh district of Jammu and Kashmir state in northern India is an oligotrophic, closed alpine lake with a cold semi-arid climate and a summer (SW) monsoon precipitation maximum. Mansar Lake in Udhampur district of Jammu and Kashmir state in northern India is a subtropical tectonic lake in the Lesser Himalayas. Lonar Lake in Buldhana district of Maharashtra state in central India is an anoxic, eutrophic crater lake in the core monsoon zone. Pookode Lake in Wayanad district of Kerala state in south India is an oxic, meso- to eutrophic lake that receives some winter (NE) monsoon precipitation in addition to the SW monsoon rains. Table 1 summarises some general and environmental

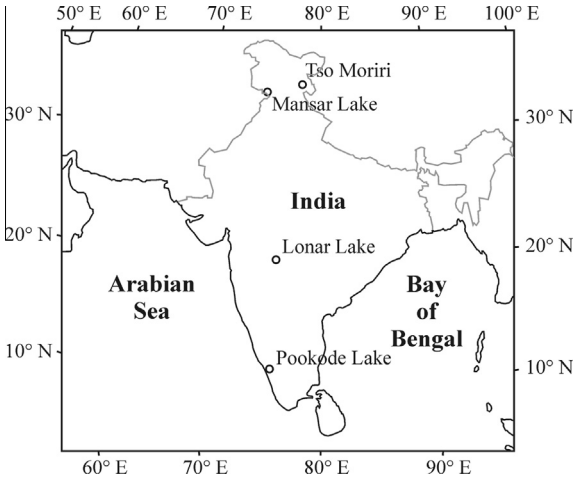

Fig. 1. Map showing the locations of the four investigated lakes.

Table 1
Locations as well as hydrological and meteorological properties of the four lakes, Tso Moriri, Mansar Lake, Lonar Lake, and Pookode Lake.

	Tso Moriri	Mansar Lake	Lonar Lake	Pookode Lake
Latitude	32° 55′ N	32° 42′ N	19° 59′ N	11° 33′ N
Longitude	78° 19′ E	75° 09′ E	76° 30′ E	76° 02′ E
Elevation (m a.s.l.)	4500	650	480	770
N-S Extension (km)	27[a]	1.2 (NW-SE)[d]	1.2[g]	0.3[k]
E-W Extension (km)	5–7[a]	0.6 (NE-SW)[d]	1.2[g]	0.2[k]
Surface area (km^2)	150[a]	0.6[d]	1[h]	<0.1[k]
Max. depth (m)	105[a]	38[d]	7[i]	7[k]
pH	9–9.5[a]	8–8.5[e]	9–10.5[i]	6–7[l]
Dissolved oxygen (mg/l)	5.4–6.6[a]	7.1–9.8[e]	0.1–16.4[i]	6.3–7.4[l]
Conductivity (mS/cm)	1.6[a]	0.19–0.20[e]	13–21[i]	0.03–0.05[l]
Annual Precipitation (mm)	100 – 300[b]	1500[d]	700[j]	4400[l]
Min. annual air Temp. (°C)	−40[c]	+1[f]	+11[j]	+7[k]
Max. annual air Temp. (°C)	+30[c]	+42[f]	+42[j]	+35[k]

[a] Mishra et al. (2014).
[b] Bookhagen and Burbank (2010).
[c] Mishra and Humbert-Droz (1998).
[d] Das et al. (2010).
[e] Al-Mikhlafi et al. (2003).
[f] Trivedi and Chauhan (2009).
[g] Prasad et al. (2014).
[h] Menzel et al. (2013).
[i] Basavaiah et al. (2014).
[j] http://indiawaterportal.org/met_data/.
[k] Veena et al. (2014).
[l] Nirmala et al. (1991).

properties of the four lakes. Further information on lake chemistry and vegetation of the catchments is given in the Appendix.

3. METHODS AND MATERIAL

3.1. Sampling

Sets of surface sediments, soil and terrestrial plant samples were collected in January 2007 and May 2008 from various locations in and around Lonar Lake and in July 2011 from Tso Moriri. Additionally, terrestrial plant material was sampled and suspended particulate matter from shallow (0.5 m) and deep (4 m) water at 2 locations was filtered from Lonar Lake in February 2011. Sediment trap samples at ca. 5 m water depth from two stations were collected for the intervals February to May 2011, and May to October 2011 at Lonar Lake. Water samples for filtering were retrieved using a Niskin water sampler attached to a hydrocable and activated by a GO Devil messenger (1000MG); suspended matter and sediment trap material were filtered onto pre-combusted and pre-weighed Whatman GF/F filters (0.45 μm), rinsed with distilled water, and air-dried. Using a UWITEC piston corer, sediment cores were retrieved in December 1998 from Mansar Lake (core length: 24.30 m), in May 2008 from Lonar Lake (core length: 10.04 m), in July 2011 from Tso Moriri (core length: 7.24 m), and in May 2012 from Pookode Lake (core length: 0.49 m). The sediment cores were opened in the laboratory and sub-sampled in 0.5 cm resolution, except for the Mansar Lake core, which was sub-sampled in 2–4 cm resolution. All samples were freeze-dried and afterwards ground manually in an agate mortar. Amino acid analyses were carried out on 91 Lonar Lake core samples, 86 Tso Moriri core samples, 50 Mansar Lake core samples, and 24 Pookode Lake core samples.

3.2. Analytical methods

Total carbon (TC) and total nitrogen (TN) contents of the samples were determined on a Carlo Erba NC2500 element analyser. A fraction of grounded sample material was weighted and wrapped into pre-combusted tin capsules and analysed via flash combustion in the element analyser. The total organic carbon (TOC) content of samples was determined following the same procedure after decalcification of sample fractions with 20% HCl in pre-combusted silver capsules. Calibration standard for these measurements was acetanilide. Precision of this method is 0.05% for carbon and 0.005% for nitrogen.

AA analyses were carried out on a Biochrom 30 Amino Acid Analyser according to the method by Roth and Hampa (1973). Before analysis, samples were hydrolysed for 22 h with 6 mol/l HCl under a pure argon atmosphere at 110 °C. Un-reacted HCl was removed from the hydrolysate by evaporation using a vacuum rotating evaporator (Büchi). The residue was resolved into an acidic buffer (pH 2.2) and injected into the analyser. Using this method, we quantified the 18 AA monomers 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-aminobutyric acid (γ-Aba), histidine (His), ornithine (Orn), lysine (Lys), and arginine (Arg) as well as the 2 hexosamines (HA) glucosamine (Gluam) and galactosamine (Galam). Asp and Glu potentially include the respective contributions from asparagine and glutamine after hydrolysis with HCl. All AA and HA molar concentrations were calculated against a standard (SIGMA AA-S-18 with addition of Orn, β-Ala, γ-Aba, Gluam and Galam), which was analysed prior to the measurements. Duplicate measurement of the standard solution resulted in a relative error of 0.1% to 1.3% for the concentrations of individual AA monomers. Duplicate measurement of a single sediment sample revealed a relative error of <1% for AA concentrations, <10% for low concentrated (<1 mol%) AA monomers, and <2.5% for higher concentrated (>1 mol%) AA monomers.

3.3. Approach

The total AA contributions to the samples were normalized with respect to TOC and TN content of samples by calculating the AA-bound carbon/TOC and nitrogen/TN percentages. These values are named AA-C and AA-N, respectively. And, whereas AA-C of sediment samples is influenced by the state of degradation but much more dependent on the ratio between TOC-rich but AA-poor terrestrial plant material and TOC- and AA-rich aquatic OM, AA-N is less source dependent but much more influenced by the state of organic mater degradation (Cowie and Hedges, 1994).

To assess the state of OM degradation, we also calculated ratios and indices based on the monomeric distribution of the AAs, the reactivity index (RI), which was invented by Jennerjahn and Ittekkot (1997), and the degradation index (DI), developed by Dauwe and Middelburg (1998) and Dauwe et al. (1999).

Briefly, the RI is the ratio between the sum of the two aromatic AA Tyr and Phe and the sum of the two non-protein AA β-Ala and γ-Aba:

$$\mathrm{RI} = \frac{\mathrm{Tyr} + \mathrm{Phe}}{\beta - \mathrm{Ala} + \gamma - \mathrm{Aba}}$$

Since the aromatic AAs are relatively enriched in cell plasma, they are preferentially lost during decay processes (Hecky et al., 1973). The abundance of non-protein AAs in fresh OM is minimal but increases during degradation due to the fact that the non-protein AAs are metabolic products of microbial proteinogenic AA decay (Cowie and Hedges, 1992). Hence, high RI values indicate fresh OM while low values characterise degraded OM.

The DI is calculated on the basis of the molar percentages of the 14 protein AAs Asp, Thr, Ser, Glu, Gly, Ala, Val, Met, Ile, Leu, Tyr, Phe, His, and Arg. It compares the monomeric distribution of the AAs of a sample with the data set of Dauwe et al. (1999) according to the formula:

$$\mathrm{DI} = \sum_i \left[\frac{\mathrm{var}_i - \mathrm{AVGvar}_i}{\mathrm{STDvar}_i} \right] \times \mathrm{fac.coef.}_i$$

where var_i is the original mole percentage of each AA in the sample, AVGvar_i and STDvar_i are the arithmetic average and the standard deviation, and $\mathrm{fac.coef.}_i$ the factor coefficient of the first axis of a principle component analysis (PCA) of the individual AAs in the data set of Dauwe et al. (1999). Positive values indicate less degraded and negative values more degraded state of the OM compared with the average of the data set of Dauwe et al. (1999).

In addition to the above mentioned AA-based indices, we performed principal component analyses of the 18 individual AA monomers for every investigated lake (*see* the Appendix) and for the combined data set to calculate a new, lake-specific AA index on the basis of the DI calculation (Dauwe and Middelburg, 1998; Dauwe et al., 1999). The PCA is a statistical method to reduce the number of variables to a few interpretable linear combinations of the data. Each linear combination will correspond to a principal component which explains some of the variability within the data set. The first principal component is the linear combination of variables that has maximum variance. Further principal components are calculated in the order of the amount of the variance they can explain. For each original variable, factor loadings are calculated that show the contribution of the variable to the variance of the respective principal component. Site scores are calculated for each sample on the basis of the original variables weighted by the respective factor loadings and indicate the position of the individual samples on the principal components axes. By comparing the score and loading plot, the relationships between samples and variables can be identified, as samples that show positive site scores are enriched in variables with positive factor loadings and depleted in variables with negative factor loadings and vice versa (Ingalls et al., 2006).

Furthermore, we calculated other AA-based degradation indices, such as ratios between proteinogenic AAs and their non-protein degradation products (Henrichs et al., 1984; Ittekkot et al., 1984a), the Ox/Anox ratio, which distinguishes between aerobic and anaerobic degradation (Menzel et al., 2013), and the percentage of Gly of the sum of Gly, Ser, and Thr (Lomstein et al., 2006). Furthermore, organic matter source indices, such as the Asp/Gly ratio (Ittekkot et al., 1984a,b) and the sum of Gly, Ser, and Thr (Lomstein et al., 2006), were calculated and their applicability examined.

4. RESULTS

The results of the AA analyses of the four lakes are summarised in Table 2 and results of the individual samples are available at http://doi.pangaea.de/10.1594/PANGAEA.843154.

Highest AA concentrations are present in suspended particulate matter (SPM) samples, followed by sediment trap samples collected from Lonar Lake (Table 2). The vascular plants, which were sampled at Tso Moriri and Lonar Lake, show AA content of about one third of that of SPM. The AA-C values of the sediment core samples from Tso Moriri, Mansar Lake, and Pookode Lake are in the same range, whereas the Lonar Lake core sediments show lower

Table 2
Average TOC, C/N, AA, AA-C, and AA-N values of specific groups of samples of the four lakes.

	TOC (%)	TOC/TN (atomic)	Amino acid content (mg/g)	AA-C (%)	AA-N (%)
Tso Moriri					
Vascular plants	46.2	31.6	92.1	9.3	52.7
Soils	0.7	11.5	1.6	9.7	30.3
Surface sediments	1.7	10.3	5.5	13.2	37.6
Sediment core	0.8	10.2	1.7	7.6	20.1
Section 0 m–3.9 m	1.2	9.0	2.9	10.0	25.2
Section 3.9 m–7.3 m	0.4	11.1	0.5	5.5	15.7
Mansar Lake					
Sediment core	3.6	12.0	5.8	7.4	23.7
Section 0 m–16.8 m	1.7	9.6	4.0	8.9	24.8
Section 17 m–24.3 m	6.3	15.2	8.2	5.5	22.2
Lonar Lake					
SPM	31.9	7.7	283.9	40.0	77.6
Vascular plants	43.1	39.6	85.6	8.7	51.2
Soils	0.9	13.8	3.0	13.4	38.0
Sediment trap material	24.1	6.9	196.4	35.9	64.5
Surface sediments	2.6	10.7	10.5	17.6	48.3
Sediment core	3.4	24.9	2.2	3.8	19.0
Section 0 m–3.1 m	1.7	15.4	3.7	9.2	33.9
Section 3.1 m–6.1 m	1.7	26.6	1.0	2.6	17.1
Section 6.1 m–9.1 m	5.2	29.7	2.3	2.1	14.8
Section 9.1 m–9.8 m	1.3	18.8	0.2	0.7	3.3
Section 9.8 m–9.9 m	0.4	13.1	0.2	1.7	6.8
Pookode Lake					
Sediment core	16.7	13.6	45.2	11.8	44.1
Section 0 cm–42.5 cm	15.0	13.7	40.7	11.7	44.6
Section 44 cm–48.5 cm	28.3	12.4	76.9	12.0	40.8

AA-C values. On the other hand, similar average AA-N values are present in Tso Moriri, Mansar Lake, and Lonar Lake core sediments, whereas the Pookode Lake samples show higher values. The AA-C values of vascular plant samples are much lower compared to SPM and sediment trap samples, whereas AA-N values of vascular plants are less depleted with respect to SPM and sediment trap samples (Table 2).

As shown in Fig. 2 A, the monomers Gly, Asp, Ala, and Glu contribute most (>9 mol%) to the AA assemblages of the different lake core sediment samples. The Lonar Lake sediments are an exception; here, Leu, Ala, Val, and Gly are the most abundant (>9 mol%) monomers. The vascular plant samples from Tso Moriri and Lonar Lake are characterised by high AA monomer contributions of Glu, Asp, Gly, Ala, and Leu (8.6 mol%–13 mol%), whereas the soils of the vicinity of the two lakes show AA spectra dominated by Asp, Gly, Glu, and Ala (10.6 mol%–16.7 mol%). Suspended particulate matter filtered from Lonar Lake is highly enriched in Glu (17.6 mol%), followed by Ala, Asp, and Gly (9 mol%–11.5 mol%).

4.1. AA variability within the Tso Moriri sediment core

The most pronounced differences concerning the AA results within the Tso Moriri core can be seen between the upper ca. 3.9 m of the sediment sequence and the underlying ca. 3.4 m.

The AA content of the upper part of the core shows a mean value of 2.9 mg/g dry sediment, whereas the lower part only contains 0.5 mg/g. The mean AA-C and AA-N percentages of the upper part of the core are 10.0% and 25.2%, respectively. The lower part of the core shows mean AA-C and AA-N values of 5.5% and 15.7%, respectively.

The monomeric AA assemblage of the upper part of the core is relatively enriched in Gly, Thr, Ser, Lys, and Ala and depleted in Met, Orn, β-Ala, γ-Aba, Glu, Arg, Ile, Val, Tyr, and Leu compared to the lower part (Fig. 2B).

4.2. AA variability within the Mansar Lake sediment core

The results of the AA analyses of the Mansar Lake sediment core have been published by Das et al. (2010) and interpreted with respect to palaeo-climate variability. Broadly, the core can be divided into an upper part from 0 m to 16.8 m and a lower part from 17 m to 24.3 m.

The mean AA content of the upper part of the core is 4.0 mg/g and generally decreases downcore. The lower part of the core shows a mean AA content of 8.2 mg/g with no marked internal trend. Average AA-C and AA-N percentages in the upper part are 8.9% and 24.8%, respectively. Similarly to the AA content, both AA-C and AA-N show a decreasing trend with increasing depth. The lower part of the core is characterised by mean AA-C and AA-N values of 5.5% and 22.2%, respectively.

The monomeric AA assemblage of the two parts of the core differs with Tyr, Gly, Asp, Glu, and Ser being relatively enriched in the upper part and γ-Aba, Orn, β-Ala, Ile, Val, Leu, Phe, Met, Lys, and Ala being enriched in the lower part (Fig. 2C).

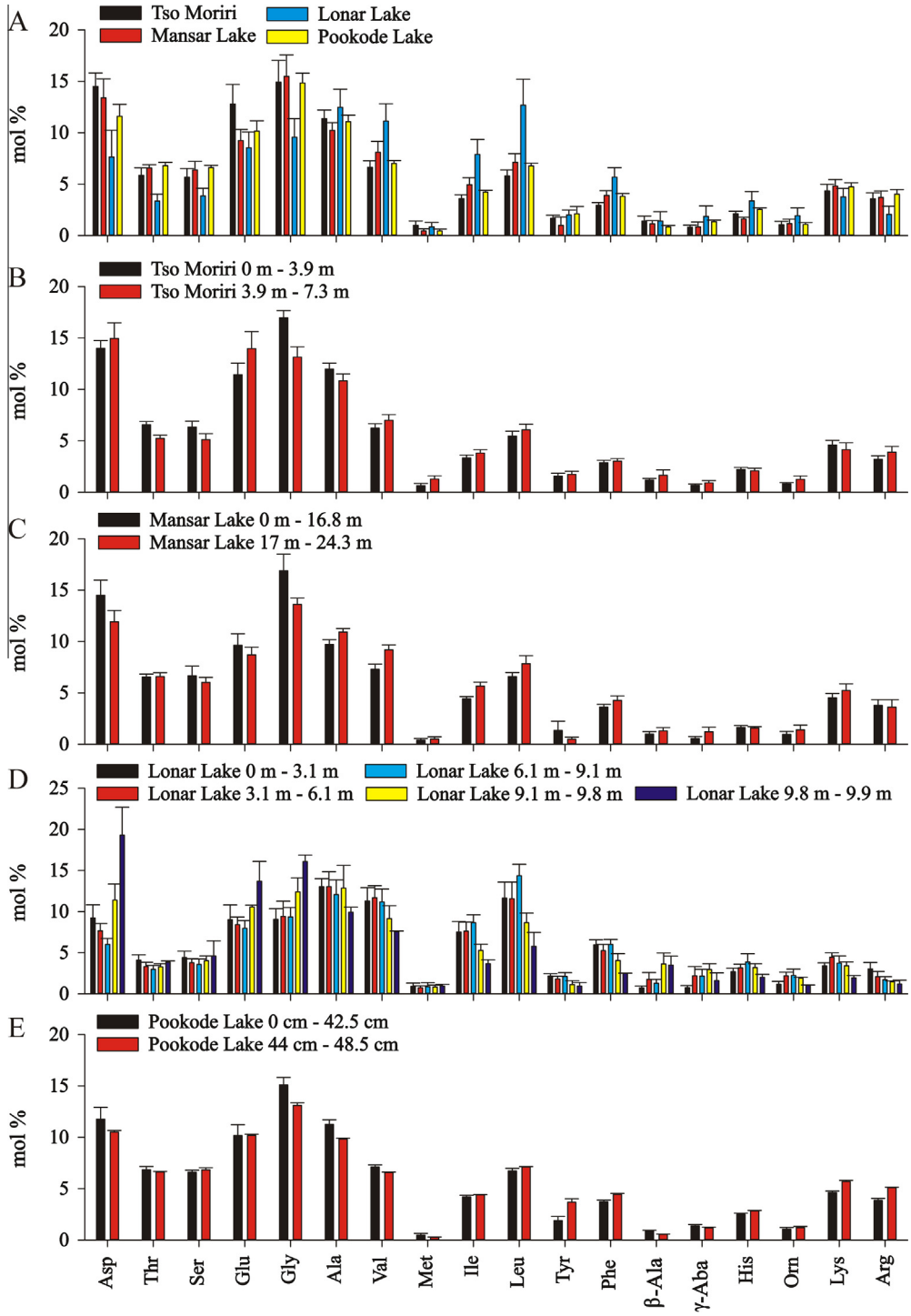

Fig. 2. Monomeric AA and HA assemblages of the sediment core samples of the four lakes. (A) comparison of the four lake cores; (B) comparison of Tso Moriri core sub-sections; (C) comparison of Mansar Lake core sub-sections; (D) comparison of Lonar Lake core sub-section; (E) comparison of Pookode Lake core sub-sections. Filled bars indicate average values, error bars indicate standard deviations.

4.3. AA variability within the Lonar Lake sediment core

The Lonar Lake sediment core has been analysed for different proxies and interpreted with respect to palaeo-climate (Anoop et al., 2013; Menzel et al., 2014; Prasad et al., 2014). According to the AA analyses and supported by the findings of the afore-mentioned authors, the Lonar Lake sediment core can roughly be divided into five subunits: the first subunit comprising the upper part of the core between 0 m and 3.1 m, the second subunit between 3.1 m

and 6.1 m, the third subunit from 6.1 m to 9.1 m, the fourth subunit between 9.1 m and 9.8 m, and finally, the fifth subunit at the bottom of the core (9.8 m–9.9 m) comprising a palaeosol and underlying hard clay.

The mean AA content, AA-C, and AA-N values of the single subunits are given in Table 2.

The average monomeric AA assemblages of the individual subunits are shown in Fig. 2 D and reveal some major differences. Compared to the mean AA assemblage of the Lonar Lake sediment core, the first subunit is enriched in Arg, Thr, Asp, Ser, and Tyr and depleted in γ-Aba, β-Ala, Orn, His, and Lys. The second subunit is relatively enriched in Lys, β-Ala, γ-Aba, and Orn and depleted in Met and Tyr. The third subunit shows relatively elevated percentages of Leu, Ile, His, Orn, and γ-Aba and diminished percentages of Asp, Thr, Arg, and β-Ala. The fourth subunit is enriched in β-Ala, γ-Aba, Asp, Gly, and Glu and depleted in Tyr, Ile, Leu, Arg, Phe, Val, and Lys, whereas the fifth subunit shows enrichment of Asp, β-Ala, Gly, Glu, Ser, and Thr and depletion of Phe, Leu, Ile, Tyr, Lys, Orn, Arg, His, Val, Ala, and γ-Aba.

4.4. AA variability within the Pookode Lake sediment core

According to the AA data, the Pookode Lake short core can be divided into a top part from 0 cm to 42.5 cm and a bottom part from 44 cm to 48.5 cm.

The mean AA content of the top part of the sediment core is 40.7 mg/g dry sediment, whereas the mean AA content of the bottom part of the core is 76.9 mg/g dry sediment. The AA-C and AA-N percentages of the two parts of the core are quite identical, being 11.7% and 44.6% in the top part and 12.0% and 40.8% in the bottom part, respectively.

In comparison, the monomeric AA assemblage of the top part of the core is relatively enriched in Gly, Ala, Asp, β-Ala, Met, and γ-Aba, whereas the bottom part is relatively enriched in Tyr, Arg, Lys, Phe, His, and Orn (Fig. 2E).

5. DISCUSSION

In the following sections, we test the applicability of AA-based indices, which were commonly developed on the basis of investigations on marine sediments with negligible contribution of terrestrial OM, to samples from different lacustrine environments.

Detailed discussions of the AA assemblages of the individual lakes and a comparative examination of these can be found in the Appendix.

5.1. AA-C and AA-N

AA-C can serve as a degradation proxy in environments that show comparable OM sources (Cowie and Hedges, 1994; Colombo et al., 1998; Lomstein et al., 2006; Carstens and Schubert, 2012). In lakes this is not possible as our data demonstrate. AA-C values of suspended particulate material from Lonar Lake are in the range of 33%–49%, whereas vascular plant samples from Lonar Lake (Menzel et al., 2013) and Tso Moriri show AA-C values of 2%–18% (Table 2). Thus, AA-C is less suitable as a degradation proxy in lake sediments, but can be used as source indicator, with low values relative to AA-N indicating higher amounts of vascular plants.

AA-N, on the other hand, shows less variation between aquatic and terrestrial OM than AA-C (Cowie and Hedges, 1992, 1994; Menzel et al., 2013). A possible bias by woody vascular plant material with low AA-N values can be ignored due to its very low AA and N concentrations (Cowie and Hedges, 1992). This is corroborated by our data, which show comparable AA-N values for the sediment cores from Tso Moriri (22.1%), Mansar Lake (23.7%), and Lonar Lake (19.0%). Other indices confirm similar states of OM degradation within these three cores, as suggested by the AA-N values, whereas AA-C values are much higher in Tso Moriri (8.1%) and Mansar Lake (7.4%) compared to Lonar Lake (3.8%) that shows the highest mean TOC/TN (C/N) ratio of the three lakes, indicating higher contribution of terrestrial OM.

5.2. Degradation indices: DI, RI, new Lake Index (LI)

The degradation index (DI) (Dauwe and Middelburg, 1998; Dauwe et al., 1999) and reactivity index (RI) are often applied to environmental AA analyses to assess and compare the state of OM degradation (Unger et al., 2005; Gaye et al., 2007; Gupta and Kawahata, 2007; Lahajnar et al., 2007; Möbius et al., 2011; Carstens and Schubert, 2012). However, some studies on AA contribution to marine, fluviatile, and lacustrine sediments have shown that the DI and RI cannot universally be used (Unger et al., 2005; Gupta and Kawahata, 2007; Davis et al., 2009; Möbius et al., 2011; Carstens and Schubert, 2012). We only find a significant positive correlation between the two indices in the Pookode Lake (Fig. 3).

To decipher if the RI or the DI are suitable to assess the degradation rate, we performed PCAs of the AA assemblages of the four lakes separately (*see* the Appendix) as well as for the combined lake samples (Fig. 4) and compared them to the original data set used for the DI

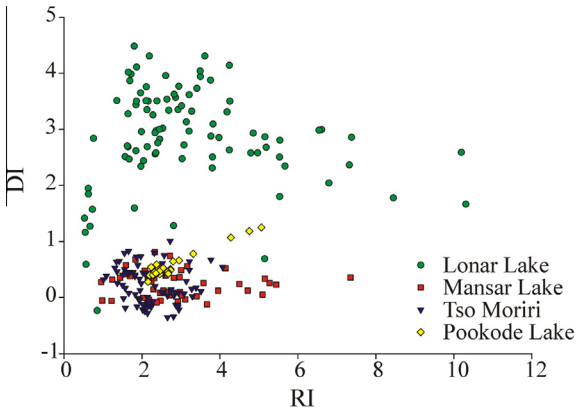

Fig. 3. Cross-plot of DI and RI values of the sediment core samples of the four lakes.

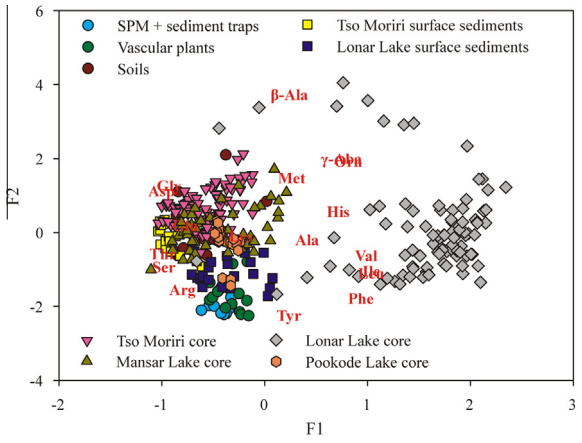

Fig. 4. Cross-plot of first and second PCA axis factors of the PCA of the monomeric AA contribution of the combined data set.

calculation (Dauwe et al., 1999). Lonar Lake core sediments with unusually high DI values are enriched in Leu, Val, Ile, His, and Phe and depleted in Gly, Asp, Arg, Thr, Ser, and Glu compared to the DI data set of Dauwe et al. (1999). The fact that this deviation is most pronounced in core sections that show highest C/N ratios, indicating strongest contribution of terrestrial OM, suggests that the DI might in general not be suitable to decipher the degradation status of sediments from environments that show high contribution of terrestrial OM. The interpretation of the monomeric AA assemblages of the different sediment cores (*see* the Appendix for a detailed description) indicates that specific monomers show different behaviour during degradation in our data compared to their factor loadings for the DI calculation (Dauwe et al., 1999). These deviations from the DI show that it is recommended to calculate an individual PCA of AA results from a specific study site. The incorporation of additional source specific data into such a PCA (such as C/N ratio as an indicator of aquatic vs. terrestrial OM) might further enhance its interpretability. In our individual PCAs of the four lakes, one of the first two factors of the PCA was sensitive to the state of degradation whereas the other was sensitive to organic matter sources (the Appendix).The results of a PCA comprising the entire AA analyses, including the four lake sediment cores and the surface sediment, soil, vascular plant, SPM, and sediment trap samples, indicates that the first axis, explaining 49.3% of the variability of the data, seems to be sensitive to redox conditions and the contribution of degraded terrestrial, especially woody, OM to the samples. In contrast, the second axis of this PCA, explaining 13.3% of the variance, seems to be most sensitive to the state of OM degradation with relatively labile monomers showing negative factor loadings and monomers that are mostly associated with degraded organic matter showing positive factor loadings (for a more detailed discussion on the PCA, refer to the Appendix). Therefore, we calculated a lake sediment degradation index (LI) according to the DI calculation (Dauwe et al., 1999), but based on the factor loadings of the second axis of the PCA of our whole data set. The arithmetic mean, standard deviation, and second PCA-axis factor loading of the individual AAs of our data set for the LI calculation, are listed in Table 3. This index might be applicable to other aquatic environments, especially other lake sediments, too. Furthermore, application of the LI to marine sediments seems also reasonable. For example, a comparison of newly calculated LI values to reported DI values of a marine sediment core of the Mediterranean Sea, covering sediments of highly diverse state of OM degradation (multicore #569; Möbius et al., 2010), shows a very good correlation ($R^2 = 0.904$). The LI produces values of about −1 to −3 for relatively fresh samples, such as plankton, limnic sediment trap, terrestrial plant, and less degraded sediment samples. Moderately degraded samples, such as most of our lake sediment core samples and relatively less degraded samples from multicore #569 (Möbius et al., 2010) show LI values of about 0–2. Highly degraded lake sediments of the Lonar Lake core show LI values of about 4, whereas the most degraded samples of multicore #569 (Möbius et al., 2010), which show non-protein AA concentrations of >20 mol%, are characterised by LI values of 8–12. The LI, therefore, correlates negatively with indicators of organic matter freshness such as the AA-N, RI, and, with some limitations (as discussed above) with the AA-C as well as with ratios between proteinogenic AAs and their degradation products (Table 4). It correlates positively with the %Gly/(Gly + Ser + Thr) and the Ox/Anox indicator, which both rise with increasing degradation (see Sections 5.3 and 5.4). Additionally, the LI is independent of terrestrial and aquatic source indicators such as C/N and Gly + Ser + Thr (Table 4).

The results of the PCA of the combined lake samples indicate that the RI is suitable to decipher the state of degradation of OM in lakes as the aromatic AAs are the most labile (most negative LI factor loadings), whereas the non-protein AAs are the most stable AAs (most positive

Table 3
Average molar percentages, standard deviations, and factor coefficients of each AA monomer in the whole data set, which were used for LI calculation.

	Avg (mol%)	SD (mol%)	Fac. coeff.
Tyr	1.78	0.76	−0.223
Phe	4.08	1.21	−0.177
Arg	3.31	1.02	−0.153
Leu	8.18	3.12	−0.109
Ile	5.10	1.96	−0.103
Ser	5.63	1.36	−0.092
Val	8.06	2.21	−0.061
Thr	5.46	1.50	−0.056
Ala	11.43	1.44	−0.018
Lys	4.14	0.81	−0.008
Glu	11.01	2.50	0.020
His	2.42	0.92	0.058
Asp	11.97	3.30	0.114
Gly	13.16	3.05	0.128
Met	0.70	0.41	0.149
Orn	1.16	0.70	0.194
γ-Aba	1.02	0.79	0.203
β-Ala	1.13	0.65	0.376

Table 4
Correlation between different AA-based OM source and degradation indices as well as C/N ratio of the combined data set.

	C:N	AA-C	AA-N	Asp: β-Ala	Glu: γ-Aba	Arg: Orn	Thr + Ser + Gly	%Gly (T + S + G)	Ox: Anox	RI	DI
LI	−.059	−.515**	−.658**	−.545**	−.327**	−.421**	.048	.686**	.491**	−.531**	−.198**
C:N	1	−.486**	−.162*	−.205**	−.221**	.043	−.535**	−.020	−.576**	−.120	.688**
AA-C		1	.819**	.770**	.657**	.375**	.351**	−.446**	.160*	.724**	−.342**
AA-N			1	.650**	.476**	.475**	.273**	−.606**	−.018	.578**	−.198**
Asp: β-Ala				1	.753**	.646**	.063	−.516**	−.004	.900**	−.083
Glu: γ-Aba					1	.465**	.079	−.357**	.067	.896**	−.123
Arg: Orn						1	.002	−.442**	−.018	.554**	−.005
Thr + Ser + Gly							1	−.134	.598**	−.057	−.878**
%Gly (T + S + G)								1	.133	−.458**	.123
Ox: Anox									1	−.137	−.834**
RI										1	.050

* $p < 0.01$.
** $p < 0.001$.

LI factor loadings). This is due to the fact that the aromatic AAs are enriched in cell plasma, which is easily degradable, and the non-protein AAs β-Ala and γ-Aba become enriched during degradation as they are decomposition products of Asp and Glu, respectively (Ittekkot et al., 1984a). However, OM of terrestrial origin can be enriched in γ-Aba compared to OM of aquatic origin (see Section 5.5), especially when vascular plants undergo environmental stress, as for example extreme temperature, drought, highly alkaline or saline soils (Kinnersley and Turano, 2000). At Tso Moriri, the vascular plant samples show higher contribution of γ-Aba than all other samples, including soil and sediment core samples. Nevertheless, this effect is to some extent countered by elevated aromatic AA content, especially Phe, in undegraded terrestrial OM (Cowie and Hedges, 1992), making RI a reliable proxy to evaluate the state of OM degradation in environments with different OM sources. However, it should be noted that if non-protein AAs are considered individually, only β-Ala content should be taken as an indicator of organic matter degradation.

5.3. Specific organic matter source indices

The most important difference in OM origin in lacustrine environments certainly is the ratio between aquatic and terrestrial OM contribution to the sediments. Several studies have deciphered the differences in AA assemblages of various aquatic and terrestrial organisms (Hecky et al., 1973; King, 1977; Ittekkot et al., 1984a,b; Cowie and Hedges, 1992), suggesting that these differences are transferred into the sediments. However, to estimate the percentage of aquatic versus terrestrial OM contribution to sediments, the calculation of the simple ratio between organic carbon and total nitrogen usually shows universal applicability (Meyers, 1994). C/N ratios of all samples correlate positively with Leu, Ile, Val, Phe, His, γ-Aba, and Orn and negatively with Asp, Gly, Arg, Thr, Glu, and Ser, suggesting that the former are enriched in land plants and soils whereas the latter are enriched in aquatic material. In Lonar Lake, showing highest C/N ratios and thus highest terrestrial contribution, the correlation is positive between C/N and Orn, Leu, His, γ-Aba, and Ile and negative between C/N and Asp, Thr, Ser, Arg, and Glu. The missing correlation between C/N and Val, Phe, and Gly in Lonar Lake sediments is probably due to the exceptional plankton assemblage in Lonar Lake, comprising mostly of cyanophyceae, which are relatively enriched in Val and Phe and depleted in Gly (Becker, 2007) compared with most other phytoplankton (Lee, 1988), especially those including substantial contribution of diatoms (Cowie and Hedges, 1992).

We also tested other AA-based OM source indices used to identify high contribution of specific organisms to environmental samples. Dominance of Asp over Gly in suspended and sinking material is commonly interpreted as being evidence of high calcareous OM contribution, whereas dominance of Gly over Asp is interpreted as being evidence of high siliceous OM contribution (Ittekkot et al., 1984a,b; Müller et al., 1986). This is based on findings that

show high contribution of Gly to siliceous organisms (Hecky et al., 1973; King, 1977; Cowie and Hedges, 1992) and high contribution of Asp to calcareous organisms (Degens, 1976; King, 1977; Carter and Mitterer, 1978). However, these indices of siliceous and calcareous OM sources can only be applied to relatively undegraded OM. Gly can be highly enriched during degradation, due to its significant contribution to microbial produced OM (Keil et al., 2000) and its relatively reduced decomposability compared to most other AAs (Sigleo and Shultz, 1993), whereas Asp might be preferentially enriched during aerobic degradation (Cowie et al., 1995). To assess the contribution of specific OM sources to sediments, other indices are needed. The relative contribution of siliceous OM to even more degraded sediments can be reconstructed from the molar percentage of Gly, Ser, and Thr of the total AA assemblage in combination with the percentage of Gly of the afore mentioned three AA monomers [%Gly/(Gly + Ser + Thr)] (Lomstein et al., 2006). Since siliceous OM is enriched in Gly, Ser, and Thr (Hecky et al., 1973; King, 1977), sediments with high contribution of siliceous OM show contributions of the sum of Gly, Ser, and Thr of ca. >27 mol%, as for example in the Pookode Lake sediment core and the upper parts of the Tso Moriri and Mansar Lake sediment cores. To assure that the high values of this sum are not driven by strong contribution of microbial-originated or degradation-related enrichment of Gly, %Gly/(Gly + Ser + Thr) needs to be calculated. Percentages of ca. >60% might indicate Gly enrichment due to enhanced degradation, which should be confirmed by relatively low AA/Galam ratios, as Galam is present in bacterial cell walls (Benner and Kaiser, 2003), or high β-Ala content of the respective samples. Since the samples of Pookode Lake and the upper parts of Tso Moriri and Mansar Lake sediment cores show %Gly/(Gly + Ser + Thr) values of <60%, the high contribution of Gly, Ser, and Thr indicates strong siliceous OM contribution. This is corroborated by the abundance of bacillariophyceae in modern Pookode and Mansar Lakes (Zutshi et al., 1980; Nirmala et al., 1991) and enhanced biogenic silica contribution in the upper part of the Tso Moriri sediment core (Prasad, unpubl. data).

None of the four lakes investigated during this study shows high contribution or evidences of former dominance of calcareous organisms. Thus, related AA-based indices could not be tested.

5.4. Redox index

Different degradation mechanisms during aerobic and anaerobic decomposition potentially affect the monomeric AA assemblage of OM (Cowie et al., 1995; Menzel et al., 2013). According to findings of changes in monomeric AA assemblages due to different redox conditions (Cowie et al., 1995), Menzel et al. (2013) calculated a simple ratio between AAs that become relatively enriched and those that become relatively depleted during aerobic degradation:

$$\mathrm{Ox/Anox} = \frac{\mathrm{Asp} + \mathrm{Glu} + \beta - \mathrm{Ala} + \gamma - \mathrm{Aba} + \mathrm{Lys}}{\mathrm{Ser} + \mathrm{Met} + \mathrm{Ile} + \mathrm{Leu} + \mathrm{Tyr} + \mathrm{Phe}}$$

Especially the imprint of the redox conditions during the most effective, early stages of OM degradation in the water column and at the sediment–water-interface may be preserved in lake sediments. Palaeo-environmental reconstructions showed that the whole Tso Moriri core, the upper part of the Mansar Lake core, and the bottommost part of the Lonar Lake core were deposited under oxic conditions (Das et al., 2010; Mishra et al., 2014; Prasad et al., 2014; Menzel et al., 2014). Part of the Mansar and Pookode Lake sediments were deposited under low oxygen concentrations (Das et al., 2010; Veena et al., 2014). Anaerobic conditions were encountered in most of the Lonar Lake and the deepest Pookode Lake sediments (Prasad et al., 2014; Menzel et al., 2014; Veena et al., 2014). The oxic sequences usually show Ox/Anox values of $\geqslant 1.5$, whereas the anoxic sequences show values of $\leqslant 1$.

5.5. Ratios between proteinogenic AAs and their non-proteinogenic degradation products

Commonly, ratios between protein AAs and their non-protein degradation products or intermediates, namely Asp/β-Ala, Glu/γ-Aba, and Arg/Orn, or equivalent combinations of these (Gupta and Kawahata, 2007) are used to compare the state of degradation of different samples (Lee and Cronin, 1982; Cowie and Hedges, 1994; Dauwe and Middelburg, 1998; Das et al., 2010). However, varying OM sources in terrestrial environments potentially bias these ratios by contributing relatively high amounts of non-protein AAs, as γ-Aba and Orn percentages are elevated in terrestrial OM. Also, the relative enrichment of Asp and Glu during aerobic degradation (Cowie et al., 1995) might lead to elevated Asp/β-Ala and Glu/γ-Aba ratios, as for example in the bottommost part of the Lonar Lake sediment core, which comprises a palaeosol on top of an underlying hard clay. Both samples indicate strong microbial degradation under aerobic conditions, and whereas the palaeosol shows respective Asp/β-Ala and Glu/γ-Aba ratios of 4.0 and 5.3, indicating strong degradation, the hard clay shows ratios of 8.0 and 16.1. A low to moderate degradation of the hard clay is not supported by other indices, such as AA-N, RI, Ox/Anox, or %Gly/(Gly + Ser + Thr). Hence, the ratios between protein AAs and their non-protein degradation products and intermediates exhibit some weaknesses in deciphering the state of OM degradation in terrestrial environments.

Nevertheless, the contribution of β-Ala to fresh OM of both aquatic and terrestrial origin is relatively low and increases during progressing degradation with slightly elevated values in surface sediments and higher values in more degraded sediment core samples (Cowie and Hedges, 1992; Menzel et al., 2013). Hence, the contribution of β-Ala seems to be more sensitive to OM degradation than to OM origin and might be used to trace OM decomposition even in less degraded samples, whereas the ratios between protein AAs and their non-protein degradation products, the molar percentage of γ-Aba, or the sum of non-protein AAs might only be useful to identify moderately or highly degraded samples. However, different redox conditions during OM degradation can have considerable influence on the

formation of β-Ala and other non-protein AAs in sediments and should be considered during interpretation (Cowie et al., 1995).

6. CONCLUSIONS

The investigation of sediment cores of four Indian lakes from different climatic regimes confirms that AA-based indices are capable of deciphering the state of OM degradation and can also be used to identify specific sources of OM to lake sediments. However, some commonly used proxies show limitations in lacustrine environments, dominantly due to their interference with varying amounts of different OM sources. During our study, the following proxies have proven to be applicable to lake sediment studies comprising samples from different climate regimes with varying contribution of aquatic and terrestrial OM and of different OM degradation state.

- AA-N shows high potential in deciphering the state of OM degradation. Fresh OM dominantly shows AA-N values of $\geqslant 50\%$, linearly decreasing with progressing degradation. AA-C on the other hand is highly depending on the percentage of terrestrial vs. aquatic OM, typically showing values $\geqslant 30\%$ in aquatic and values $\leqslant 15\%$ in terrestrial OM, and should not be used as a degradation proxy.
- The RI and the newly calculated LI are applicable to identify the freshness of OM in lake sediments. The DI, invented on the basis of marine sediment, shows some weaknesses in sediments with high terrestrial OM contribution. Thus, the use of RI and LI should be preferred. LI values of about -1 to -3 indicate fresh OM, whereas moderately degraded lake sediment core samples show LI values of 0–2. Highly degraded lake sediment core samples and moderately degraded marine sediment core samples are characterised by LI values of about 4, and highly degraded marine sediment core samples show values between 8 and 12.
- The relative contribution of the non-protein AA β-Ala to the AA assemblage of sediments seems to be dominantly attributed to the state of OM degradation. The non-protein AAs γ-Aba and Orn, which also accumulate during degradation, can be significantly enriched in terrestrial OM compared to β-Ala and might therefore potentially be biased when it comes to the assessment of OM degradation.
- To identify the percentage of terrestrial and aquatic OM contribution to lake sediments, the commonly used C/N ratio should be used, since AA-based indices might not contribute superior information.
- The accumulation of microbial OM, often a by-product of progressing OM degradation, might be assessed using %Gly/(Gly + Ser + Thr), with values >60% usually pointing to enhanced microbial contribution.
- Sediments that show notable contribution of siliceous OM are usually characterised by elevated percentages Gly + Ser + Thr. Values of >27 mol% seem to identify such sediments in our data set, as long as %Gly/(Gly + Ser + Thr) does not indicate prominent contribution of microbial OM, which would bias this interpretation. Thus, Gly + Ser + Thr might also be applicable to other lacustrine studies and more reliable than the Asp/Gly ratio, which can be biased by microbial OM contribution, different state of degradation, as well as different redox conditions during degradation.
- The use of the Ox/Anox ratio provides reliable information about the dominant redox conditions during OM degradation in our data set, with approximate values $\geqslant 1.5$ indicating distinct aerobic degradation and $\leqslant 1$ indicating anaerobic degradation. Thus, this ratio might be applicable to other study sites too.
- Furthermore, the calculation of an individual PCA of any AA data set is highly recommended, as it yields fundamental information about the most important factors controlling the variability in AA assemblages and might help to identify anomalies within the investigated system.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2015.03.028.

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