

**Trace Contaminants Association with Colloidal
Macromolecular Organic Matter in Galveston Bay:
Implications for Bioavailability**

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Dr. Peter Santschi, Professor of Oceanography at Texas A&M, has received his PhD in Chemistry from the University of Bern, Switzerland, in 1975. He has extensive experience in Marine Isotope, Trace Element and Natural Organic Matter Geochemistry. He has conducted many scientific studies of transport and speciation of radionuclides, trace elements and organic matter over the past three decades. Dr. Santschi served as Principal Investigator of over 30 multidisciplinary projects dealing with radiochemistry and trace element geochemistry in estuaries, shelf and slope waters of the Gulf of Mexico, and other parts of the Earth. For example, he and his associates and graduate students dated the sediments of Sabine Lake, Galveston Bay, Lavaca Bay, and the Mississippi Delta region in order to reconstruct the pollution history of these sites, and conducted extensive studies on the role of colloidal organic matter in trace element cycling in these waters. Recently, he just completed a 1 Mio \$ project, funded by the Department of Energy's Ocean Margins Program, studying the isotope and trace element geochemistry and transport of organic matter from the continental margin to the open ocean in the Gulf of Mexico and the Middle Atlantic Bight. In another project, funded by the Office of Naval Research, he conducted extensive research on trace element binding to natural organic matter in Galveston Bay. He published extensively on this subject in the peer-reviewed literature, and is the author of over 130 scientific articles in the peer-reviewed literature.

TRACE CONTAMINANT ASSOCIATION WITH COLLOIDAL MACROMOLECULAR ORGANIC MATTER IN GALVESTON BAY: IMPLICATIONS FOR BIOAVAILABILITY

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Most trace metals in Galveston Bay have only been reliably determined in recent years using state-of-the-art ultra-clean methodology (e.g., Benoit et al., 1994; Stordal et al., 1996; Wen et al., 1997, 1998). Without such methodology, samples get contaminated by sampling gear and during handling, and as a consequence, previously reported concentrations are, in most cases, many orders of magnitude too high. However, to reliably determine total concentrations is only the first step towards a better understanding of fate, bioavailability and food chain transfer. Bioavailability and toxicity of trace metals are profoundly affected by the speciation of the element. For example, trace metal bioavailability and toxicity to organisms is greatly enhanced when metals are present as labile ionic species. Hence, the use of the free ion model is prevalent. However, small hydrophobic metal chelates are bioavailable as are, possibly, macromolecular species through coagulation with food particles.

Many environmental regulations are still written in terms of the "dissolved" forms. However, the traditionally defined "dissolved" phase contains not just truly dissolved species (defined as <1 kDa) but also a considerable portion of colloidal (e.g., 1 kDa to 0.4 μm) metals (Benoit et al., 1994; Stordal et al., 1996a; Wen et al., 1997, 1998), with different physical, chemical and biological properties than truly dissolved forms. Furthermore, colloidal organic carbon (Guo and Santschi, 1997) also has different properties than low molecular weight forms. Thus, it is important to learn more about the properties of dissolved organic matter, DOM.

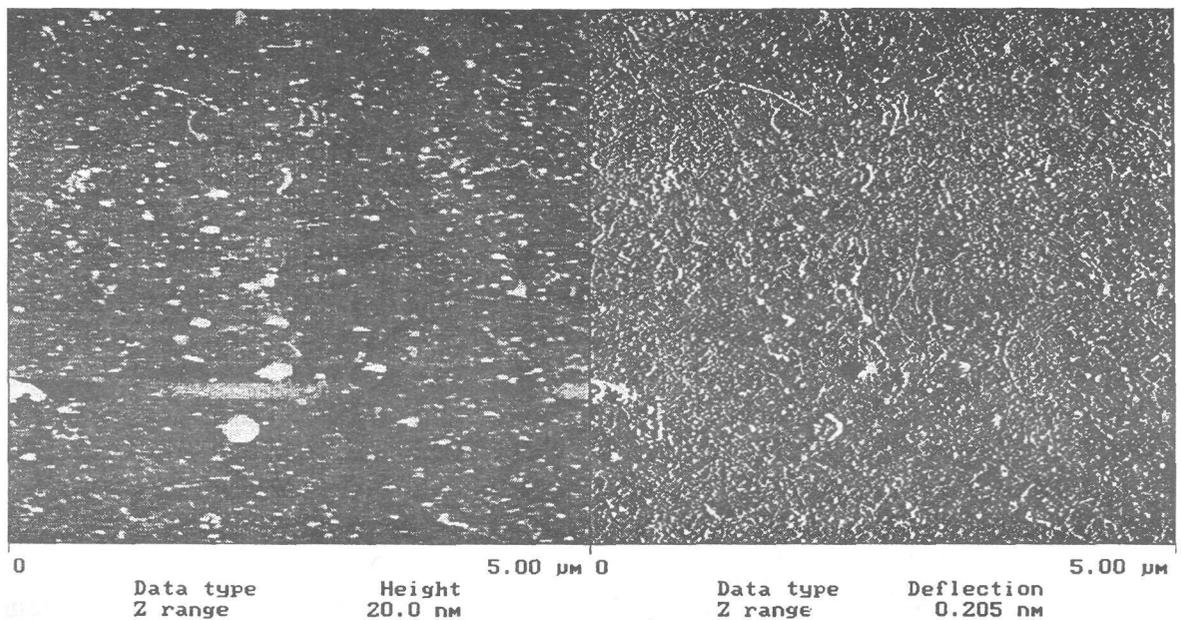
Estuarine dissolved organic carbon (DOC) is a mixture of inputs from riverine inflow, autochthonous primary production, and allochthonous contributions from adjacent coastal ecosystems (Burton & Liss 1976). Recent studies in estuaries and coastal waters have focused on sources of DOC (Bianchi et al. 1997a, Guo & Santschi 1997a), photochemical and bacterial consumption of DOC (Wetzel et al. 1995, Amon & Benner 1996a, b), as well as the role of natural organic matter in controlling the transport and fate of trace metals and radionuclides (Baskaran & Santschi 1993, Benoit et al. 1994, Wen et al. 1997). A significant fraction of the DOC in estuarine waters is composed of colloidal or macromolecular organic matter (e.g., Guo & Santschi 1997a), which plays an important role in the carbon cycle, trace metal scavenging, and biogeochemical processes (e.g., Guo & Santschi 1997b, Santschi et al. 1997b). Due to recent improvements of sampling and pre-concentration techniques, the abundance of colloids, DOC molecular weight distribution, and geochemical behavior in estuaries can be more effectively characterized (Benner et al. 1992a, Guo & Santschi 1997a).

It can be expected that biomolecules such as polysaccharides and proteides can be found in

the operationally defined colloidal fraction in harbor, estuarine and coastal waters, and function as strong metal chelators. Depending on the time scale of their involvement in biological processes, they can continue to do that for days and weeks after their release from aquatic organisms.

In recent years, our group has made great progress in collecting sufficient amounts of natural organic matter using rigorously calibrated methodologies in order to use it for characterization and experimental studies (e.g., Quigley et al., 1996; Guo and Santschi, 1997; Santschi et al., 1995, 1997; Stordal et al., 1996a,b, Wen et al., 1997). NOM was characterized isotopically (e.g., Santschi et al., 1995; Guo et al., 1997), chemically (e.g., Wen et al., 1998), and by shapes and forms (Santschi et al., 1998). Large fractions of transition and B-type metals were found to be organically bound, in part to thiols (e.g., Santschi et al., 1998b). Some of A-type metals were found to be most tightly bound by acid polysaccharides (e.g., Quigley, 1998).

We provided, for the first time, direct visual, chemical and isotopic evidence for the ubiquitous nature of marine polysaccharide fibrils, using atomic and electron microscopy (Santschi et al., 1998). These authors collected colloid samples from the Gulf of Mexico (GOM) and the Middle Atlantic Bight (MAB) of nominal sizes 1-200 nm by cross flow ultrafiltration, diafiltered and freeze dried. Rehydrated colloids were analyzed in parallel by Atomic Force Microscopy, AFM, and Transmission Electron Microscopy, TEM, using standardized techniques. Results from estuarine, surface and deep water samples, showed, for the first time, that an important fraction of COM consists of fibrillar material (Fig. 1), which is rich in polysaccharides, and "fresher" (i.e., has younger radiocarbon age) than the bulk COM. These results are important since COM makes up 30-70% of oceanic and estuarine nominally "dissolved" organic matter (Guo et al., 1995a; Guo and Santschi, 1997, and references therein). Other micro-particles appear quasi-spherical, often attached to the fibrils like pearls. In the surface waters of the Gulf of Mexico (GOM), the Middle Atlantic Bight (MAB) and the Trinity River estuary, fibrils with diameters of 1-3 nm and lengths of 100-2000 nm were predominant in the COM fraction. Although fibrils were also observed in samples from the benthic nepheloid layer in the GOM (1600 m) and the MAB (2600 m), a much greater heterogeneity of colloid/macromolecule shapes and sizes was observed in these deeper waters. Acid polysaccharide-rich fibrils are thus seen in all size or molecular weight fractions, i.e., in filter-passing fractions, as shown here, as well as in filter-retained fractions, as was shown previously for "marine snow" (e.g., Alldredge and Silver, 1988; Mopper et al., 1995).



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Figure 1. Atomic force micrographs (AFM) of colloidal organic matter collected from Galveston Bay (from Santschi et al., 1998a), showing fibrils and pedogenic organic matter. Since AFM is enlarging horizontal dimensions, vertical thickness needs to be determined separately. The polysaccharide-rich fibrils shown here have a thickness of the order of 1-3 nm, and a length of the order of 100's to 1000's of micrometers.

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