The Role of Margin-derived Inputs on Natural Iron Fertilization in the Southern Ocean

Matt Charette,Marine Chemistry & Geochemistry
Alex Rao, Marine Chemistry & Geochemistry

1. Background

While the discharge of terrestrially-derived groundwater in the coastal ocean has been recognized for centuries, these "invisible" flows have not been widely studied until recently because of sampling difficulties and the misconception that material fluxes due to SGD are insignificant (Burnett et al., 2006). However, with the development of new measuring techniques in the last two decades, numerous studies have demonstrated significant SGD in coastal regions worldwide (e.g., Cable et al., 1996; Charette et al., 2001; Moore, 1996, 1997; Tsunogai et al., 1996; Burnett and Dulaiova, 2003). These studies have used multiple approaches (e.g., seepage meters, piezometers, geochemical tracers) to estimate local and regional-scale SGD inputs to the coastal ocean. In this study, we have applied some of these techniques to better understand of benthic nutrient and trace metal sources along the southern Patagonian coast, including SGD and remineralization in sediments.

There is ample evidence for Fe limitation in oceanic 'high-nitrate, low-chlorophyll' (HNLC) regions. As the largest HNLC region, the Southern Ocean is of great interest to ocean biogeochemistry, with the potential for major changes in carbon export exerting a great influence on atmospheric CO_2 and global climate on anthropogenic and geologic timescales. The importance of Southern Ocean phytoplankton Fe limitation has been the focus of both mesoscale Fe fertilization studies (e.g., SOIREE, EisenEx, SOFeX) and shipboard Fe enrichment incubation studies (e.g., Boyd et al., 2000; Coale et al., 2004; Hopkinson et al., 2007). The relative significance of airborne *vs*. upwelling Fe inputs in fueling Southern Ocean productivity is also a subject of much debate. There is some evidence that Southern Ocean blooms can be initiated by mesoscale activity or upwelling of micro- and macronutrients where the Antarctic Circumpolar Current (ACC) crosses bathymetric features (Sokolov and Rintoul, 2007). According to Charette et al. (2007), vertical mixing is particularly important in entraining deep-water Fe into the surface mixed layer downstream of Southern Ocean islands, in addition to horizontal mixing of Fe from island runoff. However, Cassar et al. (2007) argued that airborne soluble Fe inputs can explain much of the variability in Southern Ocean net community production and gross primary production, particularly downwind of dry continental areas. Lateral Fe inputs from ocean margins are frequently invoked as a natural iron fertilization process in this region (Hopkinson et al., 2007), but this source has received comparably little direct attention.

2. Field Sampling

A field campaign was conducted in January and February of 2009, covering both the western and eastern sectors of the Magellan Strait (Figure 1). WHOI investigators A. Rao, M. Charette, M. Gonneea and S. Bertrand were joined by Chilean scientists from the Universidad de Magallanes (Osvaldo Vasquez, MSc and Dr. Bibiana Jara Vergara), the Cientro de Investigación en Ecosistemas de la Patagonia (Dr. Rodrigo Torres), and the Wildlife Conservation Society (Claudia Silva, MSc), and Belgian scientists from the Université de Liège (Dr. François de Vleeschouwer and Virginie Renson, MSc).

The Magellan Strait, at the southern tip of South America, separates Patagonia from Tierra del Fuego, in the Subantarctic Zone between the Subtropical and Subantarctic convergences. The climate here is primarily controlled by prevailing westerlies in this upper mid-latitude belt (40-60˚S) and the Andean Cordillera, which causes a dramatic west-east climatic gradient. Rainfall is intense (400-5000 mm/yr) in the western part of the Strait, between Punta Arenas and the Pacific coast, whereas the Atlantic sector receives much less precipitation (250-350 mm/yr). The eastern sector is dominated by a strong semidiurnal macrotidal regime (tidal range up to 9-10 m) and strong tidal currents. Tidal ranges in the Pacific sector are much lower (1-2 m; Brambati et al. 1991). Sediments in this region also follow a latitudinal gradient. Sands and gravel prevail in the highly energetic Atlantic sector, while muds dominate the central and southern parts of the Basin of Punta Arenas, Bahia Inutil and Seno Magdalena. In the Pacific sector, sands and gravels alternate with dominantly muddy sediments (Brambati et al. 1991). Little is known about the hydrogeology of this region, although it is likely influenced by the concurrent regional gradients in climate and sediment type.

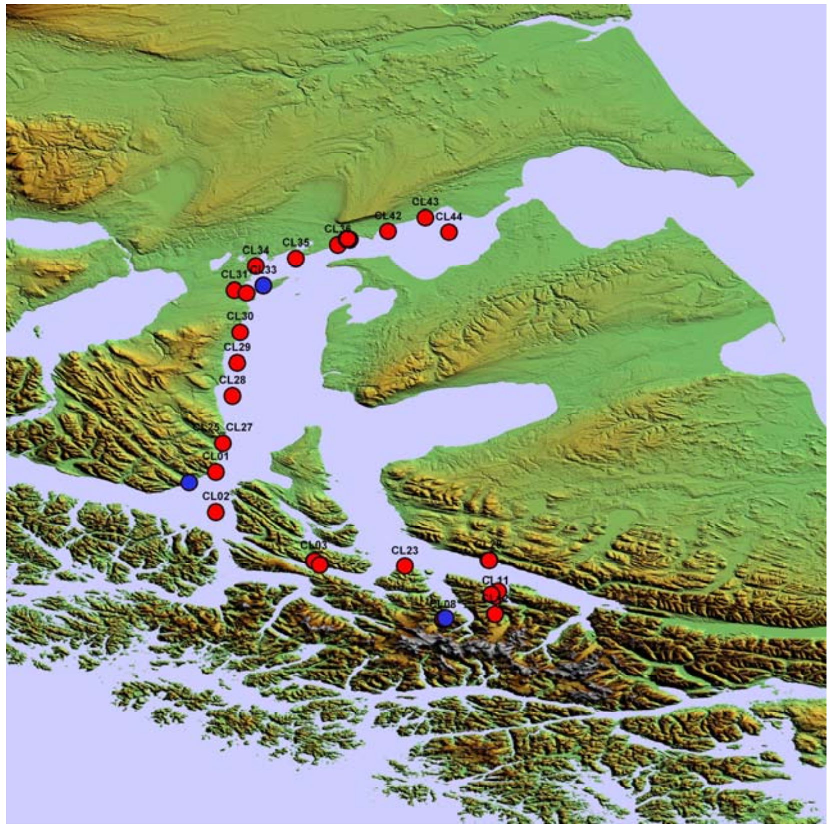


Figure 1. Map of sampling sites. Sediment cores for incubations were collected at sites indicated in blue.

Surface and groundwater samples were collected for nutrients, metals, radionuclides, and other ancillary measurements (e.g., pH, alkalinity, salinity, dissolved O_2) using PushPoint samplers and an AMS retract-a-tip piezometer system. Ra isotopes and ^{222}Rn, which are naturally enriched in groundwater, were used to estimate rates of groundwater discharge. SGD time-series measurements were conducted in the Rio Susanna estuary in the eastern sector of the Magellan Strait. Sediments were collected at select sites for porewater microprofiling, solid phase analyses and core incubations to determine benthic respiration rates and nutrient and trace metal fluxes across the sediment-water interface.

3. Analyses

Dissolved oxygen, salinity, pH, and E_h were measured in surface and groundwater samples in the field using a YSI multi-probe sonde, while high-precision salinity measurements were conducted with a Guideline AutoSal.

Sediment core incubations for nutrient and trace metal fluxes were conducted under a laminar flow hood on board the vessel. Following incubations, a Clark-style amperometric oxygen microelectrode with guard cathode was used to measure oxygen microprofiles in sediment cores. Nutrient analyses were conducted in the Charette lab nutrient facility using standard methods. Trace metal analyses of diluted samples were conducted in the WHOI plasma facility, respectively. Methods for the measurement of $\sum Fe_d$ in samples from sediment core incubations at higher precision using preconcentration, matrix removal, and isotope dilution techniques are currently under development.

4. Results

4.1 *Groundwater-derived nutrients*

Radium isotopes were used to estimate submarine groundwater discharge. As shown in Figure 2, samples of groundwater and glacial meltwater streams were enriched in Ra relative to river and coastal ocean water in both the eastern and western sectors. However, Ra isotopes in coastal ocean water appear to follow conservative mixing between the observed river and ocean endmembers. These observations preclude a significant groundwater Ra source in this region.

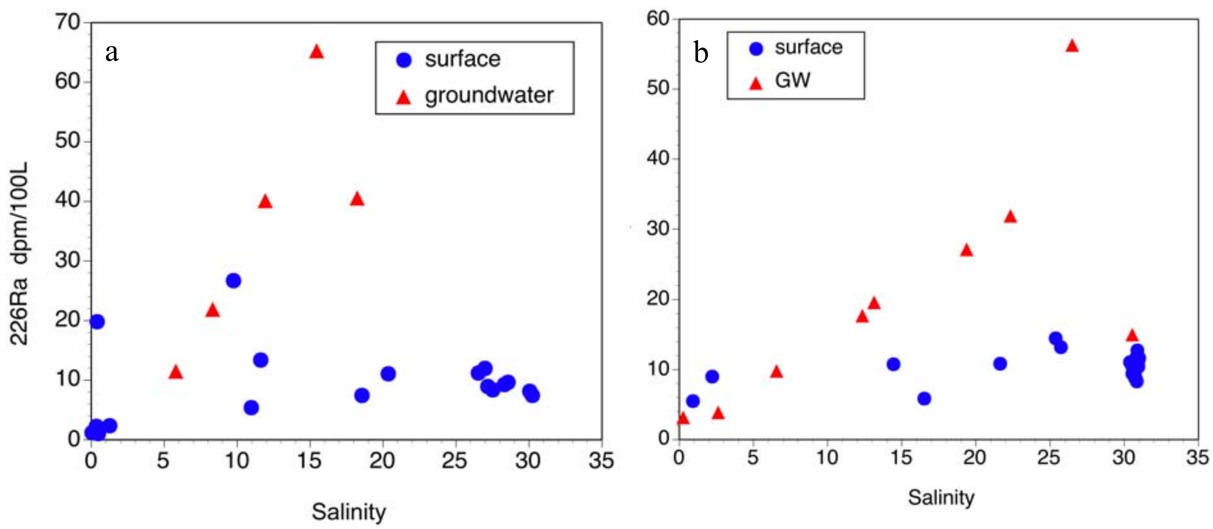
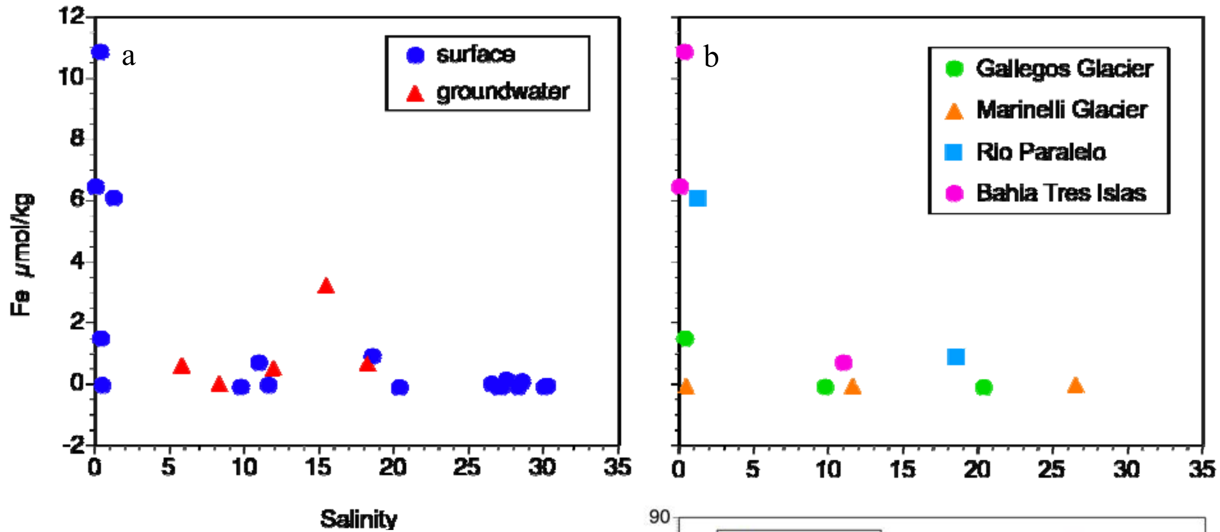


Figure 2. ^{226}Ra activity in surface and groundwater samples in the (a) Pacific and (b) Atlantic sectors of the Magellan Strait.

While groundwater inputs may not appear high in this region when integrating over large areas, SGD may play a significant role in individual estuarine systems, such as the Rio Susanna estuary in the Atlantic sector of the Magellan Strait. A tidal time-series study conducted at this site showed increasing long-lived Ra activities from flood to ebb tide, representing a high area-normalized rate of submarine groundwater discharge (0.26 m^3 m^{-2} d^{-1}). Even on the scale of this estuarine system, however, the complex relationship between Ra and DIN in surface water (*data not shown*) prevents the identification of a groundwater nitrogen source, although groundwater appears to be elevated in DIN. This may be due to the relative importance of other nitrogen sources, sinks and transformations of N in this estuarine system in surface water and in surface sediments at the groundwater seepage face.



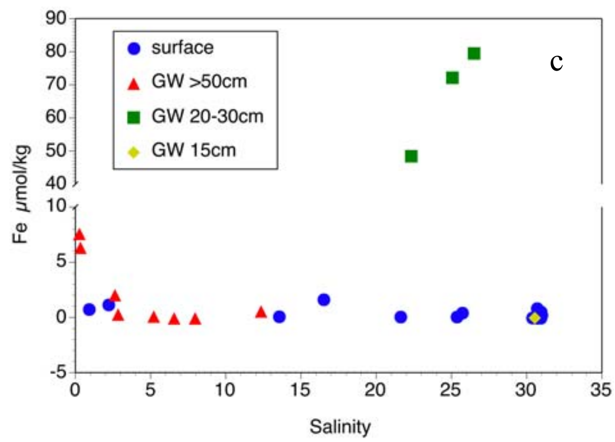


Figure 3. Summary of $\sum Fe_d$ concentration *vs.* salinity in samples collected in the Pacific and Atlantic sectors of the Magellan Strait. In the Pacific sector: (a) groundwater and surface water, and (b) rivers and glacial meltwater streams. In the Atlantic sector: (c) groundwater and surface water.

Total dissolved iron ($\sum Fe_d$) concentrations were highest in the Pacific sector in samples collected from rivers and glacial meltwater streams, intermediate in groundwater, and lowest in coastal ocean water (Figure 3a,b). These observations suggest that rivers and glacial meltwater may represent an important source of Fe to the coastal zone, with groundwater fluxes playing a secondary role. The removal of Fe by flocculation during estuarine mixing was indicated by decreasing $\sum Fe_d$ in surface waters at increasing salinity. In the drier Atlantic sector, PushPoint and piezometer samples of porewater and groundwater were highly enriched in $\sum Fe_d$ relative to the coastal ocean (Figure 3c). At

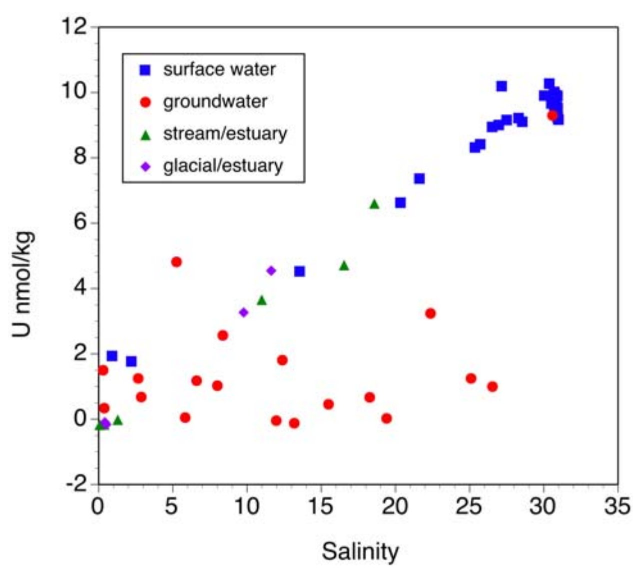


Figure 4. Summary of measured uranium concentrations *vs.* salinity in all samples.

the Rio Susanna estuary, $\sum Fe_d$ concentrations notably increased from 0-10 µmol/kg in porewater samples collected below 50 cm depth in sediments, to 50-80 µmol/kg at 20-30 cm depth. Above this depth, $\sum Fe_d$ concentrations once more declined. This distribution of $\sum Fe_d$ in sediments most likely reflects the release of soluble reduced iron in suboxic and anoxic sediments by microbial remineralization of organic matter, and iron reoxidation and iron oxide precipitation in the presence of oxygen in surface sediments. Sediment core incubations were conducted to examine the sediment-water flux of $\sum Fe_d$ resulting from organic matter remineralization in surface sediments.

Trace metal analyses also revealed an enrichment in dissolved manganese in select groundwater/porewater samples, which tracked the enrichment in $\sum Fe_d$ (*data not shown*). Mn is also remobilized in porewater following Mn-oxide reduction by microbial organic matter oxidation in sediments, suggesting a similar diagenetic source for dissolved Mn and Fe in surface sediment porewater. While strontium appears to behave conservatively in surface and groundwater, uranium in groundwater deviated significantly from the conservative behavior observed in surface waters, reflecting removal under reducing conditions as observed in previous studies (Figures 4 and 5; e.g., Charette et al. 2005, Windom and Niencheski 2003).

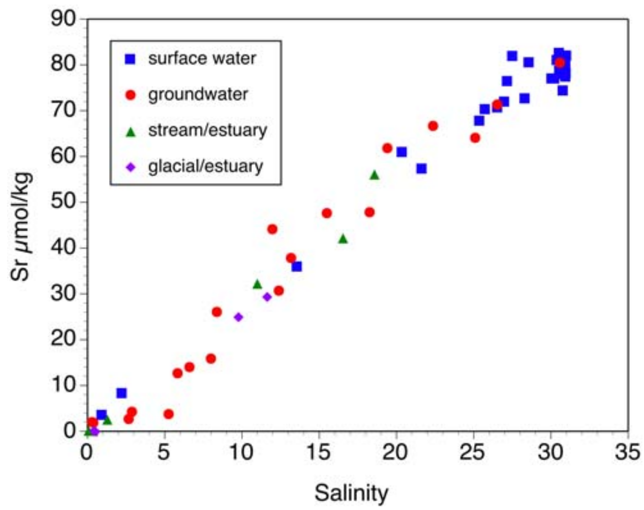


Figure 5. Summary of measured strontium concentrations *vs.* salinity in all samples.

4.2 *Sediment respiration: Oxygen demand and benthic nutrient supply*

Sediment cores were collected at three locations, including fine-grained moraine deposits in the Gallegos glacier, and fine- and coarse-grained sediments in Bahia San Nicolas and Whitsand Bay, respectively. Preliminary results from dark sediment core incubations show the highest oxygen consumption rates and sediment-water dissolved inorganic nutrient fluxes in Whitsand Bay (Table 1). The shallow oxygen penetration depth observed in these sediments is consistent with high microbial activity in these coarse sediments (Figure 6). In contrast, lower oxygen consumption rates and sediment-water nutrient effluxes (Table 1), and deeper oxygen penetration (Figure 6) were observed in fine-grained sediments at Bahia San Nicolas and at the Gallegos glacier moraine. Although the analysis of dissolved iron has been delayed due to the necessary development of higher precision methods for $\sum Fe_d$ determination, these samples were collected during core incubations and will allow us to determine benthic iron fluxes.

Table 1. Summary of O_2, NO_3^-, NH_4^+, and PO_4^{3-} fluxes in cores from Whitsand Bay (n=3), Bahia San Nicolas (n=3), and the Gallegos glacier deposits (n=2).

	O_2 (ave ± s.d.)	NO_3^- (ave ± s.d.)	NH_4^+ (ave ± s.d.)	PO_4^{3-} (ave ± s.d.)
Whitsand Bay	-11.8 ± 8.1	2.51 ± 6.86	1119.73 ± 925.32	45.42 ± 51.90

Bahia San Nicolas	-1.6 ± 0.4	16.26 ± 14.34	34.25 ± 46.67	0.55 ± 1.93
Gallegos Glacier	-0.7 ± 0.01	29.93 ± 8.01	196.05 ± 42.15	-4.58 ± 0.95

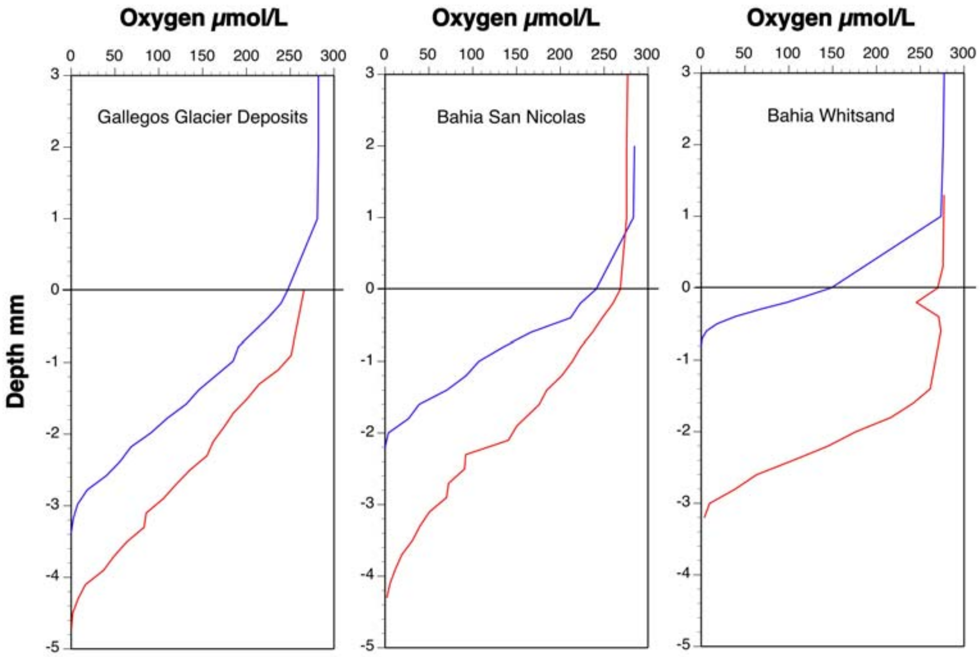


Figure 6. Oxygen microprofiles in sediment cores collected in Bahia Whitsand, Bahia San Nicolas, and in Gallegos glacier deposits.

5. <u>References Cited</u>

Boyd, P. W. et al. 2000. *Nature* **407**, 695.

Brambati, A., G. Fontolan, and U. Simeoni. 1991. *Boll. Ocean. Teor. Appl.* **9(2-3)**, 217.

Burnett, W. C., P.K. Aggarwal, A. Aureli, H. Bokuniewicz, J.E. Cable, M.A. Charette, E. Kontar, S. Krupa, K.M. Kulkarni, A. Loveless, W.S. Moore, J.A. Oberdorfer, J. Oliveira, N. Ozyurt, P. Povinec, A.M.G. Privitera, R. Rajar, R.T. Ramessur, J. Scholten, T. Stieglitz, M. Taniguchi, J.V. Turner. 2006. *Science of the Total Environment*. 367: 498–543.

Burnett, W. C. and H. Dulaiova. 2003. *Journal of Environmental Radioactivity.* 69: 21–35.

Cable, J. E., W. C. Burnett, J. P. Chanton, and G. L. Weatherly. 1996. *Earth and Planetary Science Letters.*

Cassar, N. et al. 2007. *Science* **317**, 1067.

Charette, M. A., K. O. Buesseler, and J. E. Andrews. 2001. *Limnology and Oceanography.* 46(2): 465-470.

Charette, M. A., E. R. Sholkovitz, and C. M. Hansel. 2005. *Geochimica et Cosmochimica Acta.* 69(8): 2095-2109.

Charette, M. A. et al. 2007. *Deep-Sea Res. II* **54**, 1989.

Coale, K. H. et al. 2004. *Science* **304**, 408.

Hopkinson, B. M., B. G. Mitchell, R. A. Reynolds, and H. Wang. 2007. *Limnology and Oceanography* **52(6)**, 2540.

Moore, W. S. 1996. *Nature*. 380: 612-614.
Moore, W. S. 1997. *Earth and Planetary Science Letters*. 150: 141-150.
Sokolov, S. and S. R. Rintoul. 2007. *J. Geophys. Res.* **112**, C07030.
Tsunogai, U. J. Ishibashi, H. Wakita, T. Gamo, T. Masuzawa, T. Nakatsuka, Y. Nojiri, T. Nakamura. 1996. *Earth and Planetary Science Letters.* 138: 157-168.
Windom, H. and F. Niencheski. 2003. *Marine Chemistry.* 83: 121-130.