

# Foreword

Few of us really have intuitive concepts of the differences among ocean ecosystems. Ecosystems on land clearly look different from one another – contrast, for example, the outward appearances of deserts and savannas. Yet oligotrophic gyres and continental shelves, the oceanic analogs of these terrestrial systems, look nearly identical to the unaided eye, and we have to look more deeply (sometimes literally) to perceive the differences. Nearly all terrestrial ecosystems rest, physically and functionally, on an organic-rich soil foundation. Dissolved organic matter (DOM) is the soil of the sea – a large, biochemically resistant reservoir of organic matter providing a substrate for life, and a source for nutrient regeneration, ion exchange capacity, light and heat absorption, and so on. Marine DOM, however, is much less conspicuous than terrestrial soil. It is, in fact, nearly invisible. In this book, Hansell and Carlson and the many contributing authors tell the story of making DOM, the soil of the sea, visible.

Recently I was asked to provide a list to the International Geosphere-Biosphere Program (IGBP) of the top accomplishments and failures of the Joint Global Ocean Flux Study (JGOFS). I polled hundreds of scientists and students accessible via US JGOFS' e-mail lists and received numerous opinions about both the program's successes and failures. Interestingly, and as syndicated columnist Dave Barry would say, "I am not making this up," *one* topic was on both lists – dissolved organic carbon, DOC! This book attests to the success of DOM studies in JGOFS (including carbon, nitrogen and phosphorus), and throughout ocean biogeochemistry over the past decade. Was it also a story of failure? The question is provocative and I want to explore it here, at least briefly.

DOM has a long and distinguished history in marine chemistry and biology, dating to the early controversy as to whether or not this apparently large reservoir of organic matter was an important source of nutrition for marine animals (Krogh, 1934; Jorgensen, 1976). Duursma's (1963) monograph on the seasonal dynamics of DOC in the North Sea and North Atlantic revealed that the pool was an active and variable component of the marine ecosystem. The first radiocarbon dating of

DOC by Williams et al. (1969) indicated that the vast majority of this globally significant carbon pool was long-lived and refractory – in both the deep as well as surface oceans. By the late 1980's, as JGOFS began to focus on properties of the ocean carbon system, DOC was perceived as uninteresting – just a large, inert pool without much discernable vertical structure or horizontal gradients. I recall Peter LeB. Williams showing me the DOC analyzer he developed. “Here's the world's best instrument for analyzing the ocean's most boring property!”, he said. Added to this was controversy over the best analytical approach to quantify the bulk pool, which went back to Krogh and Keys (1934).

Given this backdrop, the seminal paper on DOC analysis by Sugimura and Suzuki (1988) was greeted with great surprise and excitement. In demonstrating a new analytical method and some of its early results, they presented oceanic DOC profiles with surface gradients of several 100's of  $\mu\text{M}$  and overall very much higher concentrations than revealed by earlier approaches. These findings made DOC interesting in several ways. Marine chemists seeking improvements to the thermodynamic description of the carbonate system in seawater saw in DOC a potential source of additional protolytes (Bradshaw and Brewer, 1988). Peter Brewer, the new Chair of U.S. JGOFS, was particularly energetic in advancing Suzuki's method and a newly recognized role for DOC in the carbon cycle. Perhaps the greatest push for the new, high DOC levels came from modelers. The 3-dimensional ocean modeling community became very interested in a DOM pool that had a longer lifetime than sedimenting particles and could be transported horizontally for long distances. In this behavior they saw the possible answer to the problem of nutrient trapping in models of the equatorial Pacific Ocean. Ray Najjar modeled DOM export to address the problem in his Ph.D. thesis (Najjar et al., 1992). Robbie Toggweiler discussed other aspects of high DOC levels in a still widely cited paper (Toggweiler, 1989).

It was clear that a large and influential segment of the ocean community was prepared to embrace these exciting results. Suzuki's results led to upward revisions of the oceanic DOC inventory, and to an explosion of research on marine DOM, its chemistry, analysis and ecology. Yoshimi Suzuki became an overnight celebrity. He participated in the U.S. JGOFS North Atlantic Bloom Experiment, and measured DOC in May 1989 in close conjunction with Ed Peltzer from Brewer's lab at WHOI, again demonstrating high concentrations and spectacular variations in space and time. Perplexingly, there were no known biological processes to maintain variations in euphotic zone DOC stocks of about 1 mole C as found over scales of a few days or a few km. Yet his analyses made on the same cruise established one of the first direct estimates of DOC utilization by bacteria, and resulted in an influential estimate of bacterial growth efficiency (Kirchman et al., 1991). U.S. JGOFS sponsored two workshops, including a “bake-off” (alluding to high-temperature combustion techniques) to validate Suzuki's method (Williams, 1991). Although large segments of the community wanted the new results to be true, many marine

chemists remained very skeptical. Reporting on the workshop results, Peter M. Williams reported,

“Most strikingly, the ranges of variation in the mean DOC concentrations of the same water samples by the same types of DOC analyzer were almost as great as the entire data set. . . . The DOC data from the different seawater analyses plot along three roughly parallel lines until reaching the high extreme of the measured range. . . . and thus do not vary randomly. One explanation for this pattern is that analyses made by different instruments include blanks of varying magnitude.” (Williams, 1991, p. 11).

Williams had it right, as was later demonstrated by Benner and Strom (1993) in the special issue of *Marine Chemistry* reporting the scientific results of the 1991 bake-off workshop. High-temperature, catalytic oxidation techniques for DOC analysis suffered from high instrument blanks that were not easily evaluated or corrected, leading to variable and high offsets in apparent DOC concentrations. In the meantime, Eiichiro Tanoue measured DOC in the same region of the northwestern Pacific assessed earlier by Sugimura and Suzuki (1988), finding much lower concentrations and less pronounced vertical gradients (Tanoue, 1992). In response to these new findings, Suzuki began a reassessment and reanalysis of his original results. In a statement of extraordinary courage and grace he retracted the results that had caused so much excitement (Suzuki, 1993; *see also* Hedges et al., 1993).

Thus, we see in this series of events a scenario familiar in the history of science. An idea, stimulated by technological innovation, was advanced and tested. Great excitement ensued and the new results suggested new solutions to recognized problems. More scientists saw a subject in a new way. But with increased scrutiny, the method was found wanting and the results were ultimately rejected. I think this is the reason some scientists have tended to regard oceanic DOC measurement as a failure. . . . the initial results didn't hold up. To some, Suzuki is the villain of the story, too quick to accept apparently spectacular results without adequate testing. I view the situation differently. As a result of the excitement generated by the original paper, and by Brewer's and others' strong advocacy of it, many others began to think in new ways about DOM in the sea. They wrote proposals and started new research. The technical aspects of DOC analysis were examined in an unprecedented manner, resulting in new instruments with great precision, capable of resolving 1  $\mu\text{M}$  differences in DOC concentration. There is today a recognized DOC analytical standard. These developments made possible direct detection of bacterial utilization of the bulk DOC pool, thus allowing us to assess the varying lability of the bulk DOM pool, insights expanded upon the results of Barber (1968) and Ogura (1972) a generation earlier. Following the idea pursued by Najjar and colleagues, DOC eventually became recognized as an important vector of export production (Copin-Montegut and Avril, 1993; Carlson et al., 1994). Increased precision enabled detection of deep-ocean DOC concentration gradients and basin-scale differences in DOC (Hansell and Carlson, 1998), opening its use

as a new geochemical tracer. Although the NABE study lacked reliable DOC data, all subsequent JGOFS studies had successful DOC research components. Oceanic DOM is now recognized as an important component of the biogeochemical system and possibly a barometer of global change (Church et al., 2002). Most importantly, we can today regard marine DOC as a dynamic component in the global carbon cycle. Success or failure? Read this book and be the judge.

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