Discharge-driven harmful algal blooms in the NE Gulf of Mexico

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The state of Alabama (USA) has only 100 km of coastline but has had recurring harmful algal blooms (HABs) at two shallow-water hot-spots. Both are in the same hydrological unit on the eastern margin of Mobile Bay. The first, Weeks Bay, is a sub-estuary on the eastern margin of Mobile Bay and is the site of diverse dinoflagellate blooms that cause hypoxia and fish-kills. The second, the Gulf of Mexico shoreline adjacent to Little Lagoon, a shallow and saline lagoon, is the site of toxic blooms of the diatom *Pseudo-nitzschia* spp. Initiation of both dinoflagellate and diatom blooms is correlated with discharge from the aquifer.

Microalgal community composition appears to be driven by the interaction of temperature and submarine groundwater discharge. Dinoflagellates bloom in Weeks Bay during periods of low discharge in both winter (*Prorocentrum minimum*) and summer (*Karlodinium veneficum*). *Pseudo-nitzschia* spp. bloom predominantly in the spring after periods of high discharge [1], as part of a cohort of diatoms that includes other bloom-forming taxa [2]. Comparison of community composition with physico-chemical characteristics of Little Lagoon showed a very high correlation between the degree of dominance by diatoms and water age (inferred from the excess ^{224}Ra:^{223}Ra ratio) when subsurface resistivity showed that the water table was high. There was no correlation between community indices and water age when the water table was low.

The surficial aquifer is contaminated with very high N (up to c. 5 mM DIN plus DON) and the sediments in Weeks Bay and Little Lagoon have even higher concentrations of both N and P. Although the supply of nutrients by groundwater is important in supporting very dense blooms, the magnitude of discharge is likely as important in structuring the community. The conditions under which both dinoflagellate and diatom blooms occur are consistent with ordination of their niches in terms of habitat productivity and stability [3]. Because global climate change is predicted to alter seasonal patterns of precipitation, hence aquifer discharge, it is likely that the niches for these HAB taxa will expand.

[1] Liefer et al. (2009) *Harmful Algae* **8**: 706-714. [2] MacIntyre et al. (2011) *J. Plankt. Res.* **33**: 273–295. [3] Grime (1977) *Amer. Natur*. **111:** 1169-1194.

Nanodiamonds and carbonaceous grains in Bull Creek Valley, Oklahoma

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Sediments in the Bull Creek Valley document the Pliestocene-Holocene transition, including the period corresponding to the Younger Dryas climate anomaly. Conflicting reports of nanodiamond presence/ absence, spatial/ temporal distribution, and polymorphic phase identification [e.g., 1,2] are perhaps not surprising given the challenges of recovering and identifying such materials within bulk sediments. Nanodiamonds form extraterrestrially; their distribution in Earth sediments may relate to the intensity of extraterrestrial bombardment. It has been suggested that a nanodiamond spike in Younger Dryas strata records an impact event, contributing to cooling on a global to regional scale [1].

For this study, sediments corresponding to alluvial, paleosol, and loess horizons were collected from multiple profiles across the Bull Creek Valley at approximately 10 cm intervals. Carbon dates ranged from ~33,000 years before present to recent. The clay fraction was separated from the bulk soil and then digested by a series of strong acid treatments. Residues were resuspended in ammonium hydroxide and prepared for transmission electron microscopy (TEM) by centrifugation onto grids with carbon support films. Grids were analyzed with TEM, high-resolution TEM (HRTEM), energy-dispersive x-ray analysis (EDS), and electron energy loss spectroscopy (EELS).

Nanodiamonds were identified in multiple horizons, including sediment dated to the Younger Dryas. Individual grains ranged from approximately 3-50 nm, although most grains were 5-10 nm. Most or all grains correspond to the n-diamond polymorph, as suggested by lattice fringe spacings. Lesser amounts of cubic nanodiamonds qwere also tentatively identified. EELS of these particles was consistent with sp^3-bonded carbon. Other micron-scale particles morphologically similar with those previously identified as hexagonal diamond [3] were graphene/graphane mixtures based on electron diffraction and EELS.

[1] Kennett et al. (2009) *Science* **323**, 94. [2] Daulton et al. (2010) *PNAS* **107**, 16043-16047. [2] Kennett et al. (2009) *PNAS* **106**, 12623-12628.