The vertical flux of particulate organic nitrogen in the sea: decomposition of amino acids in the Peru upwelling area and the equatorial Atlantic

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ABSTRACT

Marine particulate matter samples were collected in moored and free-drifting sediment traps deployed off the coast of Peru during February, 1978. Three types of amino acids were analyzed in these samples: free extractable amino acids (FEA), hydrolyzed extractable amino acids (HEA) and total hydrolyzed amino acids (THA). FEA and HEA were also analyzed in moored trap samples from the PARFLUX E station in the equatorial Atlantic Ocean.

Amino acid fluxes from the two areas were related to primary productivity, POC flux and PON flux. In the Peru upwelling area, total amino acids account for 20-30% of the POC flux and 40-65% of the PON flux. Relative decomposition rates were different for the three types of amino acids and may be higher at night than during the day. Individual amino acid concentrations indicated that diagenetic reactions may be occurring on the sinking particles. The rates, sites, and mechanisms of these reactions are discussed as well as their implications for benthic metabolism.

Construction of a simple model from the Peru data indicates that about 80% of the amino acids produced in the surface waters during primary production are decomposed above 14 m, assuming all amino acids were produced as POC. However, some proportion of the amino acids are produced or excreted as DOC and decomposed in the dissolved state. About 10% of the primary production is decomposed as particulate amino acids between 14 m and 50 m, and up to 12% may reach the sea floor.

1. Introduction

Organic matter produced by living organisms in the surface waters of the ocean is subject to rapid biological decomposition. By affecting the quantity and composition of organic matter in the sea, decomposition processes can influence the geochemistry of trace elements associated with organic compounds, the nutritive value of particulate matter sinking to the sea floor, and the composition and quantity of material entering the sedimentary record (Andersen, 1977; Gagosian and Lee, 1981). Nutrients regenerated during decomposition can also affect the rate of biological production (Ryther and Dunstan, 1971).

There is strong evidence that most organic matter produced in the euphotic zone

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of the open ocean is decomposed in the upper several hundred meters (Menzel, 1967; Menzel and Ryther, 1968). Recent studies of organic matter in sediment trap samples collected in the North Atlantic Ocean support this idea (Wakeham *et al.*, 1980). However, sediment trap and *in-situ* pump studies have shown that some organic matter is being transported to the sea floor on large particles more rapidly than was once thought (Wiebe *et al.*, 1976; Bishop *et al.*, 1977, 1978; Staresinic, 1978; Honjo and Roman, 1978; Spencer *et al.*, 1978; Knauer *et al.*, 1979; Rowe and Gardner, 1979; Honjo, 1980). Since transport is rapid, the organic material reaching deep water via large particles may be less degraded and more biologically labile than material associated with smaller particles which remain suspended for longer periods.

To date, most studies of the flux of particulate organic matter have considered bulk properties such as total carbon, nitrogen and plant pigments; the individual organic compounds have received much less attention. Although total carbon values are useful, knowledge of the specific compounds provides more precise information on nutritional value, the possibility of interaction with trace elements, and mechanisms of degradation. Some of the specific compounds which have been studied are C_{15}-C_{35} hydrocarbons (Crisp *et al.*, 1979), polycyclic aromatic hydrocarbons (Prahl and Carpenter, 1979), and various lipids (Wakeham *et al.*, 1980; Gagosian *et al.*, 1982).

Decomposition and remineralization of organic nitrogen compounds are of particular importance in marine systems, since inorganic nitrogen can control biological productivity through its role as a limiting nutrient (Ryther and Dunstan, 1971; Walsh and Howe, 1976). As shown in Figure 1, particulate organic nitrogen (PON) is produced by phytoplankton in surface waters. This phytoplankton PON can sink directly out of the euphotic zone under some conditions, but usually enters the marine food chain through zooplankton grazing. Heterotrophs take up dissolved organic matter excreted by the plankton or released during cell rupture from feeding processes or after death, and convert some of the organic N in this material to inorganic N. Heterotrophs also colonize fecal pellets and particles of dead plankton, again regenerating inorganic N from organic N. This inorganic N can then serve once more as a nutrient for phytoplankton growth. Although heterotrophic decomposition processes remineralize most of the photosynthetically-produced organic matter in the upper several hundred meters of the open ocean, at least some organic matter is being transported downward on large particles. And, in shallow areas of high productivity, a larger proportion of surface primary production can reach the sea floor. Sediment trap experiments in Scottish sea lochs have shown that 30-40% of annual water column production may be transported to bottom sediments (Steele and Baird, 1972; Davies, 1975). Information on organic nitrogen in this downward flux, e.g. its nutritive value, the rates and mechanisms of decomposition processes, might be obtained by a study of specific organic nitrogen compounds.

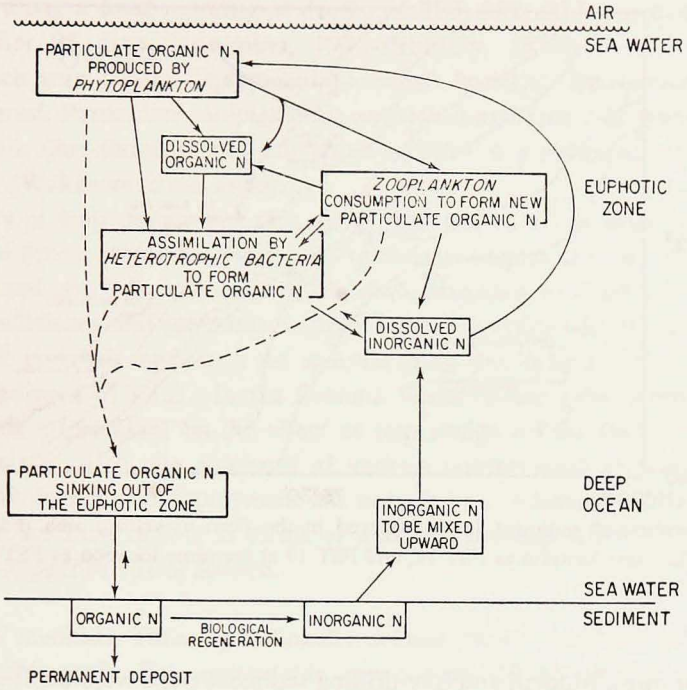

Figure 1. Simplified schematic of the marine organic nitrogen cycle.

Amino acids, the building blocks of protein molecules, make up the largest known reservoir of organic nitrogen in most organisms. Amino acids are useful indicators of decomposition in the marine environment because much is already known about their natural occurrence and geochemical behavior. Amino acids have been one of the more frequently studied classes of organic compounds in seawater (Williams *et al.*, 1976; Lee and Bada, 1977; Dawson and Gocke, 1978), marine sediments (Degens *et al.*, 1964; Schroeder, 1974, 1975; Whelan, 1977), and interstitial waters (Henrichs and Farrington, 1979; Henrichs, 1980; Jorgensen *et al.*, 1980, 1981). In addition, specific amino acid transformation reactions in the marine environment have been investigated (Schroeder and Bada, 1976; Bada and Man, 1980).

We report here measurements of amino acids in sediment trap material from the Peru coastal upwelling area and the equatorial Atlantic Ocean. The sediment trap deployments and sampling methods were designed for other studies, but samples from the two areas were kindly provided by J. Farrington, R. Gagosian, and S. Honjo. Results from the analyses are used to discuss the sites, mechanisms, and rates of decomposition of organic nitrogen in the sea.

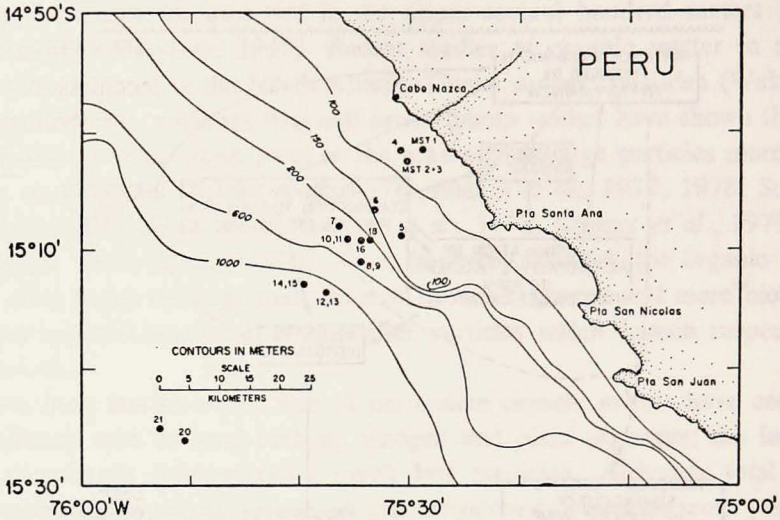

Figure 2. Location of sediment traps deployed in the Peru upwelling area. FST 17 was deployed at the same location as FST 16, and FST 19 at the same location as FST 18.

2. Methods

a. Sediment traps. Moored and free-drifting sediment traps were deployed along the Peruvian coast near the Coastal Upwelling Ecosystem Analysis Transect C during February-March, 1978 (see Fig. 2). The free-drifting traps (FST) were paired 41-cm diameter cylinders (Staresinic *et al.*, 1978) modified for easier handling at sea (Staresinic, 1978, 1982). Two identical arrays were simultaneously deployed, one at the base of the euphotic zone and one at 50 m. Three pairs of diel trap settings (FST 8 to 19) were made in water 400-1000 m deep. Several traps were also deployed in shallower (FST 4 to 7) and deeper (FST 20 and 21) water. FST deployment data and drift trajectories are reported by Staresinic (1982). Moored traps (MST) were 19-cm (dia.) cylinders (Rowe and Gardner, 1979; Rowe, 1981) suspended 3, 7, and 10 m above the bottom. One array (MST 1) was set very near the coast in 30 m of water; a diel pair (MST 2 and 3) was set a short distance away in 80 m of water. Traps were recovered 6-12 hours after deployment; no poisons were used to retard bacterial action during this short time. The particulate matter from the traps was split with a Folsom plankton splitter and the individual fractions frozen for shipment to Woods Hole. One-eighth to one-half of each sample (5-50 mg C) was available for this study.

The sediment trap experiment at the equatorial Atlantic PARFLUX E site has been described by Honjo (1980) and Brewer *et al.* (1980). Preliminary organic analyses were reported by Wakeham *et al.* (1980). The PARFLUX E station is located on the Demerara abyssal plain about 750 km from the Guyana coast (13°30.2'N, 54°00.1'W) in 5,288 m of water. Four cone-shaped sediment traps

were placed along a fixed mooring at depths of 389, 988, 3755 and 5068 m, and recovered after 98 days (November, 1977-February, 1978). Sodium azide was added to each trap before deployment to retard bacterial decomposition of the trapped material. Particulate samples were wet sieved and split with a rotary splitter (Honjo, 1980). One-sixteenth of each sample (0.03-0.4 g sediment) was available for this study (Wakeham *et al.*, 1980).

The effects of trap design and technology will not be considered in any detail here. Three different trap types were used to collect samples analyzed in this study, two moored and one free-drifting trap. The data presented have not been corrected for trapping efficiency and conclusions drawn from the results take this into account. Further work currently underway on samples from the Sediment Trap Intercomparison Experiment (S.T.I.E.) in the Panama Basin during July-December, 1979, should provide information on the effect of trap design on the flux of specific organic compounds. Also, the efficiency of various poisons used to retard bacterial decomposition during trap deployment has not yet been adequately investigated. A discussion of the Peru results in terms of bacterial decomposition of the trapped material will appear in a later section.

b. Analytical methods. Three operationally defined categories of amino acids were measured in this study. Free extractable amino acids (FEA) are those which can be extracted from the wet sample by organic solvents (toluene-methanol) and which contain a free (derivatizable) nitrogen. This category would include any free amino acids loosely associated with sinking particles and the pools of free amino acid remaining in the unruptured cells of organisms. This organic solvent extraction procedure was used to extract FEA because the samples were simultaneously analyzed for specific lipid compounds as in Wakeham *et al.* (1980). Hydrolyzed extractable amino acids (HEA) are all the amino acids in the solvent extractable material which are free after acid hydrolysis. This category will include the FEA as well as amino acids released by acid hydrolysis from lipid-associated peptides and proteins or from some other lipid-associated binding process. By far the largest category, the total hydrolyzed amino acids (THA) are those amino acids freed by acid hydrolysis from an intact, non-solvent extracted sample. Although this category includes the extractable amino acids, most of the THA is composed of the protein amino acids found in particulate material. Other bound amino acids (absorbed or chelated) may be included in the THA. Extractable amino acids in the sediment trap samples were extracted with toluene/methanol (1:1) and partitioned into saturated salt solution as previously described (Wakeham *et al.*, 1980). The salt solution was split into two fractions, one analyzed directly for the dissolved free amino acids (FEA), the second fraction hydrolyzed in 6 N double-distilled HCl under nitrogen at 110° for 19 hours. The hydrolyzates were evaporated to dryness *in vacuo*, taken up in water, and analyzed for HEA. For certain Peru samples, an additional fraction of par-

ticulates, 3/16 to 1/8 of the sample collected, was available for the determination of total amino acids. These samples were hydrolyzed in 6 N double-distilled HCl for 19 hours, filtered through a Gelman A/E combusted glass fiber filter, evaporated to dryness *in vacuo*, and analyzed for THA.

Amino acids were separated, identified, and quantified by high-pressure liquid chromatography (HPLC) of their fluorescent derivatives and comparison with known amounts of authentic standards. Preparation of the fluorescent derivatives with o-phthaldialdehyde (OPT) followed a modified procedure after Hill *et al.* (1979) and Lindroth and Mopper (1979). The OPT solution was prepared by dissolving 50 mg of OPT in 4.5 ml of methanol and adding 50 μl of ethanethiol or 2-mercaptoethanol and 0.5 ml of borate buffer. This solution was prepared daily and protected from light. The borate buffer was prepared by adjusting 0.4 M boric acid to pH 9.5 with 3 N NaOH. Ethanethiol was used to make the OPT solution for the PARFLUX E samples but was replaced by 2-mercaptoethanol for the Peru samples. The latter derivatization method was equally sensitive and formed a derivative as stable as that using the ethanethiol/OPT method, but without the permeating and unpopular odor. These OPT reagents do not form derivatives of secondary amino acids such as proline and hydroxyproline, so concentrations of these amino acids were not measured in this study.

The derivatization procedure for all samples was the same. One ml of sample (50-100 μg amino acids) was mixed with 1.0 ml of borate buffer (pH 9.5) in a 5-ml volumetric flask. Then 0.5 ml of OPT solution was added and the derivative brought to volume (5 ml) with methanol. The resulting derivative was immediately vortex mixed for one minute and then syringe filtered through a Gelman 0.45 μ Metricel filter. Exactly two minutes after the derivative was made, a 10-μl aliquot was injected into the HPLC. Standardizing the timing is critical since the response factors of the derivative vary with time (Lindroth and Mopper, 1979).

Samples were analyzed by reverse-phase HPLC using either a Micromeritics 7000 B or a Varian 5000 pumping system. Initially, a commercial 30-cm Waters μ-Bondapak C-18 column was used with a forty minute linear gradient elution program from 5% to 40% acetonitrile in 0.0125 N Na_2HPO_4 (pH 6.0) with a 10 minute hold after 15 minutes and a flow rate of 1.1 ml/min. During the course of these analyses, methods were changed to improve resolution, and best results (including separation of threonine and glycine) were obtained on 25 cm $\times$ 3.2 mm i.d. columns slurry packed at 690 atm. with Spherisorb S5 ODS, 5 μm, suspended in 25% dibromomethane in methanol. A sixty minute linear program from 10% to 60% methanol in 0.05 N Na_2HPO_4 (pH 6.0) at a flow rate of 1.0 ml/min. was used. Fluorimetric detection was accomplished with a Schoeffel Instrument Corp. FS 970 Liquid Chromatographic Fluorometer with the excitation monochrometer set at 340 nm and the emission measured with a 470 nm cutoff filter. Identification of compounds was verified by co-injection with authentic standards.

Two aliquots of each sample were derivatized and analyzed by HPLC and the results averaged. The difference between these subsamples averaged $< 5\%$. Method blanks showed total amino acid concentrations from filtration, handling, and reagent contamination to be negligible except for one peak apparently related to the OPT reagent and which eluted with valine.

3. Results and discussion

a. Extractable amino acids at the PARFLUX E site. The E station water column is characterized by a weak oxygen minimum between 200 and 400 meters and no significant nepheloid layer (Brewer *et al.*, 1980). Sinking particles at this location are carbonate-rich and the bottom sediments are a firm silty clay (Honjo, 1980). Primary productivity measured in November, 1977, when the traps were deployed, was 200 mg organic C fixed/m^2/day (Honjo, 1980).

The flux of extractable amino acids measured on PARFLUX E sediment trap material shows a rapid decrease with depth (Table 1). This decrease, like that of total lipids, is faster than that of total organic carbon (Table 2), implying that lipids and lipid-associated (extractable) amino acids are more labile than the bulk of organic carbon. Amino acids appear to decrease faster near the surface than do the lipid compounds. At 988 m, total lipids actually make up a higher percentage of organic carbon than at 389 m (see Wakeham *et al.*, 1980, for further discussion of this), while amino acids are essentially gone at this depth.

Loss rates for free and hydrolyzed extractable amino acids appear to differ as well. Although the concentrations are small, the free amino acids decrease faster than the combined extractable amino acids (Table 2). This trend is also shown by the Peru data and will be discussed later in more detail. The PARFLUX E measurements were made at an early stage of this work on a very small amount of material and some of the non-protein amino acids useful for monitoring biological degradation (e.g. β-alanine, γ-aminobutyric acid) were not analyzed. In general, the amino acids found were similar in composition to the protein amino acids in plankton and not unlike distributions found in suspended particulate matter filtered from seawater in the Pacific (Siezen and Mague, 1978).

b. Total amino acids from the Peru upwelling area. The Peru coast is one of the world's major upwelling areas. Until recently, its high productivity supported an anchoveta fishery which was the largest single fishery in the world. Zuta *et al.* (1978) in their description of the hydrologic features of this upwelling area, divide the coast into two principal upwelling zones. Our sediment trap study was conducted during the weak February upwelling in the southern zone between 14S and 16S (Fig. 2). Primary productivity measured at trap stations ranged from 2 to 4 g C/m^2/day (Staresinic, 1978; Gagosian *et al.*, 1980) which agrees well with previous

Table 1. Free and hydrolyzed lipid amino acid concentrations and fluxes at the PARFLUX E site.

FEA (μg/sample)

	E6 + E2* 388 m	E1 + E3* 988 m	E4 3755 m	E5 5068 m
asp	.021	.001		
glu	.009	.001		
ser	.022	—		
gly + thr	.047	—		
ala	.046	.005		
tyr	.037	.004		
arg				
val	.037	.002		
met	—	—		
ile	—	.002		
leu	.041	.001		
phe	—	.008		
lys	—	—		
Total	.259	.024	< .001	< .001

HEA (μg/sample)

	E6 + E2* 388 m	E1 + E3* 988 m	E4 3755 m	E5 5068 m
asp	24.3	2.9	3.7	1.7
glu	62.2	9.9	3.6	1.5
ser	17.1	1.5	—	2.4
gly + thr	35.7	3.3	2.2	3.3
ala	28.9	3.2	3.1	2.1
tyr	12.5	4.1	0.6	1.4
arg	15.5	6.8		
val	29.8	2.2	—	—
met	36.6	2.6	—	—
ile	27.0	3.3	—	
leu	37.8	4.5	—	0.3
phe	53.4	0	—	
lys	4.7	1.7	—	1.1
Total	385.5	46.0	13.2	13.8
Flux (μg/m^2/day)	2.6	0.3	0.09	0.09

* Fractions < 1 mm and > 1 mm were analyzed separately and the numbers added together.

Table 2. Organic carbon, total lipid, and amino acid concentrations in samples from the PARFLUX E site.

Depth (m)	Org C* (g)	Lipid** (mg)	HEA (μg)	FEA (μg)	Lipid / Org C (g/g)	HEA C† / Org C (mg/g)
388	1.0	295	386	.26	.30	0.18
988	0.54	190	46	.02	.35	0.04
3755	0.2	25	13	0	.13	0.03
5068	0.2	13	14	0	.07	0.03

* Honjo (1980).

** Wakeham *et al.* (1980).

† HEA C is calculated using total amino acid concentrations and assuming a weighed average amino acid of molecular weight 120.5 with 44.5% C and 12.5% N calculated from Peru FST 10 as a typical particulate amino acid distribution. Other samples varied very little from this average value for FST 10. For comparison, Jukes *et al.* (1975) calculated an average protein which contains 52% C and 17% N.

measurements (Zuta and Guillen, 1970; Ryther *et al.*, 1971). Sediments in the area are heterogeneous diatomaceous muds of high (3-5%) organic carbon content (Rosato *et al.*, 1975; Gallardo, 1978). Where the oxygen minimum zone contacts the continental slope at depths between 100 and 500 m, sulfate reduction can occur (Dugdale *et al.*, 1977) and the sediment is covered in places by a bacterial mat dominated by *Thioploca*-like sulfur bacteria (Gallardo, 1978).

Staresinic (1978, 1982) describes the material collected in the free-drifting sediment traps. Diatoms were especially abundant in material collected in the shallow traps. Anchoveta fecal pellets packed with diatom frustules in various states of destruction were found in many samples and accounted for a proportionally greater part of the 50 m flux. Night traps contained larger amounts of euphausiid molts and phytodetritus than day traps. The mean flux of particulate organic carbon (POC) across the euphotic depth (14 m) was 554 mg C/m²/day, while the mean flux of PON was 83 mg N/m²/day. Fluxes across 50 m were roughly half of these values.

The high primary productivity in Peru (2-4 g C/m²/day) resulted in a much higher measured flux of amino acids than at the PARFLUX E site where productivity was about 200 mgC/m²/day. But, it is difficult to compare results from the two areas since the shallowest PARFLUX sample came from 389 m (euphotic depth is 80 m) and the deepest Peru sediment traps were moored at 70 to 80 m (euphotic depth is 10-20 m). The free extractable amino acid flux averaged 7600 μg/m²/day in the Peru upwelling (70 m) and was 0.3 μg/m²/day at PARFLUX E (389 m); hydrolyzed extractable amino acids averaged 21,000 μg/m²/day in Peru (70 m) compared with 2.6 μg/m²/day at PARFLUX E (389 m). As might be expected, the flux of amino acids was higher in the more productive area.

Both the Peru and the PARFLUX E amino acid fluxes show a decrease with depth. This decrease is almost a factor of 30 over the 5000 m depth range of the PARFLUX E station, from 2.6 to 0.09 $\mu g/m^2/day$ for the extractable amino acids. Changes in flux between the euphotic depth and 50 m at the Peru free-drifting trap stations varied, usually decreasing by a factor of 1-2 during the day and by about 6 at night. Diel changes will be discussed in more detail later. The Peru moored traps, although deeper (70 m), measured fluxes equal to or greater than the FST fluxes. This can be attributed to resuspension of bottom sediments since the traps were moored 3-10 m off the bottom in a shallow near-shore area (Rowe, 1981), and fluxes were largest just off the bottom (see Table 3). Even when input to the moored traps from resuspension is considered, however, the amino acid results reported here suggest that this labile class of organic compounds is not completely decomposed in very productive shallow waters.

Although the amino acids are not completely decomposed in the water column, the amino acids on sinking particles in both the Peru area and the PARFLUX E site disappear faster than total carbon. Total hydrolyzed amino acids made up 20-30% of the POC and 40-65% of the PON flux in the Peru free-drifting sediment traps 8 through 11. These numbers were calculated by dividing the amino acid C and N contents (see Table 2 footnote) by the POC and PON values shown in Table 3. In almost every case where data were available, the ratio of amino acid flux to POC flux either stayed constant or decreased with depth, indicating that the amino acids were decomposed more rapidly than the bulk of the POC. On the other hand, the ratio of amino acid flux to particulate organic nitrogen flux more frequently increased with depth, implying that the bulk of PON was decomposed more rapidly than the amino acids in the shallow waters off Peru. This could be due to the presence of nitrogen compounds more labile than amino acids such as polyamines, aliphatic amines, purines and pyrimidines. Decomposition rates of these compounds in the Peru samples will be discussed elsewhere. Another explanation for increasing amino acid/PON flux ratios is that amino acids could be produced on sinking particles by heterotrophic organisms faster than, or in preference to, other organic nitrogen compounds.

The different types of amino acids measured in this study, free extractable (FEA), hydrolyzed extractable (HEA), and total hydrolyzed (THA), appear to decompose at different rates. Evidence for differences between the FEA and HEA is shown in Table 4. The ratio of FEA to HEA decreases as the probable age of the sample (time since sinking began) increases. The plankton analyzed contained almost all of their extractable amino acids (hydrolyzed extractable includes the free extractable amino acids) in the free form. The Peru free-drifting traps contained very fresh material, including recognizable phytoplankters at 10, 15 and 50 m depth. In many cases, the cells appeared to be intact (Staresinic, personal comm.). Still, the FEA to HEA ratio began to decrease between 15 and 50 m. The moored traps, set just

Table 3. Amino acid fluxes from free-drifting and moored sediment traps in the Peru upwelling area (see Fig. 2 for locations).

Free-drifting Sediment Traps

Station No.	Depth (m)	Time Day, Night	FEA mg/m²/hr	HEA mg/m²/hr	THA mg/m²/hr	Org C mg/m²/hr	Org N mg/m²/hr
4	19	D	0.38	0.56	—*	21.7†	2.6†
5	15	D	0.05	0.24	30.3	21.3	3.1
6	10	N	0.08	0.18	9.7	21.3	4.0
7	23	D	0.02	0.11	24.3	17.3	2.7
9	14	D	0.16	0.39	6.8	13.7	2.0
8	52	D	0.20	0.33	6.0	11.7	1.6
10	14	N	0.96	1.68	16.9	26.1	3.8
11	52	N	0.16	0.29	6.2	10.9	1.2
12	14	D	0.43	0.92	—	17.0	2.3
13	53	D	0.29	0.67	—	13.8	1.7
14	14	N	0.35	1.17	—	28.6	5.3
15	53	N	0.09	0.21	—	6.1	0.7
16	11	D	0.73	0.62	—	18.7	2.5
17	53	D	0.21	0.28	—	17.4	2.4
18	11	N	0.18	0.30	—	29.2	5.1
19	53	N	0.04	0.05	—	9.3	1.0
20	36	D	0.08	0.12	—	17.4	2.5
21	53	D	0.02	0.11	—	5.5	0.6

Moored Sediment Traps

MST 1	20	D	0.17	1.10	—	9.2††	1.7††
	23		0.16	0.58	9.8	17.6	2.9
	27		0.11	1.25	20.1	35.7	5.2
MST 2	70	D	0.39	0.87	—	17.3	2.6
	73		0.26	1.05	—	16.8	2.2
	77		0.76	1.52	—	12.6	1.8
MST 3	70	N	0.14	0.42	—	9.1	1.3
	73		0.24	0.65	6.6	7.4	1.0
	77		0.10	0.78	8.8	12.7	1.5

* Dashes appear where total sample was not available for hydrolysis.
† Data from Staresinic (1978).
†† Data from Rowe (1981).

Table 4. Ratio of free to hydrolyzed extractable amino acids in various samples of increasing "assumed age."

	FEA/HEA
Phytoplankton and zooplankton*	0.8-1.0
Peru free-drifting traps†	0.2-0.8
Peru moored traps†	0.1-0.5
PARFLUX E 388 m	0.0005
PARFLUX E 5068 m	0

* Average value of several individual species which were analyzed for amino acids (Lee, unpublished data).

† Average of every sample reported in Table 3.

off the bottom, showed slightly lower ratios than the free-drifting traps as might be expected since moored traps would contain slightly older material or material which contained sediment resuspended from the bottom. The deeper PARFLUX E samples showed much reduced ratios. In fact, by 3755 m no detectable FEA remained. The most obvious explanation for this decrease of free extractable amino acids with "age" is that free amino acid pools are released to the surrounding seawater when an organism dies and its cells rupture. The decrease in ratio with age would simply reflect increasing cell rupture with age of sample (or time in the trap). However, evidence presented in the next section on individual amino acids in the free extractable fraction suggest that decomposition reactions are also occurring and that dissolution is not the sole explanation.

Relative rates of decomposition of the total hydrolyzed amino acids relative to the extractable (lipid-associated) amino acids are difficult to determine from the available data. The lipid to protein ratio of organisms depends on their physiological state, so the initial ratio in the trap source organisms is not constant. Also, fewer samples were available for THA analysis. In the two cases where the source terms were similar for different depths and data were available (FST stations 9 & 8 and 10 & 11), the ratio of HEA to THA decreased with depth (0.07 to 0.05 and 0.1 to 0.05). Better evidence to show that the extractable (lipid-associated) amino acids disappear faster than the total hydrolyzed (protein) amino acids is presented in the next section.

c. Individual amino acids in Peru upwelling samples. Individual amino acid concentrations for FST stations 8 through 11 are shown in Table 5. The relative distribution of free and hydrolyzed extractable amino acid concentrations for the other Peru samples analyzed were very similar to the distributions shown here. The total hydrolyzed amino acid (THA) distribution in all four samples closely resembles that of sediment hydrolyzates from this area (Henrichs, 1980). In general, the concentrations of individual amino acids follow the same pattern of change with depth as the total concentrations.

Table 5. Individual free and hydrolyzed extractable amino acid and total hydrolyzed amino acid fluxes at two depths at a diel free-drifting sediment trap station in the Peru upwelling area.

	FEA				HEA				THA			
	9	8	10	11	9	8	10	11	9	8	10	11
	14 m	52 m	14 m	52 m	14 m	52 m	14 m	52 m	14 m	52 m	14 m	52 m
	Day	Day	Night	Night	Day	Day	Night	Night	Day	Day	Night	Night
asp	10	10	15	4	27	27	73	14	960	860	2240	590
glu	18	13	141	45	59	55	454	73	870	740	1910	690
β-glu	0	0	0	0	0	0	N	N	0	0	0	0
ser	6	8	16	4	15	11	77	8	440	350	960	440
thr	*17	27	142	17	*52	46	188	32	340	300	670	270
gly									860	810	1760	1070
?**	3	2	4	1	6	3	5	3	0	0	0	0
ala	24	31	122	17	46	43	157	27	780	650	1670	720
β-ala	10	21	N††	7	19	21	33	14	40	80	N	N
val + met	18	25	148	19	38	31	142	23	810	510	1950	660
γ-aba									190	200	500	140
tyr	†0	0	N	N	†0	0	24	7	110	80	200	110
arg									0	0	0	0
α-aba	2	1	0	1	3	2	2	2	0	0	0	0
ile	9	19	77	12	24	20	148	25	260	380	1340	380
leu	23	27	173	18	53	40	201	29	500	420	1460	400
ϕ-ala	14	15	91	10	21	19	117	21	330	400	1390	440
lys	8	6	29	5	26	13	63	12	310	260	850	330
Total ($\mu g/m^2/hr$)	162	205	958	160	389	331	1684	290	6800	6040	16900	6240

* Threonine and glycine were resolved in the extractable fraction of samples run later during this work. In every case where resolution was achieved, threonine made up between 20 and 30% of the combined total (thr + gly), as was also the case of the total hydrolyzed amino acids shown here.

** The structure of this primary amine is presently unknown. It elutes very close to but does not coelute with glucosamine.

† Where they were resolved in later extractable fractions, arginine was usually present in very small amounts, while γ-aminobutyric acid and tyrosine varied with the sample, usually being present in approximately equal amounts. In the total hydrolyzed fractions, tyr was closer to half the amount of γ-aba present.

†† N indicates that a compound is present in small amount but too small or not sufficiently resolved to be quantified.

††† A peak related to the OPT reagent frequently occurs in the blank and co-elutes with valine. These numbers therefore show a maximum value for the concentration of val + met.

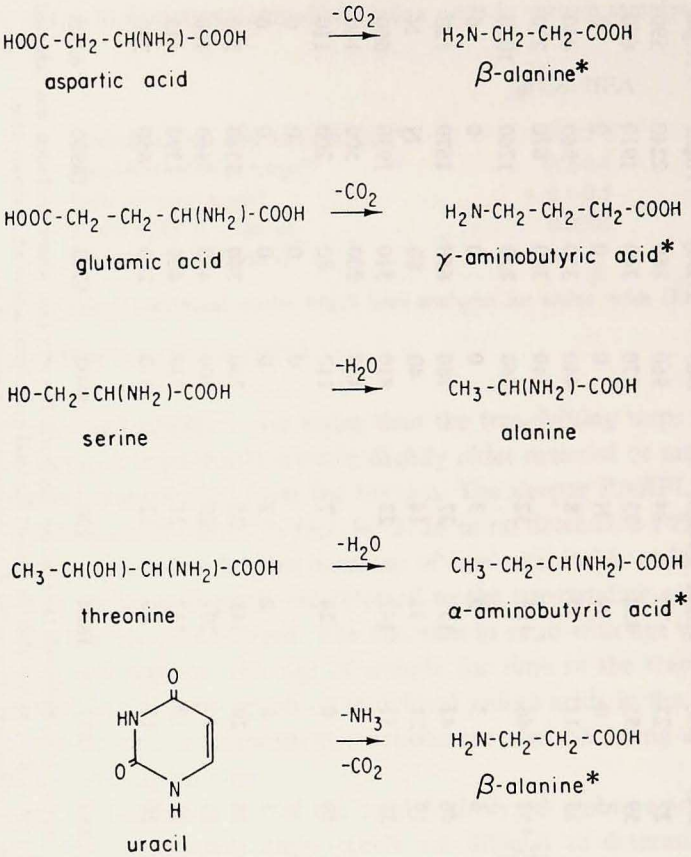

Figure 3. Some biological transformation reactions of organic nitrogen compounds resulting in the formation of amino acids (* marks the non-protein amino acids).

Do the individual amino acid distributions show any evidence that decomposition reactions are occurring in the sediment trap material? A number of biochemical reactions occur during decomposition processes. Major routes of metabolism of the amino acids present in organisms are decarboxylation and deamination. In most cases, when these reactions occur, the product is an amine or an aliphatic acid no longer detectable by our routine amino acid analyses. But diacidic amino acids such as aspartic acid and glutamic acid decarboxylate to form compounds which are still amino acids, namely β-alanine (β-ala) and γ-aminobutyric acid (γ-aba). These and other reactions to be discussed are shown schematically in Figure 3. Another diagenetic reaction is the dehydration of serine and threonine to form alanine (ala) and α-aminobutyric acid (α-aba). These dehydration reactions have been reported in seawater (Bada and Hoopes, 1979) and in foraminiferal tests from deep sea sediments (Bada *et al.*, 1978). All of these potential diagenetic products, β-ala, γ-aba, α-aba, and ala were found in the Peru sediment trap samples. Serine/

alanine ratios do not appear to decrease with depth in either the Peru or the PARFLUX sediment traps. Alanine, however, is a normal protein amino acid and is found in large concentration in organisms. Therefore, variations in organisms falling into the traps may account for the variation in this ratio. This is probably also true for threonine/α-aba ratios, but lack of good analytical separation for both threonine and α-aba in the samples prohibited determining these ratios accurately. α-Aba made up less than 1% of the total amino acids measured in the FEA and HEA and was not detected in the THA (too small proportionally to the other more concentrated amino acids). It is also possible that the dehydration reactions are slow and had not yet had time to occur to a measurable extent on the rapidly falling large particles caught in the sediment traps.

What is the source of the β-alanine and γ-aminobutyric acid in the large particle flux? These compounds are non-protein amino acids but may be occasionally found in organisms as metabolic intermediates. β-Ala is a precursor of the vitamin pantothenic acid, while γ-aba is a chemical agent for the transmission of nerve impulses (Lehninger, 1970). Meister (1965) reports that γ-aba is found in many plants in low concentration and is also commonly formed during the microbial decarboxylation of glutamic acid. Meister adds that microbial decarboxylation of aspartic acid usually occurs at the β rather than the α carboxyl group, forming alanine rather than β-alanine. Awapara (1962) suggests that β-ala is more usually formed during the degradation of the pyrimidine uracil. γ-aba has been found in high concentrations in the intracellular pools of the dinoflagellate *Gonyaulax polyhedra* (Kittredge *et al.*, 1962) and in various marine macroalgae (Scheuer, 1980). Henrichs (1980) reports the presence of both compounds in the intracellular free amino acid pool of a marine bacterium (*Pseudomonas halodurans*).

Evidence from the relative and absolute concentrations of β-alanine suggests that this compound may be produced on sinking particles (see Table 6a). In every case where the change in proportion of β-ala in the sample (Δ) could be measured, the relative proportion of β-ala increased with depth. And, in every case measureable, the increase in the FEA was greater than or equal to the increase in HEA suggesting that the formation of β-ala was faster in the FEA. Since few data were available for the THA, no conclusion could be reached regarding relative rates of formation of β-ala in this amino acid category. The actual ratios of β-ala to total amino acids decrease in the order FEA $>$ HEA $>$ THA suggesting that this could be the relative reaction rate order. However, the ratio order may simply reflect the fact that β-ala is not usually incorporated into protein. The increase in β-ala with depth might be due to a slower loss relative to the other amino acids as suggested by Henrichs (1980) for sediments, except that in some cases, the absolute flux of β-ala also increased. This absolute increase suggests that β-alanine is being produced on the sinking particles.

Table 6a. Changes in ratio of β-alanine to total amino acid concentrations with depth in Peru sediment trap pairs.

FST No.	9	8	10	11	12	13	14	15	16	17	18	19	20	21
FEA	0.06	0.1	N†	.04	.07	.07	.03	.15	.01	.04	.03	.2	.05	.10
Δ*	0.4		—		0		0.8		0.8		0.9		0.5	
HEA	0.05	0.06	0.02	0.05	0	N	0.02	0.03	0.01	0.02	0.02	0.08	0.05	0.05
Δ	0.2		0.6		0		0.3		0.5		0.8		0	
THA	0.005	0.013	N	N	—		—		—		—		—	
Δ	0.6		—											

* Δ is calculated by subtracting the shallow trap ratio from the deep trap ratio and dividing by the deep trap ratio.

Table 6b. Ratios of α-aminobutyric acid to total amino acid concentrations in Peru sediment trap depth pairs.

FST No.	9	8	10	11	12	13	14	15	16	17	18	19	20	21
FEA	0	0	N†	N	0.07	0	0.08	0.04	0.06	N	0.04	0.03	0.05	0.04
HEA	0	0	0.01	0.02	0.06	0.03	N	0.02	N	N	0.02	0.02	0.04	0.04
THA	0.028	0.033	0.030	0.023	—		—		—		—		—	

† N indicates that a compound is present in small amount but too small or not sufficiently resolved to be quantified.

But, it is also possible that new particles of higher relative β-ala concentration are being produced between 14 m and 50 m. As mentioned earlier, anchovy fecal pellets made up a proportionally larger part of the 50 m than the 14 m flux. β-Ala may be formed microbially in the anchovy gut and incorporated into fecal pellets egested below 14 m. We cannot assess the importance of this source from our present data. Alternatively, β-ala may be more resistant to digestion than other amino acids and therefore be more concentrated in the fecal pellets. However, the FEA > HEA > THA order of ratio decrease would be more difficult to explain if this were the case.

If β-alanine is being produced on the sinking particles, can we determine the mechanism of formation from the present data? β-Ala/aspartic acid ratios increase with depth in every case measured, which is consistent with the decarboxylation hypothesis. If this mechanism is correct, the changing ratios suggest that the reaction rate order is FEA > HEA > THA. On the other hand, uracil is present in these samples (Lee, unpublished data) and could be the source of the β-ala. The presence of both γ-aba and β-ala in a marine bacterium and deep-sea sediments might suggest that the mechanism of formation is similar for both compounds. But, the distribution of these two compounds in the Peru samples is very different. γ-Aba does not show the correlation with depth exhibited by β-ala (see Table 6b). The ratio of γ-aba to total amino acids in the extractable amino acids decreases or remains constant with depth in most cases. The ratio in the FEA is usually greater than or equal to the ratio in the HEA, but the largest proportion of γ-aba is in the THA. Since γ-aba has not been reported as a constituent of protein, some other binding mechanism must exist. These distribution differences between β-ala and γ-aba could be due to a different mechanism of formation or a difference in source input. As stated earlier, γ-aba is found in plants, including a marine dinoflagellate and various marine macroalgae. It is likely that variations in source organisms could contribute varying amounts of γ-aba to the sediment traps thus masking diagenetic processes.

Are sinking particles a source of β-ala and γ-aba to the sea floor? Schroeder (1975) and Whelan (1977) report both γ-aba and β-ala as a large proportion of the amino acids in marine sediments from the deep sea. Schroeder's thermal kinetic studies showed deamination and not decarboxylation to be the preferred chemical decomposition pathway for amino acids. He suggested that the decarboxylation of glutamic and aspartic acid by bacteria might instead be the source of β-ala and γ-aba in marine sediments. Henrichs (1980) analyzed sediments from the Peru upwelling area at or near the site of our sediment trap studies and found γ-aba concentrations in total sediment hydrolyzates of 1 mole % at all depths (< 1 m) in all cores analyzed. β-Ala values were similar although poor resolution from valine in her GC method makes these values less certain (Henrichs, personal comm.).

Based on her data from Peru and from the North Atlantic, Henrichs suggested that β-ala and γ-aba might be present in sinking material and that the increase in relative abundance down core which she observed in the North Atlantic was because these compounds are less readily metabolized than protein amino acids.

Indeed, our data show that sinking particles are a source of β-alanine and γ-aminobutyric acid. The Peru sediment trap THA contain about 3 mole % γ-aba and 0.4 mole % β-ala. These values account for much if not all of these compounds in the underlying sediments. Based on organic carbon content of surface sediments and on sedimentation rates determined from ^{210}Pb measurements, Henrichs (1980) calculated an average accumulation rate of 90 g C/m²/yr for the Peru sediments at depths of 90 m and 280 m. Since about 25% of this carbon is from amino acids, roughly 23 g amino acid C/m²/yr accumulates in the surface sediments. From Table 3, the THA flux through 50 m for FST 8 and 11 is 157 mg amino acid/m²/day. If an "average" amino acid is 45% C (see Table 2) and the flux of amino acids is constant over the year, we calculate a flux through 50 m of 26 g amino acid C/m²/yr. Considering the seasonal variability in POC flux and the other assumptions in these calculations, the agreement between the sinking rate of amino acid carbon on large particles and the accumulation rate of amino acid carbon in the sediments is remarkable. This agreement would suggest that most of the amino acids passing 50 m reach the sea floor without being decomposed, and that the γ-aba and β-ala on the sinking particles more than account for the amount of these compounds found in surface sediments. Chemosynthetic sulfur bacteria growing in the upper 10-20 cm of the anoxic Peru sediments likely produce new amino acids from inorganic N. The amino acid production rate of these organisms is not known, but an equivalent loss of amino acids by decomposition below the 50-m trap would balance our rough budget.

The formation and accumulation of β-alanine, γ-aminobutyric acid, and other non-protein amino acids raises an interesting question with regard to benthic nutrition. If these compounds are less readily metabolized by organisms than the protein amino acids, are they a nutritious source of nitrogen for benthic metabolism? Or, is this nitrogen locked away in a molecule which is resistant to decomposition? If the β-ala and γ-aba in deep-sea sediments, where these two compounds can make up over half of the amino acids present (Schroeder, 1975; Whelan, 1977; Henrichs, 1980), are coming from sinking particles, then part of the amino acid carbon reaching the sea floor may not be useful to bottom organisms. Although the amino acids sinking on particles in the deep sea probably make up a smaller fraction of total C than the 20-30% found in Peru, still a significant fraction may be in the form of these non-protein amino acids. This must be considered when basing nutritional content on measured values of "total amino acids" or "total protein" when the individual compounds have not been measured.

Table 7. Comparison of the amount of amino acid decomposed between 14 and 50 m to surface primary productivity.

FST Stations No.	Primary* productivity g C/m²/day	Amino acid** production mg aa C/m²/day	Amount of amino acid† decomposed, mg aa C/m²/day FEA	HEA	THA
8-11	2.2	550	4.1	7.7	52
12-15	2.8	700	3.1	6.5	—
16-19	3.4	850	7.9	7.1	—

* From Staresinic (1978).

** Assumes 25% of carbon is in amino acids.

† Calculated by subtracting the sum of the day (12 hr) and night (12 hr) fluxes at 50 m from the sum of the day and night fluxes at 14 m.

Since the formation of β-ala and γ-aba is probably microbially-mediated, one must question whether these reactions occurred while the particles were concentrating in the unpoisoned collection cups of the sediment traps. In a shipboard incubation study on this Peru upwelling area cruise, J. E. Hobbie (personal comm.) counted bacterial biomass in an offshore trap (FST #3, not sampled for amino acids) and calculated a doubling time for the bacteria of 6.3 hours at *in-situ* temperatures. However, if microbial decomposition reactions producing β-ala and γ-aba were taking place during trap deployment, one would expect larger concentrations of the products in the shallower traps, where temperatures are warmer and bacterial biomass probably higher. In fact, we see the opposite, suggesting that bacterial activity during the 6-12 hour trap deployment may not greatly alter amino acid concentrations.

If the particulate amino acids in the trap material are not changing to a significant extent with respect to their β-alanine or γ-aba composition in 6-12 hours, why is there a change between 14 m and 50 m? How long does it take for the particles to sink 36 m? Brewer *et al.* (1980) report a mean particle settling velocity of 21 m/day for the open ocean PARFLUX stations. Taguchi and Hargrave (1978) report lower sinking rates (0.1 to 1 m/day) from their trap experiments in the upper 60 m of a productive marine bay. Honjo and Roman (1978) measured fecal pellet sinking rates of 120 m/day. These estimates indicate that most particles would take days to months to fall 36 m, while a large fecal pellet could fall in only seven hours. This calculation suggests that caution must be applied when looking at diurnal variations between the 14 m and 50 m traps since the exact length of time it takes the particles to sink 36 m is unknown.

d. Factors affecting the calculation of decomposition rates for total amino acids. We have discussed relative decomposition rates in terms of categories of amino acids, such as extractable or protein, and in terms of diagenetic reactions involving specific compounds. But, we have not yet placed our data in the general context of the marine organic nitrogen cycle shown in Figure 1. Table 7 shows the calculated

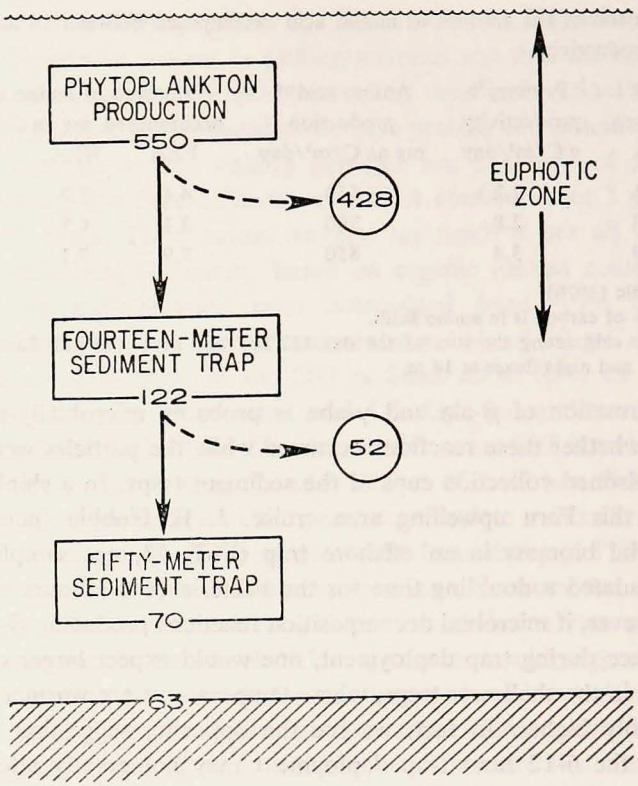

Figure 4. Budget of amino acid production, decomposition, and accumulation for FST 8-11 in units of mg amino acid carbon/m²/day.

amount of amino acid produced in primary production compared with the amount of amino acid decomposed between 14 and 50 m. Because productivity measurements, sedimentation rates, etc., are in terms of carbon, we will discuss our data in terms of C rather than N. Acknowledging the limitations of the many assumptions made, a rough budget in units of mg amino acid C/m²/day (see Fig. 4) would be the following: 550 mg is produced by phytoplankton in the euphotic zone; of this, 122 mg (22%) appears in the 14 m trap at the base of the euphotic zone; 52 mg (10%) of this trap material is decomposed or lost by other processes before reaching the 50 m trap, where 70 mg (12%) is caught; and, almost all of this 50-m trap material may reach the sediment where 63 mg aa C/m²/day is accumulating. Again, if chemosynthetic production by sulfur bacteria is significant, then more decomposition must occur below the 50-m trap. The decomposition rate calculated between 14 m and 50 m, 52 mg aa C/m²/day, is more than twice the 11-28 mg aa C/m²/day calculated for surface sediments in this area by Henrichs (1980), again assuming 25% of total sediment C is in amino acids.

But, what happened to the 428 mg aa C/m²/day difference between the material produced and that caught at 14 m? Although some POC is remineralized above 14 m, it is likely that much of this extra carbon is in the dissolved pool. It was either produced originally as DOC and released to the seawater directly by phytoplankton or during zooplankton feeding processes, or it was consumed as POC by zooplankton and excreted as a dissolved metabolic waste product. As dissolved organic matter, the free amino acids are subject to rapid removal from seawater (Hobbie, *et al.*, 1968; Lee and Bada, 1977).

Several processes serve to complicate the simple picture described above. Vertical migrators may be feeding on particles in the euphotic zone at night, and then moving down below the 50 m traps during the day to release relatively fresh material in fecal pellets. Staresinic (1982) estimated that anchovy and euphausiids could bypass the 50 m trap with 60 mg C/m²/day, which is about 20% of the flux measured by traps 8 and 11 and about 3% of the primary productivity at this station. If this is so, the agreement between the accumulation rate in the sediment and the flux through 50 m implies that the decomposition rate below 50 m is greater than our rough budget indicates.

Another complicating factor is the diel variation observed in amino acid flux. The difference in flux between the 14 m and 52 m traps is always greater at night than during the day (see Table 3), and the 14 m flux is much higher at night. This suggests that the source of sinking particles at 14 m is larger at night, and that there may be more decomposition between 14 m and 52 m then. Several processes might account for the diel differences. Vertical migrators rise to the surface to feed at night (Boyd *et al.*, 1980) and would most likely deposit their fecal pellets in the 14 m trap. Primary productivity certainly varies diurnally. Measurements taken twice a day at the Peru stations show that evening chlorophyll-*a* values are always larger than morning values (Gagosian *et al.*, 1980). Another possible explanation for the differences in particulate amino acid flux is the diel change in the magnitude of vertical mixing due to variations in wave action and thermal stratification. Staresinic (1978) discusses in more detail diel differences in POC flux and in types of organism remains found in the traps as well as reasons for these differences.

4. Conclusions

The flux of amino acids on sinking particles is related to primary productivity in surface waters. In the Peru upwelling area, amino acids account for 20-30% of the POC flux and 40-65% of the PON flux. They are not completely decomposed within the shallow euphotic zone of this highly productive region, and much of the amino acid flux may reach the bottom in this area. At the PARFLUX E site, amino acid fluxes were much lower than in the Peru upwelling area, although samples

from the same depths were not available for comparison. E site fluxes decreased by a factor of 30 over 5000 m.

Amino acids disappear faster than the bulk of particulate organic carbon but may be more resistant than some of the other nitrogen compounds present. Decomposition rates for amino acids on the particles vary according to their chemical state. Free extractable amino acids (FEA) decompose faster than hydrolyzed extractable amino acids (HEA); extractable amino acids may decompose faster than the total hydrolyzed amino acids (THA). The day and night traps in the Peru upwelling area show differences in the flux and possibly in the amount of decomposition of amino acids. These differences are not easily explained but are most likely due to the activity of vertical migrators and to diurnal changes in productivity and wind strength.

Individual amino acid concentrations suggest that diagenetic reactions may be occurring on the sinking particles in the Peru upwelling area. These reactions are almost certainly microbially-mediated rather than chemical, considering the nature of the reactions observed. It has been thought that the source of two amino acids found in large relative concentration in deep sea sediments, β-alanine and γ-aminobutyric acid, was *in-situ* microbial decarboxylation of aspartic and glutamic acid. While this process may occur, evidence from the Peru upwelling area samples shows that the source of some, if not all, of these compounds in the sediments is large particles sinking through the water column. Although some evidence suggests that microbial decarboxylation may be occurring on the particles, β-alanine may also be produced by the degradation of uracil while at least some portion of the γ-aminobutyric acid found is likely present in the source organisms.

A rough budget of the amino acid cycle in the Peru upwelling indicates that about 20% of the primary productivity reaches the bottom of the euphotic zone (14 m). Half of this is lost before it reaches 50 m. The remaining half, 10% of the surface primary productivity, passes through 50 m and may reach the sea floor.

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REFERENCES

Andersen, N. R. 1977. Concepts in marine organic chemistry. Mar. Chem., *5*, 303–368.

Awapara, J. 1962. Free amino acids in invertebrates: a comparative study of their distribution and metabolism, *in* Amino Acid Pools, J. T. Holden, ed., Elsevier, Amsterdam, 815 pp.

Bada, J. L. and E. A. Hoopes. 1979. Alanine enantiomeric ratio in the combined amino acid fraction in seawater. Nature, *282,* 822-823.

Bada, J. L. and E. H. Man. 1980. Amino acid diagenesis in Deep Sea Drilling Project cores: Kinetics and mechanisms of some reactions and their applications in geochronology and in paleotemperature and heat flow determinations. Earth Sci. Rev., *16,* 21–55.

Bada, J. L., M.-Y. Shou, E. H. Man and R. A. Schroeder. 1978. Decomposition of hydroxy amino acids in foraminiferal tests; kinetics, mechanism and geochronological implications. Earth Planet. Sci. Letts., *41,* 67–76.

Bishop, J. K. B., J. M. Edmond, D. R. Ketten, M. P. Bacon and W. B. Silker. 1977. The chemistry, biology, and vertical flux of particulate matter from the upper 400 m of the equatorial Atlantic Ocean. Deep-Sea Res., *24,* 511–548.

Bishop, J. K. B., D. R. Ketten and J. M. Edmond. 1978. The chemistry, biology, and vertical flux of oceanic particulate matter from the upper 400 m of the Cape Basin in the southeast Atlantic. Deep-Sea Res., *25,* 1121–1162.

Boyd, C. M., S. L. Smith and T. J. Cowles. 1980. Grazing patterns of copepods in the upwelling system off Peru. Limnol. Oceanogr., *25,* 583–596.

Brewer, P. G., Y. Nozaki, D. W. Spencer and A. P. Fleer. 1980. Sediment trap experiments in the deep North Atlantic: isotopic and elemental fluxes. J. Mar. Res., *38,* 703–728.

Crisp, P. T., S. Brenner, M. I. Venkatesan, E. Ruth and I. R. Kaplan. 1979. Organic chemical characterization of sediment-trap particulates from San Nicholas, Santa Barbara, Santa Monica and San Pedro Basins, California. Geochim. Cosmochim. Acta, *43,* 1791–1801.

Davies, J. M. 1975. Energy flow through the benthos in a Scottish sea loch. Mar. Biol., *31,* 353–362.

Dawson, R. and K. Gocke. 1978. Heterotrophic activity in comparison to the free amino acid concentrations in Baltic seawater samples. Oceanol. Acta, *1,* 45–54.

Degens, E. T., J. H. Reuter and K. N. F. Shaw. 1964. Biochemical compounds in offshore California sediments and seawaters. Geochim. Cosmochim. Acta, *28,* 45–66.

Dugdale, R. C., J. J. Goering, R. T. Barber, R. L. Smith and T. T. Packard. 1977. Denitrification and hydrogen sulfide in the Peru upwelling region during 1976. Deep-Sea Res., *24,* 601–608.

Fattorusso, E. and M. Piattelli. 1980. Amino acids from marine algae, *in* Marine Natural Products, Volume 3, P. Scheuer, ed., Academic Press, 229 pp.

Gagosian, R. B. and C. Lee. 1981. Processes controlling the distribution of biogenic organic compounds in seawater, *in* Marine Organic Chemistry, E. K. Duursma and R. Dawson, eds., Elsevier, Amsterdam, 521 pp.

Gagosian, R. B., T. Loder, G. Nigrelli, Z. Mlodzinska, J. Love and J. Kogelschatz. 1980. Hydrographic and nutrient data from R/V KNORR Cruise 73, Leg 2—February to March, 1978—off the coast of Peru, W.H.O.I. Tech. Rept. 80-1, 77 pp.

Gagosian, R. B., S. O. Smith and G. E. Nigrelli. 1982. Vertical transport of steroid alcohol and ketones measured in a sediment trap experiment in the equatorial Atlantic Ocean. Geochim. Cosmochim Acta, in press.

Gallardo, V. A. 1978. Large benthic microbial communities in sulphide biota under Peru-Chile subsurface counter current. Nature, *268,* 331–332.

Henrichs, S. 1980. Biogeochemistry of amino acids in interstitial waters of marine sediments. Ph.D. Thesis, W.H.O.I./M.I.T. Joint Program in Oceanography, W.H.O.I. Tech. Rept. 80-39, 253 pp.

Henrichs, S. M. and J. W. Farrington. 1979. Amino acids in interstitial waters of marine sediments. Nature, *279,* 319–322.

Hill, D. W., F. H. Walters, T. D. Wilson and J. D. Stuart. 1979. High performance liquid chromatographic determination of amino acids in the picomole range. Anal. Chem., *51*, 1338–1341.

Hobbie, J. E., C. C. Crawford and K. L. Webb. 1968. Amino acid flux in an estuary. Science, *159*, 1463–1464.

Honjo, S. 1980. Material fluxes and modes of sedimentation in the mesopelagic and bathypelagic zones. J. Mar. Res., *38*, 53–97.

Honjo, S. and M. R. Roman. 1978. Marine copepod fecal pellets: production, preservation and sedimentation. J. Mar. Res., *36*, 45–57.

Jorgensen, N. O. G., P. Lindroth and K. Mopper. 1981. Extraction and distribution of free amino acids and ammonium in sediment interstitial waters from the Limfjord, Denmark. Oceanol. Acta, 465–474.

Jorgensen, N. O. G., K. Mopper and P. Lindroth. 1980. Occurrence, origin, and assimilation of free amino acids in an estuarine environment. Ophelia, Suppl. *1*, 179–192.

Jukes, T. H., R. Holmquist, and H. Moise. 1975. Amino acid composition of proteins: Selection against the genetic code. Science, *189*, 50–51.

Kittredge, J. S., D. G. Simonsen, E. Roberts and B. Jelinek. 1962. Free amino acids of marine invertebrates, *in* Amino Acid Pools, J. T. Holden, ed., Elsevier, Amsterdam, 815 pp.

Knauer, G. A., J. H. Martin and K. W. Bruland. 1979. Fluxes of particulate carbon, nitrogen, and phosphorus in the upper water column of the northeast Pacific. Deep-Sea Res., *26*, 97–108.

Lee, C. and J. Bada. 1977. Dissolved amino acids in the equatorial Pacific, the Sargasso Sea, and Biscayne Bay. Limnol. Oceanogr., *22*, 502–510.

Lehninger, A. L. 1970. Biochemistry. Worth Publishers, New York, 833 pp.

Lindroth, P. and K. Mopper. 1979. High performance liquid chromatographic determination of subpicomole amounts of amino acids by precolumn fluorescence derivatization with o-phthaldialdehyde. Anal. Chem., *51*, 1667–1674.

Meister, A. 1965. Biochemistry of amino acids. Academic Press, New York, 2nd Ed., 1084 pp.

Menzel, D. W. 1967. Particulate organic carbon in the deep sea. Deep-Sea Res., *14*, 229–238.

Menzel, D. W. and J. H. Ryther. 1968. Organic carbon and the oxygen minimum in the South Atlantic Ocean. Deep-Sea Res., *15*, 327–337.

Prahl, F. G. and R. Carpenter. 1979. The role of zooplankton fecal pellets in the sedimentation of polycyclic aromatic hydrocarbons in Dabob Bay, Washington. Geochim. Cosmochim. Acta, *43*, 1959–1972.

Rosato, J. J., L. D. Kulm and P. S. Derks. 1975. Surface sediments of the Nazca plate. Pac. Sci., *29*, 117–130.

Rowe, G. T. 1981. Benthic production and processes off Baja California, northwest Africa and Peru, *in* Bioproductivity of Upwelling Ecosystems, R. Barber and M. Vinogradov, eds., in press.

Rowe, G. T. and W. D. Gardner. 1979. Sedimentation rates in the slope water of the northwest Atlantic Ocean measured directly with sediment traps. J. Mar. Res., *37*, 581–600.

Ryther, J. H. and W. M. Dunstan. 1971. Nitrogen, phosphorus and eutrophication in the coastal marine environment. Science, *171*, 1008–1013.

Ryther, J. H., D. W. Menzel, E. M. Hulburt, C. J. Lorenzen and N. Corwin. 1971. The production and utilization of organic matter in the Peru coastal current. Inv. Pesq., *35*, 43–59.

Schroeder, R. A. 1974. Kinetics, mechanism and geochemical applications of amino acid racemization of various fossils. Ph.D. Thesis, Scripps Institution of Oceanography, U.C.S.D.

—— 1975. Absence of β-alanine and γ-aminobutyric acid in cleaned foraminiferal shells: Im-

plications for use as a chemical criterion to indicate removal of non-indigenous amino acid contaminants. Earth Planet. Sci. Lett., *25,* 274–278.

Schroeder, R. A. and J. L. Bada. 1976. A review of the geochemical applications of the amino acid racemization reaction. Earth Sci. Rev., *12,* 347–391.

Siezen, R. J. and T. H. Mague. 1978. Amino acids in suspended particulate matter from oceanic and coastal waters of the Pacific. Mar. Chem., *6,* 215–231.

Spencer, D. W., P. G. Brewer, A. Fleer, S. Honjo, S. Krishnaswami and Y. Nozaki. 1978. Chemical fluxes from a sediment trap experiment in the deep Sargasso Sea. J. Mar. Res., *36,* 493–523.

Staresinic, N. 1978. The vertical flux of particulate organic matter in the Peru coastal upwelling as measured with a free-drifting sediment trap. Ph.D. Thesis. W.H.O.I./M.I.T. Joint Program in Oceanography, W.H.O.I. Tech. Rept. 80-4, 255 pp.

Staresinic, N. 1982. Downward flux of bulk particulate organic matter in the Peru coastal upwelling. Submitted to J. Mar. Res.

Staresinic, N., G. T. Rowe, D. Shaughnessey and A. J. Williams, III. 1977. Measurement of the vertical flux of particulate organic matter with a free-drifting sediment trap. Limnol. Oceanogr., *23,* 559–563.

Steele, J. H. and I. E. Baird. 1972. Sedimentation of organic matter in a Scottish sea loch. Mem. Inst. Ital. Idrobiol., *29* (Supplement), 73–88.

Taguchi, S. and B. T. Hargrave. 1978. Loss rates of suspended material sedimented in a marine bay. J. Fish. Res. Bd. Can., *35,* 1614–1620.

Walsh, J. J. and S. O. Howe. 1976. Protein from the sea: a comparison of the simulated nitrogen and carbon productivity of the Peru upwelling system, *in* Systems Analysis and Simulation in Ecology, Volume 4, B. C. Patten, ed., Academic Press, 593 pp.

Wakeham, S. G., J. W. Farrington, R. B. Gagosian, C. Lee, H. DeBaar, G. E. Nigrelli, B. W. Tripp, S. O. Smith and N. M. Frew. 1980. Fluxes of organic matter from a sediment trap experiment in the equatorial Atlantic Ocean. Nature, *286,* 798–800.

Whelan, J. K. 1977. Amino acids in a surface sediment core of the Atlantic abyssal plain. Geochim. Cosmochim. Acta, *41,* 803–810.

Wiebe, P. H., S. H. Boyd and C. Winget. 1976. Particulate matter sinking to the deep-sea floor at 2000 m in the Tongue of the Ocean, Bahamas, with a description of a new sedimentation trap. J. Mar Res, *34,* 341–354

Williams, P. J. LeB., T. Berman and O. Holm-Hansen. 1976. Amino acid uptake and respiration by marine heterotrophs. Mar. Biol., *35,* 41–47.

Zuta, S. and O. Guillen. 1970. Oceanographia de las aguas costeras del Peru. Boletin Instituto del Mar del Peru, *2,* 157–324.

Zuta, S., T. Rivera and A. Bustamente. 1978. Hydrologic aspects of the main upwelling areas off Peru, *in* Upwelling Ecosystems, R. Boje and M. Tomczak, eds., Springer-Verlag, 303 pp.

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