Coastal Acidification by Rivers: A Threat to Shellfish?

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Increasing atmospheric CO₂ is likely to cause a corresponding increase in oceanic acidity by lowering pH by 0.2–0.5 pH units by the end of the 21st century [Royal Society, 2005]. In light of increasing acidity, there are growing concerns about the future health of a variety of marine organisms, particularly shellfish, which in the United States is a $1.6 billion industry.

Shellfish predominantly inhabit coastal regions, and in addition to the projected stress caused by the global trend in ocean acidification, some coastal ecosystems receive persistent or episodic acid inputs as a result of interactions with river water, bottom sediments, or atmospheric deposition of terrigenous materials. Most river plumes are acidic relative to the receiving ocean, and river water is mixed extensively over the continental shelf. Moreover, the chemical nature and magnitude of discharge are changing intermittently cause suboptimal conditions for shellfish development. Better understanding of such processes in a changing world is needed to gauge future biodiversity and help communities manage coastal resources.

Shellfish Growth and Acidic Rivers

To create shell material, many organisms incorporate calcium carbonate (CaCO₃) from dissolved calcium (Ca²⁺) and carbonate ions (CO₃²⁻) through the reaction

\[ \text{CaCO}_3 + \text{CO}_3^{2-} \rightarrow \text{Ca}^{2+} + \text{CaCO}_3 \]

Organisms such as scleractinian corals, shellfish pteropods, and a variety of commercially harvested shellfish use a crystalline form of calcium carbonate called aragonite. Aragonite tends to be mechanically strong, yet it is quite susceptible to corrosion in acidic waters because it is 1.5 times more soluble than calcite, the dominant form of CaCO₃. Increasing acidity drives carbonate equilibrium toward lower CO₃²⁻ concentrations and lowers the saturation index of aragonite (Ω). In simple terms, Ω is a measure of the product of the concentrations of CO₃²⁻ and Ca²⁺ ions relative to the amount of aragonite that can be dissolved at a given temperature, salinity, and pressure. Although an Ω value of 1 represents a saturated state, shelled organisms typically require much higher Ω for optimal growth.

Lowered Ω values naturally occur around most river mouths. Rivers gather runoff from soils within the watershed; these soils typically contain carbonic acid, which is a by-product of organic decomposition.

Shellfish in the Gulf of Maine

Acidic river water mixing into the surface ocean can affect coastal chemistry on broad regional scales to an extent that could inhibit the development of certain shellfish larvae.

In particular, any phenomena that could negatively affect the Gulf of Maine’s $450-million-per-year shellfish industry is a serious concern. To learn more, we investigated the potential threat to the commercially valuable clam Mya arenaria in the western Gulf of Maine. This organism spawns when ocean temperatures reach about 10°C and has a presettlement, planktonic stage of about 21 days in which the organism floats freely in the water. During this stage, the ability to incorporate aragonite from seawater is crucial to survival, with higher rates of calcification translating to higher growth rates and more rapid movement out of the vulnerable planktonic period.

Unfortunately, timing of the early spawn sometimes coincides with maximum river discharge in spring, at which time time larval bivalves may be bathed in estuarine waters with lower than optimal Ω. In our experiments with clam larvae reared for several hours in seawater at varying Ω values, we found that larvae were unable to incorporate aragonite from seawater even under supersaturated conditions of Ω equaling 1.6 (Figure 1). This led to the question of whether such suboptimal conditions occur during periods of high river discharge in the western Gulf of Maine, and if so, how extensive the effect is.

To investigate the existence and prevalence of such suboptimal conditions for shellfish growth, we focused on the discharge plumes

Fig. 1. Laboratory results demonstrating the effect of increased acidification on soft-shelled clam larvae. The increase in alkalinity with time at Ω = 0.5 indicates that shell dissolution is occurring, as the gain in alkalinity of the solution is proportional to the decrease in shell material. Even when seawater is supersaturated at Ω = 1.6, the rate of alkalinity change (CO₃²⁻ uptake) is effectively zero. At Ω = 2.0, the decrease of alkalinity indicates shell formation and growth.

Fig. 2. Mapped Ω for the surface waters of the Kennebec plume and Casco Bay, Gulf of Maine, on 20 June 2005. Contours of Ω = 1.0 (inner) and Ω = 1.6 (outer) are shown as black curves. The 1.6 contour intersects the outer islands and peninsulas of Casco Bay, where the value of the shellfish harvest exceeds $35 million per year. The Kennebec is a moderately sized river system whose average discharge is 438 cubic meters per second.
of the Kennebec River, one of the largest rivers flowing into the Gulf of Maine. During times of high discharge and downwelling (northerly) winds, Kennebec water will enter Casco Bay and mix with waters over its commercially valuable shellfish beds. Water properties in the vicinity of the Kennebec River plume measured on monthly cruises (http://www.cooa.unh.edu/index.jsp) were used to map $\Omega$ for this region (Figure 2).

Through measurements taken from these cruises, we observed episodes of acidic river influx with values of $\Omega$ less than or equal to 1.5, corresponding to the peak spawning period for *Mya arenaria* in the region (Figure 2). We conclude that such events have the potential to adversely affect the survivability and subsequent settlement distribution of soft-shelled clams if they occur during spawning periods.

**Global-Scale Effects?**

Are the conditions observed in the western Gulf of Maine indicative of those found elsewhere on the globe? River discharge mixes with and is broadly distributed in the surface waters of the continental shelf. If the global annual discharge were poured into the ocean to form a 5-meter layer, it would cover an area equivalent to 25% of the continental shelf's surface. Dissolved and particulate constituents in river discharge vary depending on regional climate, geology, land use, residence time, and atmospheric deposition. Climate and river chemistry are the main factors determining $\Omega$, with low temperatures and carbonate favoring lower $\Omega$. For example, rivers that have a combination of cool temperatures, low alkalinity, and high CO$_2$ originating from soil and in-water respiration of organic matter will have particularly low $\Omega$.

Human intervention has profoundly altered global chemical cycles and river chemistry. Many rivers are acidic, and nearly all of the world’s large rivers have $\Omega$ lower than receiving ocean waters. Because of the widespread presence of river water along the coast, it is surprising how little is known about the relationship between discharge and $\Omega$ in coastal waters and about the potential for low $\Omega$ to interfere with early stages of shellfish development.

To consider the potential threat to shellfish on a global scale, we estimated $\Omega$ from the low-salinity region near the river mouth out into the open ocean for several of the world’s major rivers (Figure 3a). The $\Omega$-salinity relationships tend to cluster according to a combination of river chemistry and water temperature. Both polar and tropical rivers enter the ocean at low $\Omega$ because of relatively low Ca$^{2+}$ and CO$_3^{2-}$ concentrations but have different trajectories across the salinity gradient according to the dependence of CaCO$_3$ solubility on temperature. However, rivers with higher Ca$^{2+}$ and CO$_3^{2-}$ concentrations tend to have higher initial $\Omega$. The actual coastal area influenced by a gradient in $\Omega$ is complex and dependent on several factors including discharge, latitude, and buoyancy, as well as wind direction, magnitude, and persistence. The Amazon and Orinoco river plumes, for example, lower $\Omega$ in the waters northeast of South America to an impressive extent (Figure 3b).

It is not known if river-influenced depressions in $\Omega$ represent a substantial stress to aragonite-fixing organisms everywhere. It is likely that many species have developed survival mechanisms, given these conditions have existed throughout time.

However, three issues should be considered, the interactions of which warrant further study of shelled organisms along the global coast. First, the spatial and temporal patterns of global discharge have changed and will continue to do so into the future. Second, the chemical nature of discharge, including the CO$_3^{2-}$ signal, is changing, and third, any lowering of coastal $\Omega$ caused by the first two issues will be exacerbated as atmospheric CO$_2$ increases.

Priority regions for further research are the Arctic and sub-Arctic coastlines, where cool temperatures and low $\Omega$ presently prevail and which are experiencing dramatic increases in river discharge. The combination of these factors could have severe consequences for high-latitude calcifying organisms, particularly shelled pteropods, which contribute to the diet of commercially important species including salmon, herring, cod, and mackerel.

For background on this article’s figures and for more information about how data were collected, please see the electronic supplement to this *Eos* issue (http://www.agu.org/eos_elec/).

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