Ultimate Biodegradation Studies of α-Olefin Sulfonates[1]

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ABSTRACT

Single carbon cut α-olefin sulfonates (AOS) having 12, 14, 16 and 18 carbon chain lengths and several of their blends were prepared from high-quality α-olefins by continuous SO_3 sulfonation in a laboratory falling film reactor. The ultimate biodegradability of these products was studied using a modified shake flask procedure with CO_2 evolution as the major biodegradability criterion. For comparison, commercial samples of a modified Ziegler-based AOS, linear alkylbenzene sulfonates (LAS), and an alcohol ethoxysulfate (AEOS) were included. The results showed the AOS products biodegraded to CO_2 more completely than LAS and slightly less extensively than AEOS. CO_2 evolution decreased slightly in amount and rate as AOS carbon chain length increased in the C_{14} to C_{18} range.

INTRODUCTION

α-Olefin sulfonates (AOS) have been formulated into a number of detergent products over the past 10 years. They have been finding use in light-duty liquid detergents and shampoos where they exhibit high foaming characteristics, mildness, and cost/performance advantages. Laboratory screening studies (1-4) have also shown AOS to be particularly promising in heavy-duty laundry formulations. In these applications, AOS demonstrates better foaming characteristics and less sensitivity to water hardness than linear alkylbenzenesulfonates (LAS).

AOS is produced from linear detergent range α-olefins by sulfonation followed by hydrolysis (5). Olefin feedstock has originated from 2 routes; thermal wax cracking and Ziegler polymerization of ethylene. Since 1977, an additional 140 million lb of detergent range (C_6-C_{20}) linear α-olefins derived from ethylene has become available via new oligomerization technology. The higher purity of ethylene-derived olefins makes them prime candidates for conversion to AOS and other derivatives.

From a biodegradability viewpoint, AOS may be considered to represent a third generation in the evolution of sulfonate surfactants. The first, tetrapropylene-derived alkylbenzenesulfonates, were poorly biodegradable and find less extensive use today. The second is alkylate-based LAS which is much more biodegradable and is the current workhouse of anionic surfactants. The relatively few biodegradation studies reported for AOS indicate that is is more rapidly and completely biodegradable than sulfonates such as LAS which contain an aromatic ring. In several of these studies, biodegradation criteria such as surface tension (4) and methylene blue active substance (MBAS) colorimetry (2,3,6) showed AOS to be slightly more biodegradable than LAS. However, a molecule can undergo primary biodegradation—loss of properties exhibited by the molecule in an undegraded state—yet leave large quantities of partially degraded material which resist ultimate biodegradation to CO_2, water and inorganic salts. More recent studies in which the disappearance of dissolved organic carbon (DOC) was measured in river dieaway (7) and shake culture (8) tests showed AOS to be considerably more biodegradable than LAS. Determination of AOS biodegradability by CO_2 evolution has not previously been reported. However, CO_2 evolution criteria for ultimate biodegradability of other surfactants have been recently reported by Sturm (9) and Gledhill (10). CO_2 evolution should be the preferred method over DOC because DOC results may be confused by adsorption of a starting material and/or metabolites on bacterial colonies.

This report covers a study of AOS biodegradation in which CO_2 evolution was used as the major criterion of biodegradability.

TABLE I

Products Used in AOS Ultimate Biodegradation Study

Product	Source and/or composition	% (wt) Active matter
C_{12} AOS	Lab-sulfonated pilot plant olefins[a]	23
C_{14} AOS	Lab-sulfonated pilot plant olefins[a]	33
C_{16} AOS	Lab-sulfonated pilot plant olefins[a]	36
C_{18} AOS	Lab-sulfonated pilot plant olefins[a]	32
C_{14}/C_{16} AOS	65/35 blend of C_{14}/C_{16} AOS[b]	35
$C_{14}/C_{16}/C_{18}$ AOS	20/40/40 blend of $C_{14}/C_{16}/C_{18}$ AOS[b]	37
C_{14}/C_{16} AOS (modified Ziegler)	Commercially sulfonated 65/35 blend of C_{14}/C_{16} olefins[c]	38
$C_{12\text{-}15}$ AEOS	$C_{13.2}$ average, 3 EO average[d]	60
C_{12} LAS	Soap and Detergent Association; blend of 3 commercial samples of C_{12} LAS	39
C_{13} LAS	Soap and Detergent Association; blend of 2 commercial samples of C_{13} LAS	48
Dextrose	Matheson, Coleman, and Bell	100

[a] NEODENE® α-olefins; Shell Chemical Company.

[b] Prepared from NEODENE α-olefins.

[c] C_{14}/C_{16} α-olefin blend; Ethyl Corporation.

[d] NEODOL® 25-3S; Shell Chemical Company.

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MATERIAL AND METHODS

Surfactants used in this study are shown in Table I. AOS samples were derived from single carbon cut pilot plant, high-quality α-olefins produced from ethylene via new oligomerization technology. Typical composition of these olefins is compared with Ziegler-derived olefins in Table II. Preparation was by conventional continuous SO_3 sulfonation in a falling film reactor, followed by neutralization, hydrolysis and hypochlorite bleaching (5). The AOS products contained ca. 50% alkene sulfonates and 50% hydroxyalkane sulfonates. $C_{14\text{-}16}$ and $C_{14\text{-}18}$ AOS blends were prepared from the single carbon cut AOS products. For comparison, a $C_{14\text{-}16}$ AOS blend derived from olefins produced in a modified Ziegler process, $C_{12\text{-}15}$ alcohol ethoxysulfate (AEOS), C_{12} LAS, and C_{13} LAS were included in the study. The C_{12} LAS and C_{13} LAS were derived from linear alkylbenzene (LAB) blends containing mostly C_{10} through C_{14} alkyl chain lengths. The 2-phenyl content of the LAB blends was 23% for both the C_{12} and C_{13} LAS.

Dextrose was included in this study as a positive biodegradability standard.

As the surfactants biodegraded, the amount of evolved CO_2, trapped as $BaCO_3$, was determined by titrating the entire charge of $Ba(OH)_2$ with 0.1 N HCl to the phenolphthalein end-point.

Primary biodegradation was determined by measuring residual surfactant using the standard MBAS colorimetric procedure (11). To avoid sample degradation during storage before analysis, formaldehyde was added as a preservative at a volume of 1%.

Dissolved organic carbon (DOC) was determined using an Oceanography Model 0524B Total Carbon System on supernatant solutions taken from samples which had been centrifuged at 18,000 rpm for 20 min. For these samples, $HgCl_2$ at 50 mg/L was used as the preservative agent.

Benzene ring degradation of the LAS materials was determined by monitoring the intense ring absorption band in the UV at 223 nm following the procedure of Swisher (12). A Carey Model 15 spectrophotometer was used.

The shake-flask CO_2-evolution test system as described by Gledhill (10) was used to assess the complete mineralization of the surfactants to CO_2, water and inorganic salts. A minor change in reactor vessel design was incorporated to facilitate experimental work. Instead of the prescribed 2-L Erlenmeyer flask, a modified 1-L flask with a 10-in. extended neck (Fig. 1) was used. The modified vessel provided sufficient oxygen gas cap volume for complete conversion of the surfactant to CO_2, thereby permitting the use of 24 flasks on the platform of a gyratory shaker. These changes enabled us to test all of the surfactants in duplicate in one series of experiments (24 test units) using a common acclimated inoculum.

Acclimation of microorganisms to the test compound was accomplished by inoculating a nutrients-supplemented (Difco vitamin-free casamino acids and yeast extract) minimal salts-vitamin (MSV) solution (10) with 5% by vol of unchlorinated, secondary municipal wastewater effluent from the Houston West District Sewage Treatment Plant. Acclimated cultures were prepared for each test compound by incremental addition (10 mg/L on day 0, 20 mg/L on day 7, and 10 mg/L on day 11) during a 14-day incubation period at room temperature in the dark and under quiescent conditions. On the 14th day, the acclimated inocula were pooled and 5 vol of the composite inocula were mixed with 1 vol of fresh secondary wastewater effluent to form the inoculum used for the subsequent biodegradation experiments.

TABLE II

Typical Composition of High Quality Ethylene-Based α-Olefins

	New technology[a] % (wt)	Ziegler % (wt)	Modified Ziegler % (wt)
Linear α-olefins	96	94	85
Branched olefins[b]	2	4	10
Internal olefins[c]	2	1	5
Paraffins	< 0.2	< 1.5	< 0.5

[a] NEODENE® α-olefins, Shell Chemical Company.

[b] Mainly vinylidenes, 2-ethyl and 1-butyl α-olefins.

[c] Mainly *cis*- and *trans*-2-olefins.

For the biodegradation test, the shake-flask CO_2-evolution test unit was charged with 60 mL of the freshly prepared, acclimated inoculum and 440 mL of MSV solution. The test compound was added to obtain a surfactant concentration of 30 mg/L (basis active matter). An automatic 10-mL pipet dispenser was used to charge a constant vol of 0.2 N $Ba(OH)_2$ solution into the center reservoir of the test unit to absorb the evolved CO_2. To provide sufficient oxygen for complete surfactant oxidation, the system was sparged with 70% vol O_2-N_2 gas. The unit was sealed, wrapped with aluminum foil to minimize algal growth, and shaken at 150 rpm at room temperature (24 ± 1 C) for 30 days.

Biodegradation progress was monitored by sampling the reaction media and removing the entire charge of $Ba(OH)_2$ for analysis on days 1, 3, 7, 14, 21, 28 and 30. After sam-

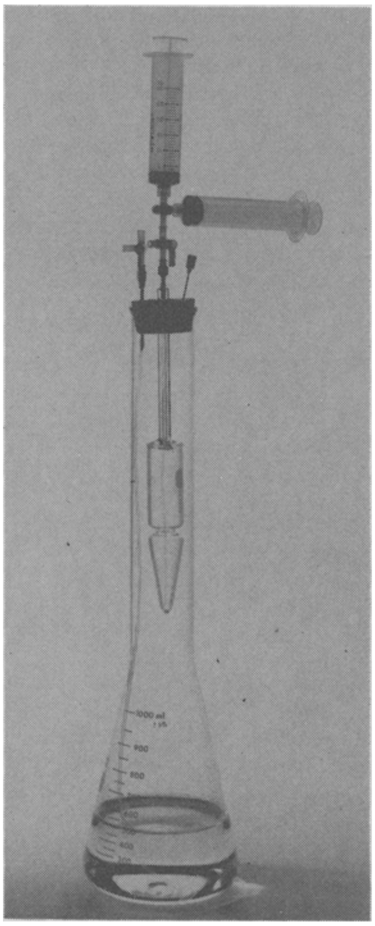


FIG. 1. Modified shake flask with CO_2 absorber and sampling tubes in place.

pling, fresh $Ba(OH)_2$ was charged into the reservoir, and the system sparged with 70% O_2-N_2 gas prior to continuation of the test. On the day prior to the end of the test, 3 mL of 20% H_2SO_4 was added to each medium to convert the carbonates to CO_2.

Along with the test compounds, duplicate control blank runs were included which contained only inoculum and MSV media. The results from analysis by methylene blue active substance (MBAS) or evolved CO_2 of these controls were subtracted from the corresponding values of the test compound. The net result is the measure of surfactant biodegradation.

RESULTS AND DISCUSSION

Ultimate Biodegradation

Percentage biodegradability as determined from CO_2 evolution data is summarized in Figures 2-5. The vertical bars in the figures represent the range of values in testing replicates of each compound. Values of 80 and 75% mineralization of dextrose to CO_2 occurred. In all cases, the rate of evolution reached a maximum by the third day. Carbon chain length of the AOS was shown to affect its biodegradability. Although the C_{12} AOS degraded similarly to the C_{14} AOS, increasing the alkyl chain length from C_{14} to C_{18} decreased the rate and the amount of evolved CO_2. The degree of ultimate biodegradation also decreased with increasing carbon chain length (Fig. 4).

The AOS blends showed behavior comparable to their corresponding monocarbon cuts (Fig. 3). The effect of carbon chain length on biodegradability can also be seen with C_{14-16} AOS biodegrading to a greater extent than C_{14-18} AOS (Fig. 4).

In general, the Ziegler-derived C_{14-16} AOS blend biodegraded similarly to the C_{14-16} AOS blend prepared from olefins via new non-Ziegler technology.

The C_{12-15} AEOS sample was found to biodegrade faster and more extensively than any of the AOS materials in this series (Fig. 3). Interesting is that this surfactant was observed to begin degrading to CO_2 during the first day of the test, whereas the AOS products required a slightly longer induction period. The ease of biodegradability of AEOS is further demonstrated by the 75% of theoretical CO_2 production achieved compared to 66% for the most degraded AOS sample (C_{12} AOS). On this basis, the biodegra-

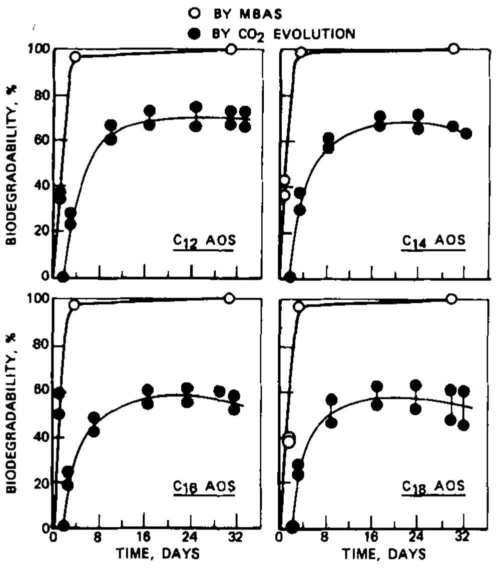


FIG. 2. Biodegradability of monocarbon cut AOS.

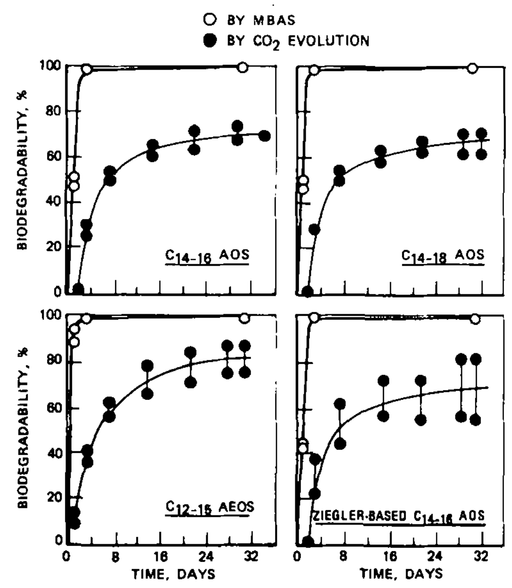


FIG. 3. Biodegradability of AOS blends compared to a Ziegler-based C_{14-16} AOS blend and C_{12-15} alcohol ethoxysulfate.

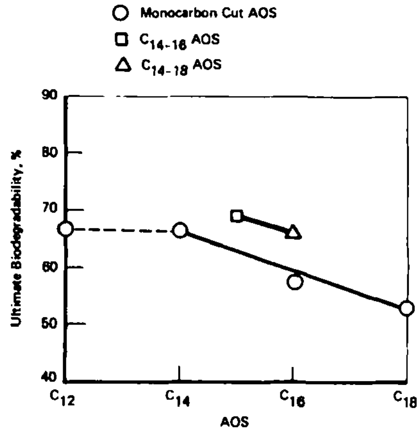


FIG. 4. Effect of carbon chain length on AOS ultimate biodegradability.

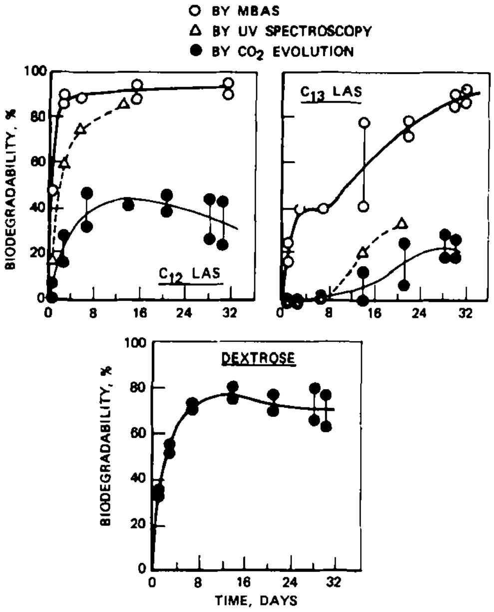


FIG. 5. Ultimate biodegradation of commercial LAS and dextrose.

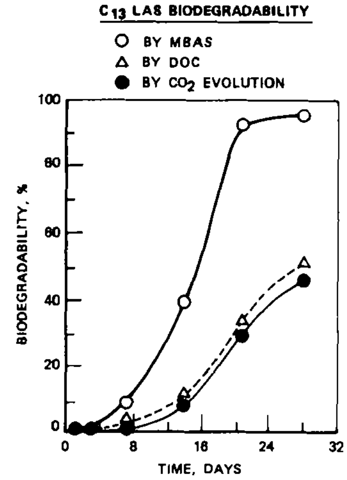


FIG. 6. Biodegradability of C_{13} LAS measured by MBAS, DOC, CO_2 evolution.

dation of AEOS is comparable to the 78% biodegradation obtained with dextrose (Fig. 5).

It is notable that the monocarbon cut AOS compounds required significantly less time to attain their maximal extent of biodegradability than any of the AOS blends (14 vs 24 days). This may be due to such factors as population and types of microorganisms capable of metabolizing the test compound and endogenous respiration. The observed apparent decline in cumulative CO_2 production of the monocarbon cut AOS, LAS, and dextrose compounds after attaining their maximal level of biodegradation can also be attributed to these same factors affecting the blank control samples. As stated earlier, test compound biodegradation is determined by the difference in amount of CO_2 evolved between the blank control and the test sample. In the latter stages of the experiment, CO_2 evolution from the blanks significantly affected results.

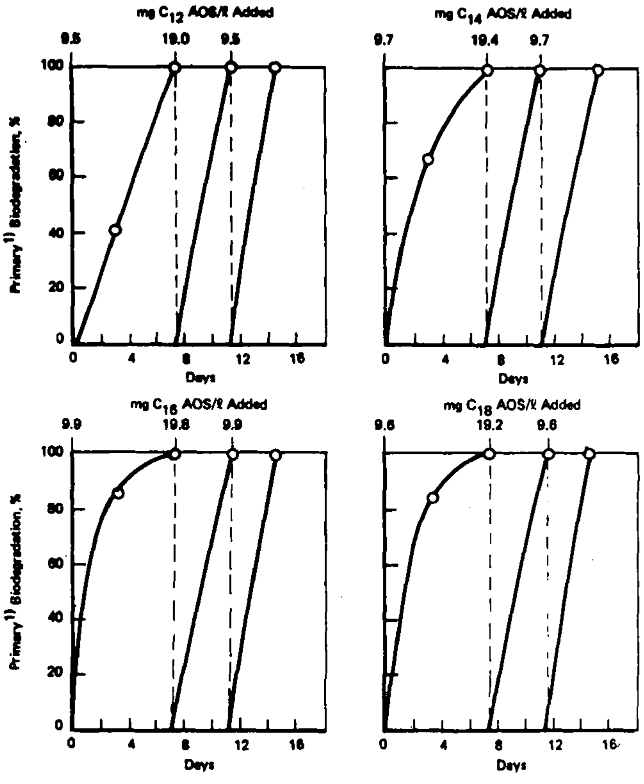
The 2 commercial LAS samples were found to be the least biodegradable substrates in this study. The C_{13} LAS sample produced significantly less CO_2 than the C_{12} LAS. These results are in line with previous studies (10,13) which show an inhibiting effect on increasing alkyl chain length on commercial LAS biodegradability. In this work, alkyl chain length affected the biodegradability of LAS more severely than AOS.

Loss of aromaticity is also shown for the LAS samples in Figure 5. The data indicate considerable degradation of the benzene ring in C_{12} LAS and much less in C_{13} LAS. In addition, capability of inoculum to degrade the C_{13} LAS benzene ring was not attained until after the seventh day. Aromatic disappearance in LAS biodegradation studies have been reported as high by some workers (12,14) and low by others (15). The use of different test conditions and/or LAS substrates may have contributed to these disparate results (16).

Primary Biodegradation

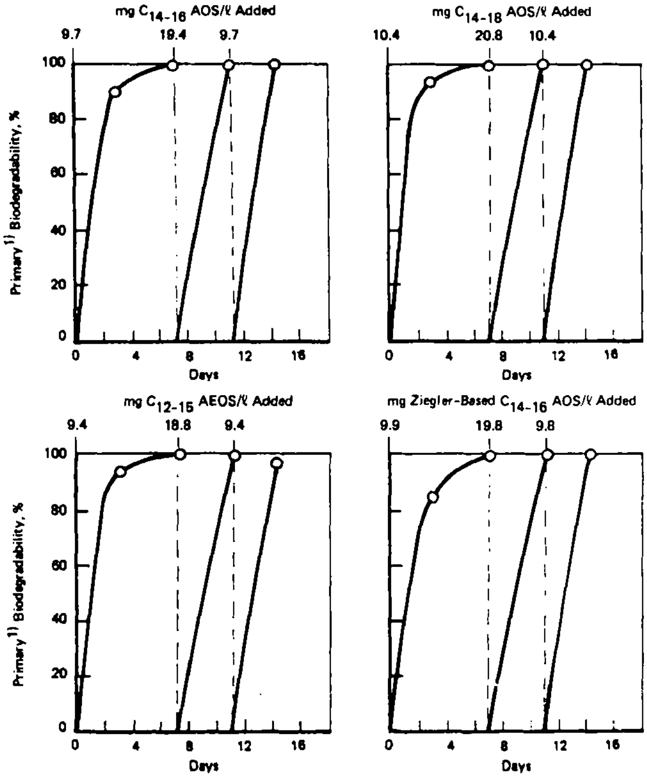
The primary biodegradability of the anionic surfactants tested as measured by MBAS indicate 98-99% disappearance of AOS and AEOS starting materials (Figs. 2 and 3) by day 3. In contrast to these results, C_{12} and C_{13} LAS, in particular, degraded at significantly slower rates (Fig. 5).

The MBAS results are unrealistic as indices of ultimate biodegradation, particularly for the LAS samples for which the difference between MBAS and CO_2 evolution data indicate that considerably higher levels of LAS metabolites persist compared to AOS. In a separate study involving C_{13} LAS, biodegradation was evaluated by DOC, CO_2 evolution



1) Basis MBAS Analysis

FIG. 7. Microbial acclimation of monocarbon cut AOS.



1) Basis MBAS Analysis

FIG. 8. Microbial acclimation of AOS blends and C_{12-15} alcohol ethoxysulfate.

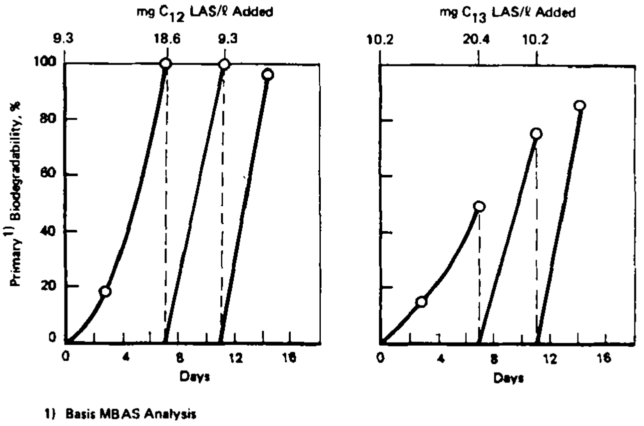


FIG. 9. Microbial acclimation of commercial LAS.

and MBAS measurements (Fig. 6). The much higher levels of biodegradation as measured by MBAS indicate CO_2 and DOC data to be considerably more realistic in defining the extent of ultimate biodegradability.

Acclimation Studies

Microbial acclimation to the test compounds was done via incremental addition of the surfactants under quiescent conditions. To observe whether this environment would exhibit biodegradation characteristics significantly different from the conditions of the shake flask test, the progress of surfactant disappearance was also monitored. In general, the MBAS results showed inoculum acclimation to the AOS and AEOS was achieved at a faster rate than the LAS surfactants. This is noticeably evident during the first incremental surfactant addition of 10 mg/L (Figs. 7-9). The apparent slightly slower rate of biodegradation of the C_{12} and C_{14} AOS in comparison to the rest of the AOS products for the same time frame may be due to greater adsorbance of C_{16} and C_{18} AOS on bacterial inoculum. Separate control experiments of a centrifuged inoculum residue confirmed the presence of adsorbed surfactant based on MBAS analysis. In later stages of the experiment, the surfactants were shown to desorb from the biota.

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