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Response to Comment on “Physical Model for the Decay and Preservation of Marine Organic Carbon”

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Fast enzyme deactivation rates are not required by our physical model of organic matter decay. Instead, low effective diffusivities arising from sorption of enzymes and physical protection by minerals are sufficient. Our model predicts observed temporal trends in organic-matter decay rather than specific rate constants. Existing statistical models of intrinsic reactivity explain observed trends empirically but not theoretically.

Our physical model (1) for the decay of marine organic carbon assumes that organic matter differs only in its accessibility to microbial degradation but not its intrinsic reactivity. The model additionally assumes that a characteristic distance r_b between microbes is much greater than the characteristic distance β^{-1} that an enzyme diffuses over a typical enzyme lifetime α^{-1} . In other words, we require that the dimensionless quantity $R \equiv \beta r_b \gg 1$, where $\beta = (\alpha \bar{D})^{1/2}$ and \bar{D} is an effective diffusivity. Our fits to data suggest that $R \cong 5.6$.

The issue of inferred enzyme deactivation rates is more appropriately examined in terms of the length-scale ratio R . When $R \gg 1$, steady-state spatial distributions of active enzymes are much more concentrated in the immediate vicinity of microbes than away from them. When $R \ll 1$, enzymes remain functional over a sufficiently long period of time such that steady-state diffusive gradients should be negligible. Recast in these terms, the argument of Boudreau *et al.* (2) suggests that typical known values of the quantities α , \bar{D} , and r_b are inconsistent with $R \gg 1$, by at least two orders of magnitude. Their numbers instead suggest a well-mixed regime in which physical accessibility to enzymes is spatially homogeneous.

In addressing this issue in our paper (1), we hypothesized that $R = (\alpha \bar{D})^{1/2} r_b \gg 1$ might derive from an effective diffusivity \bar{D} that is much less than the bare diffusivity D cited by Boudreau *et al.* We suggested two mechanisms: shielding of organic matter in clay-rich aggregates and sorption of enzymes to surfaces.

Sorption retards diffusive transport. A standard calculation (3) using characteristic sorption parameters (4) shows that \bar{D} decreases by about two orders of magnitude. If sorbed enzymes deactivate

at the same constant rate α as in solution, R then increases by a factor of about 10. In the extreme case of deactivation only and always upon sorption, a purely geometric calculation (5) based on a porosity of 0.8 and a typical specific surface area of 10^5 cm^{-1} (4) yields $R \sim 100$. If, however, enzymes do not deactivate on surfaces (6), then α decreases with \bar{D} and there is no effect on R .

Shielding, proposed earlier by Mayer (7), implies a patchy distribution of organic matter that is to some extent physically protected by minerals. Consideration of diffusive transport in tight percolation networks (8) then provides a natural mechanism for locally driving \bar{D} orders of magnitude below D , potentially increasing R by up to an order of magnitude or more.

There are also questions concerning whether the relevant r_b should be obtained from surface sediments or, for example, depths of meters. Because microbial populations decrease roughly like the square root of depth (9), the deeper case would imply increasing r_b (and R) by about a half-order of magnitude. Finally, we note that the longer enzyme lifetimes cited by Boudreau *et al.* (2) require sorption to surfaces, which, as stated above, results in decreasing \bar{D} .

These considerations do not apply to well-mixed laboratory experiments. However, the observation that a single rate constant measured in a well-mixed experiment without sediment matches a rate constant measured in a different experiment with sediment does not invalidate our model. Instead it suggests, as we state in (1), that “both chemical and physical mechanisms must play a role” in the degradation of organic matter. Our study shows how reasonable physical mechanisms can give rise to observed temporal trends without the invocation of intrinsic heterogeneity. We cannot rule out, however, the possibility that our reactivity distribution, which we derived from physical principles, derives instead from biochemical mechanisms, ecological interactions, or both.

Indeed, a wide class of statistical mixture models can give rise to the Middelburg (10) scaling relation $K(t) \sim b/t$, where K is the effective time-dependent reaction rate and the prefactor

$b \cong 0.2$. Boudreau *et al.* (2) provide the example of a gamma distribution. They show that beyond a transient time a , $K(t) \propto v/t$, where a and $v > 0$ are parameters of the gamma distribution. This result, obtained earlier by Tarutis (11), can be generalized. One need only assume that the initial distribution $g(k,0)$ has an asymptotic expansion (12) for $k \rightarrow 0$ with leading order behavior $g(k,0) \sim k^{\nu-1}$. Then the application of Watson's lemma (12) to the Laplace integrals of the reactive-continuum model (13) yields $g(t) \sim t^{-\nu}$ and $K(t) \sim v/t$ in the long-time limit. Thus, at long times, the Middelburg prefactor b may be identified with the exponent ν .

However, this asymptotic analysis can only be regarded as a “prediction” of the Middelburg scaling law if $\nu \cong 0.2$ is itself predicted and the asymptotic scaling occurs at relevant finite times. The analysis of Boudreau *et al.* (2) does not satisfy this requirement. Instead, it shows that the Middelburg scaling is consistent with a particular choice of $g(k,0)$ chosen for its fit to a single experiment.

Our point is not that our physical model fits data better than the statistical model of Boudreau *et al.* The principal value of our work lies instead in the predictions it makes for the extreme case of a system in which heterogeneous reaction rates derive purely from physical dynamics. Comparison of these predictions with data then allows, at minimum, an opportunity to reject the physical hypotheses of our model. The reasonably successful fit to the 23 data sets analyzed in (1) does not, however, suggest rejection.

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References and Notes

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