Biodegradation rates of crude oil in seawater

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ABSTRACT: Measurements of the rate of biodegradation of crude oil in seawater in laboratory, mesocosm, and field systems from 16 published reports were reviewed and compared. Volumetric biodegradation rates range widely from approximately 0.01 to 1 000 gC/m^3-d. Laboratory studies report rates at the higher end of this range, while field and mesocosm studies, of which there are fewer, suggest much lower rates ranging from 0.01 to 0.3 gC/m^3-d. Possible explanations for the discrepancy between measurements made at different scales are differences in oil concentration and in mixing energy. When temperature-scaled degradation rates from all systems are plotted versus initial oil concentration on a log-log scale, the data are approximately linear ($r^2 = 0.86$) over several orders of magnitude. The slope of the regressed line is near 1, indicating that the process can be interpreted as first order with respect to oil concentration. The half-life for biodegradation is estimated to be approximately two months at 20°C. This analysis suggests that crude oil biodegradation in seawater is relatively slow and indicates that further research is required to bridge the gap between laboratory and field systems. *Water Environ. Res.*, **65,** 845 (1993).

KEYWORDS: biodegradation, oil, seawater, temperature.

To what extent can biodegradation influence the fate of crude oil spilled at sea? The widespread presence of microorganisms capable of degrading petroleum hydrocarbons highlights the potential for biodegradation, but the practical impact of biodegradation, as manifested by the overall process rate, remains difficult to gauge. This article reviews published measurements of the rate of crude oil degradation in seawater. One objective of this study has been to update previous citations of the order of magnitude of oil degradation rates, many of which can be traced back to calculations made by Claude ZoBell nearly thirty years ago (1964). A second objective was to compare laboratory measurements of biodegradation rate with field or mesocosm measurements. Such analysis of rate information is essential in evaluating engineering measures to enhance biodegradation rates, and can aid in identifying research needs.

Measurements of marine oil biodegradation rates have been compiled in one previous review (National Academy of Sciences, 1985). We drew on this list as a starting point, adding to it to approximately double the number of cited experimental measurements. In addition, we have correlated the rate of degradation with the initial concentration of oil to gain information about the reaction order and the time scale for biodegradation.

Methods

Measurements of oil biodegradation rates (Table 1) were selected based on the following criteria: crude oil used as the sole carbon source, experiments conducted in seawater or artificial seawater, temperature and initial oil concentration reported, and sufficient quantitative data available to calculate a degradation rate in consistent units. The rates are given in units of grams of carbon consumed per cubic meter per day (gC/m^3-d). To convert values reported in different units in the literature, the following conversion factors have been applied, where experiment-specific data were lacking: 0.85 g carbon/g petroleum hydrocarbons (Purdy, 1958); 0.7 g carbon/g BOD (McCarty, 1975); and 0.5 g carbon/g biomass (Roels, 1983). Investigations using marine sediments or beach material, or those conducted with single hydrocarbon species, were excluded.

The particulars of each data set are also noted in the table. Many of the measurements were made with weathered or topped crude oils. Supplemental nitrogen and phosphorus were added in most of the laboratory experiments. We have classified the experiments into one of four categories depending on whether the measurements were made in a laboratory or in a field/mesocosm system, and whether or not nutrients were added. Laboratory and mesocosm experimental systems were distinguished by the degree of mixing and aeration. Laboratory measurements used agitated shake flasks, sparged vessels, or similar apparatus with vigorous mixing and aeration, whereas field or mesocosm experiments relied on natural circulation or gentle mixing. Most of the experiments included explicit controls for abiotic loss of hydrocarbons.

Results

Measured rates of crude oil biodegradation in seawater vary over several orders-of-magnitude, from approximately 0.01 to 1 000 gC/m^3-d. Laboratory measured rates range from approximately 1 to 1 000 gC/m^3-d, while field or mesocosm measurements range from about 0.01 to somewhat less than 1 gC/m^3-d. To further compare these data, which were measured at temperatures ranging from 1 to 32°C, the rates have been scaled to a reference temperature of 20°C using a Q_{10} value of 2.7 (Gibbs *et al.*, 1975). The temperature corrected rates are plotted as a function of initial oil concentration in Figure 1. This analysis uses a log-log transformation to estimate the reaction order and the first-order rate coefficient (that is, the exponent n and the parameter k in the equation $R = -kC^n$). The data are approximately linear over several orders of magnitude ($r^2 = 0.86$), with a slope of 1.1 (standard error 0.1), suggesting that the process can be interpreted as first-order with respect to oil concentration. The first-order time constant for this data set, as given by the least squares estimator of $\ln(k)$ with $n = 1$ is 0.011 d^{-1} ($+0.004$, -0.003 d^{-1}). This is equivalent to a half-life of roughly two months. The results of this analysis are relatively insensitive to the choice of Q_{10}; changing Q_{10} from 2.0 to 3.0 changed the estimated parameters and the correlation coefficient by less than 10%.

Table 1—Measured biodegradation rates of crude oil in seawater.

Initial oil concentration g/m³	Temperature °C	Volumetric degradation rate, gC/m³ · d	Volumetric degradation rate at 20°C, gC/m³ · d	Experiment type,[a] weathered?[b]	Reference
6 970	28	271	122	A, N	(Atlas and Bartha, 1972a, 1972b, 1973a)
8 800	15	34.3	56.4	A, Y	(Chianelli, *et al.*, 1990)
308	20	13.2	13.2	A, N	(Kator, *et al.*, 1971)
4 270	20	625	625	A, Y	(Ballerinin, *et al.*, 1981)
6 880	28	845	382	A, N	(Dibble and Bartha, 1976)
792	25	9.5	5.78	A, Y	(Hughes and McKenzie, 1975)
293	14	0.563	1.02	A, Y	(Gibbs, 1975)
880	15	2.38	3.90	A, Y	(Venosa, *et al.*, 1991)
417	32	66.6	20.2	A, N	(Horowitz, *et al.*, 1975)
417	29	24.8	10.2	A, N	(Horowitz, *et al.*, 1975)
697	15	4.65	7.63	A, N	(Walker and Colwell, 1976)
6 970	5	16.2	71.8	A, N	(Atlas and Bartha, 1972c)
61.6	30	1.85	0.684	A, Y	(Bridie and Bos, 1971)
61.6	30	0.246	0.091 3	B, Y	(Bridie and Bos, 1971)
4.49	18	0.063 4	0.077 3	C, N	(Atlas and Bartha, 1973b)
4.49	18	0.010 6	0.012 9	D, N	(Atlas and Bartha, 1973b)
68.6	1	0.015 0	0.098 7	D, N	(Laake, *et al.*, 1984)
1.58	10	0.016 7	0.045 1	D, Y	(Aminot, 1981)
42.2	10	0.091 5	0.247	D, N	(Robertson, *et al.*, 1973)

[a] A—laboratory with nutrients; B—laboratory without nutrients; C—field or mesocosm with nutrients; D—field or mesocosm without nutrients.
[b] Y—yes; N—no.

Discussion

There are several difficulties with extrapolating these conclusions regarding degradation kinetics to the marine environment in general. Most of the experiments were conducted in laboratory systems using aerated vessels with high mixing energies, and supplemented with nutrients. Although these experiments can provide evidence of the susceptibility to and requirements for degradation, it is unclear whether rate information from this type of system is applicable to understanding biodegradation as it proceeds in the environment. Another problem with the analysis presented here is that a single rate has been ascribed to what is in reality a complex mixture of chemicals that degrade at different rates. In virtually all of the experiments analyzed, some oil remained at the end of the experiment, a residue that was either recalcitrant or that degraded considerably more slowly than the bulk of the oil. The analysis also does not attempt to account for differences between crude oils. In spite of these difficulties, the derived time scale may be useful in that it constitutes an upper bound on the attainable rate of oil biodegradation in seawater.

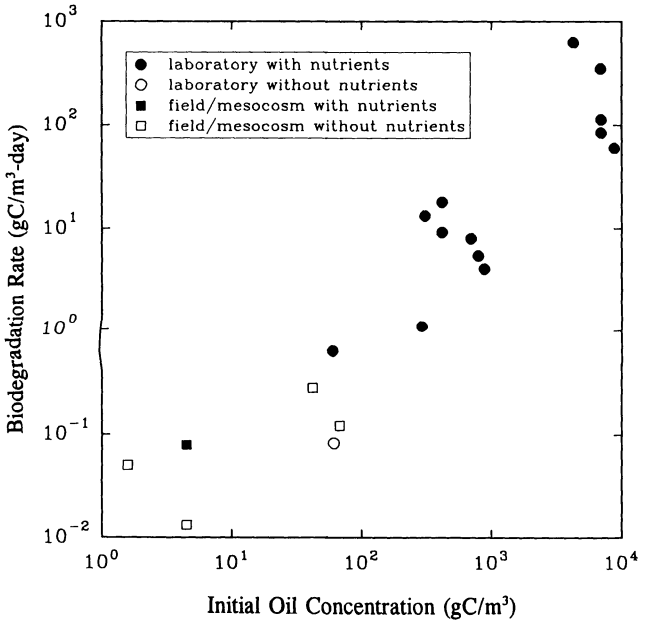

Figure 1—Concentration dependence of crude oil biodegradation rate.

A more realistic estimate of the actual rate of crude oil removal by biodegradation in the marine environment can be made from the field and mesocosm measurements. These experiments suggest degradation rates in the range of 0.01 to 0.3 gC/m³-d at 20°C. This range of rates is similar to that offered by others (Hughes and McKenzie, 1975; National Academy of Sciences, 1985). Attempts to calculate environmental biodegradation rates have also led to values in this range. Assuming a bacterial concentration, ZoBell calculated an oil degradation rate equivalent to approximately 0.5 gC/m³-d at 20°C (1964). This frequently cited value, while not unreasonable, appears to be at the ceiling of environmentally observed rates. Gibbs calculated rates equivalent to 0.15 gC/m³-d at 20°C by assuming that the overall rate was limited by nitrogen cycling (1975).

Biodegradation rates can be placed in perspective by comparing them to other microbiological process rates. The highest volumetric reaction rates for microbiological processes have been achieved in bioreactors. One such application with particular

relevance to oil spill remediation is the production of microbial protein from petroleum. Volumetric productivities of about 30 000 gC/m^3-d can be attained in this process (Fong, 1975; Kanazawa, 1975). Another well-established technological application of microbiological processes is for the treatment of domestic or industrial wastewater. Volumetric reaction rates achieved with biological wastewater treatment systems range from approximately 10 to 10 000 gC/m^3-d (Metcalf & Eddy, Inc., 1979). Marine bacterial production rates, which reflect the natural flow of carbon through marine bacteria, range from .02 to .04 gC/m^3-d (White *et al.*, 1991). Observed environmental biodegradation rates of crude oil in seawater lie at the lower end of this spectrum of microbiological process rates, and are apparently of the same order of magnitude as background carbon cycling through marine bacteria. This is not a particularly surprising observation, but it does invite consideration of engineering measures to enhance biodegradation rates.

From an engineering perspective, one of the variables likely to be important in determining the rate of biodegradation is the mixing energy of the system. Mixing delivers oxygen to the hydrocarbon-degrading microorganisms and increases the surface area of the oil-water interface by dispersing the hydrocarbon. Mixing has been poorly characterized in the experimental work performed to-date. Differences in the degree of mixing may be responsible for some of the unexplained variability in the data in Figure 1. The influence of mixing energy on biodegradation rates deserves closer attention in future experimental work.

Summary and Conclusions

In conclusion, measurements of the rate of crude oil biodegradation in seawater were reviewed and found to range widely from approximately 0.01 to 1 000 gC/m^3-d. Laboratory studies invariably yield rates at the higher end of this range, while field and mesocosm studies, of which there are fewer, suggest much lower rates. The data collectively suggest a first-order dependence of degradation rate on oil concentration and a half-life of approximately two months at 20°C. Because laboratory studies dominate the data set, this time scale for crude oil biodegradation is best interpreted as an upper bound estimate. Actual crude oil biodegradation rates in the marine environment, as observed in field and mesocosm studies, range from approximately 0.01 to 0.3 gC/m^3-d. This analysis highlights the discrepancy of at least an order of magnitude between rates measured in the laboratory and those measured in mesocosm or field experiments, and indicates that further research is required to bridge this gap. Experiments in controlled mesocosms, conducted under conditions of mixing and nutrient supply that more realistically reflect actual environmental conditions, would seem to be in order.

Acknowledgments

Credits. This study was funded through the Bechtel Technical Grant Program. Mr. Stewart sincerely acknowledges partial support from the Center for Biofilm Engineering (cooperative agreement ECD-8907039 between the National Science Foundation and Montana State University) and from the Center Industrial Associates. The authors thank Martin Hamilton for statistical advice.

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Submitted for publication May 11, 1992; revised manuscript submitted November 12, 1992; accepted for publication January 29, 1993. The deadline for discussions of this paper is March 15, 1994. Discussions should be submitted to the Executive Editor. The authors will be invited to prepare a single Closure for all discussions received before that date.

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