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MARINE HUMIC ACIDS AS AN IMPORTANT CONSTITUENT OF THE DISSOLVED ORGANIC CARBON FLUX IN THE BERING AND CHUKCHI SEA ECOSYSTEMS

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ABSTRACT

The oceans play a key role in maintaining the present-day level of CO_2 concentration in the atmosphere through active gaseous exchange at the sea-air interface. The most intense transport of CO_2 from the surface to the deep ocean occurs in subarctic sea ecosystems. To further understand the role of dissolved organic carbon flux in carbon cycling, the humic acid content distribution patterns in the Bering/Chukchi Seas were considered in the context of physical and biological features intrinsic to these high-latitude regions. An earlier investigation using the direct fluorometric method indicated that humic acid concentration was two to three times higher in Chukchi Sea waters than in the photic layer of the Bering Sea. The Humic acid concentration gradient exhibited strong coupling to hydrographic as well as biological conditions in the Bering/Chukchi Seas ecosystem providing a basis to consider HA distribution as a quasi-conservative parameter reflecting long-term production and decomposition coupling. Data presented show that carbon cycling in the Bering Sea has global significance.

INTRODUCTION

The oceans play a key role in maintaining the present-day level of the CO_2 concentration in the atmosphere through the active gaseous exchange at the sea-air interface. Deep-water mass formation due to surface cooling could be a major transport mechanism of atmospheric CO_2 to the deep ocean, especially in high-latitude seas. For example, the Bering Sea and Arctic Ocean have extended shallow shelves that allow rapid winter cooling followed by sequestering of the surface water supersaturated with CO_2 to the adjacent deep basins (Walsh et al., 1989).

A second transport mechanism, referred to as a "biological pump" (Longhurst and Harrison, 1989), occurs through the sinking of particulate organic matter (POM). This global flux provides an annual vertical transport of 0.6-2.6 Gt of organic carbon from the surface to the deep ocean (Jahnke, 1990). So far, it has been considered as a major input mechanism of organic material to the deep sea (Bacastow and Meier-Reimer, 1990). But recent investigations of dissolved organic carbon (DOC) vertical profiles in the Northern Pacific using a new method of high-temperature catalytic oxidation, developed by Sugimura and Suzuki (1988), have shown the existence of a near 1:1 correlation between decreasing DOC and increasing apparent oxygen utilization (AOU) with depth. It suggests that most of the water-column respiration is supported by the direct transit of DOC from the photic layer and not by sinking particulate material. This global DOC flux is estimated at 1-3 Gt C / yr on the basis of polar deep-water formation rates of 20×10^6 m^3/s (Toggweiler, 1988; Christensen et al., 1989) and average DOC concentration in surface waters of 100-300 µmol C / l (Druffel et al., 1989; Sugimura and Suzuki, 1988). Thus, the role of DOC input could be as important as that of POM flux.

Moreover, the high concentrations of DOC as measured by Sugimura and Suzuki (1988) could be interpreted as indicative of a new large class of organic compounds in seawater (Toggweiler, 1989; Christensen et al., 1989), which are biologically degradable, but the decomposition rate is on the order of decades or centuries. These compounds are located mostly in the surface (0-200 m) layer; they are younger than refractory dissolved organic carbon (DOC_{UV}) according to radiocarbon signatures (Druffel et al., 1989); and have higher molecular weight (over 20,000 dalton) (Sugimura and Suzuki, 1988).

The properties of these newly discovered biopolymers (DOC_{HTC}) allow the speculation that DOC_{UV} is diagenetically downstream of DOC_{HTC}. This could be the long-sought pool of biopolymer precursors of humic acids (HA) (Hedges, 1988).

To further understand the role of the DOC flux in global carbon cycling, the distribution and composition of both of these DOC pools, that is, the refractory (mostly of humic origin) and the biodegradable (HA precursors) should be thoroughly studied. This problem is of special significance in subarctic ecosystems, where the most intense transport of CO_2 from the surface to the deep ocean occurs.

GLOBAL SIGNIFICANCE OF CARBON CYCLING WITHIN THE BERING AND CHUKCHI SEAS

According to the latest estimates, during the growing season of phytoplankton 0.19 Gt and 8.2 Mt C are produced over the Bering and Southern Chukchi Seas, respectively (Zeeman, 1992), demonstrating the great importance of these regions in the global carbon flux. A substantial portion of this fixed carbon is transported northward through the Bering Strait into the adjacent deep basins of the Arctic Ocean. Recent independent assessments based on the AOU demands (Walsh et al., 1989) and the amount of carbon required for dissolution of calcium carbonate within the basins' halocline (Anderson et al., 1990) suggest a total carbon input into the Arctic interior of 3.2-115 Mt C/yr. Under present rates of "new production" within waters under the ice pack of the Arctic basins and the shallow Arctic shelves, such a carbon budget can be balanced only in case of the input of 0.1 Gt C fixed south of the Arctic ocean and entrained north through the Bering Strait, with a concomitant import of "new" dissolved nitrogen to the Arctic shelves (Walsh et al., 1989).

The nutrient-laden Bering Strait influx of > 1.0 Sv transits the Arctic Ocean directly as a subsurface layer, going under the ice cap (Aagard et al., 1985). In this transpolar drift, it entrains about twice its volume of dense and saline water produced on the shallow Arctic shelves during seasonal ice formation (Aagard et al., 1981). In six years, these modified North Pacific waters crossing Fram Strait enter the Iceland Sea, contributing to the formation of the North Atlantic Bottom Water (NABW) (Swift, 1984). Thus, creation of waters forming North Atlantic Deep Water (NADW) directly depends on advection of modified Pacific water.

In terms of the present anthropogenic CO_2 release of 5.0 Gt C/yr to the atmosphere (IPCC,1992), an Arctic sink of 0.1 Gt C/yr is small. But keeping in mind the projected greenhouse warming of 4-5° C in this region by 2050, followed by the melting of the Arctic ice pack (IPCC,1992), a future carbon sink may increase up to 0.5 Gt C/yr as a result of the increase in primary production over the Bering Sea - Arctic shelves (Walsh et al., 1989). Besides, through the teleconnection of the Pacific and Atlantic Oceans via Bering and Fram Straits, such a change in primary production could greatly affect today's ventilation of the World Ocean, which has a strong feedback with global climate formation.

CARBON FLUXES THROUGH THE BERING STRAIT

An estimation of the total carbon flux and its components through the Bering Strait allows further understanding of the role of subarctic sea ecosystems in global carbon cycling. According to Zeemans data (1991), 0.82 Gt dissolved inorganic C are transported northward annually through the Bering Strait. But this estimate could not be considered as a total carbon flux, taking into account a very high productivity characteristic of the region under study. This is demonstrated by a number of quantitative estimates based on the data on phytoplankton particulate carbon (POC) (Walsh et al., 1989; Zeeman, 1992) and the total POC and DOC content in the water column in the strait region (Loder, 1971; Lyutsarev et al., 1988; Glebov et al., 1992; Pershina, 1992), assuming the average flow-rate through the Bering Strait of about 1 x 10^6 m^3/s (Walsh et al., 1989). These estimates are presented in Table 1.

A salient point to consider here is that there is a rather good coincidence of estimates within a single approach, but based on different measuring procedures. The low magnitudes of POC flux, based solely on the content of phytoplankton particulate carbon, are related to underestimation of the detritus input into the POC flux. Subtraction of the value of phytoplankton flux of 1.3 Mt C/yr from the total POC flux of 13-19 Mt C/yr allows an estimate of detritus contribution to the total POC flux of 12-18 Mt C/yr. This magnitude is tenfold higher than for phytoplankton flux, demonstrating a major role of detrital material in the particulate flux transporting through the strait. North of the Bering Strait, in the weak-flow regime of the Chukchi Sea, a substantial, but yet unknown, portion of this particulate material sinks to the bottom forming a large carbon depocenter with a high (6:1) C:N ratio (Grebmeier et al., 1989), which fuels enormous benthic populations here. The remainder of the particulate flux finds its way to the Arctic Ocean, contributing to "new production" in the polar basins.

Table 1. Estimates of POC and DOC fluxes transported through the Bering Strait.

Flux-value (Mt C/yr)	Method of POC and DOC determination	Reference
13	POC by dry combustion	Glebov et al., 1992
19	POC by wet combustion	Loder, 1971
13	POC by wet combustion	Lyutsarev et al., 1988
1.3	POC by phytoplankton biomass	Walsh et al., 1989
3.2	POC by phytoplankton biomass	Zeeman, 1992
42	DOC by wet combusion	Loder, 1971
29-32	DOC by HA content	Pershina, 1992

In connection with the new concept of the role of DOC in supporting deep-water metabolism, it is of interest to estimate the role of DOC flux in the northward carbon transport through the Bering Strait. According to Table 1, DOC flux of 29-42 Mt C/yr is two to three times the total POC flux. Considering the two or three times higher DOC concentrations measured by Sugimura and Suzuki (1988) and recently confirmed by other investigators (Druffel et al., 1989; Cauwet et al., 1990), the given value could be a low estimate. This means that the average concentration through the water column of 1.22 mg/l (Loder, 1971) might be increased at least twice, yielding an annual DOC flux of 80 Mt C/yr. In addition, Pershina's (1992) results on HA distribution allow inclusion of refractory organic carbon into the corrected total DOC flux. Based on the average HA concentration in the strait region of 2.0 mg/l (Pershina, 1992), the flux of refractory organic carbon is about 23 Mt C/yr, or 29% of the total DOC flux. This value is in good agreement with data of Sugimura and Suzuki (1988), who discovered 35% refractory carbon in the DOC samples of the North Pacific.

As it is exported farther north, the DOC is partitioned over the shallow (~40 m) extended area (~1x10^{12} m^2) of the Chukchi/East Siberian Seas shelves and may be entrained into the pycnocline of the Arctic Ocean during intense deep-water formation. Under the annual 1 Sv influx of saline-dense (<33.5%) shelf water to the Arctic interior (Aagard et al., 1981), it can provide the total DOC input of 63 Mt C/yr, consisting of 45 Mt C/yr relatively biodegradable DOC and 18 Mt C/yr refractory (humic acids) DOC with residence time on the order of 600-6000 years (Druffel et al., 1989; Romankevich and Lyutsarev, 1990; Skopintsev, 1981). Due to the longevity of humics in comparison with the Arctic basin's deep-water residence time of 200 years (Aagard et al., 1981), these compounds could be transported laterally over long distances providing homogenous vertical DOC distribution below 1500 m.

To further understand the role of the DOC flux and its components in the carbon cycling within subarctic sea ecosystems, recent results on the HA content distribution pattern in the Bering / Chukchi Seas are considered below in the context of major physical and biological features intrinsic to these high-latitude regions.

HUMIC ACIDS IN THE BERING AND CHUKCHI SEAS

The HA distribution in the Bering and Chukchi Seas was investigated by the direct fluorimetric method (Pershina, 1987) during the growing season (July - August) of 1988. The results are presented in Figure 1. Maximum HA concentrations of 75-80 g/m^2 or 1.8-2.0 mg/l were detected in the Bering Strait. High concentrations of 60-70 g/m^2 or 1.5-1.7 mg/l were characteristic for the Chirikov Basin and the Southern Chukchi Sea. As a whole, HA concentration in Chukchi Sea waters (except for the northern-eastern part, adjacent to the East Siberian Sea) was two to three times higher than it was in the photic layer of the Bering Sea.

The results are rather consistent oceanographically. More than 60% of the flow passing through the Bering Strait is dominated by cold saline water from the Gulf of Anadyr (AW). The remainder of water on the eastern side of the strait is a mixture of Yukon River and Southeastern Bering Shelf Water, termed Alaska Coastal Water (AC), whereas on the western side of the strait, it is a mixture of Siberian Rivers and East Siberian Sea Water, termed Siberian Coastal Water (SC) (Walsh et al., 1989). At the stratified interfaces of AC and SC with AW, referred to as eastern and western front, respectively, where vertical mixing is inhibited, enhanced plant production should be expected. Indeed, detailed study of nitrogen cycling in the strait region by Walsh et al. (1989) showed that the greatest rates of nitrogen uptake of 1.5-3.0 mg-at N m^2/hr (twice that found in the AW) were observed in these boundary water parcels. This nitrogen uptake would result in a daily primary production of 2 to >10 g C /m^2/day at the edges of the AW (McRoy et al., 1972) versus ~4 g C /m^2/day within Anadyr Water and ~0.33 g C /m^2/day within Alaska Coastal Water (Walsh et al., 1989). Such high primary production implies high biosedimentation rates of phytodetrital material providing a food source for large benthic populations south of the Bering Strait as well as north. The surficial sediments south of the Bering Strait are characterized by low organic carbon content and a high C:N ratio exhibiting rapid mineralization rates of incoming detritus in the Chirikov Basin (Grebmeier et al., 1989). In the Chukchi Sea, on the contrary, underlying sediments are characterized by high organic content, low C:N ratio (better food quality), high sulfide concentration (as a result of sulfate-reduction mineralization mechanisms) and intense urea-fluxes (Walsh et al., 1989). Latter conditions, concomitant with very high primary

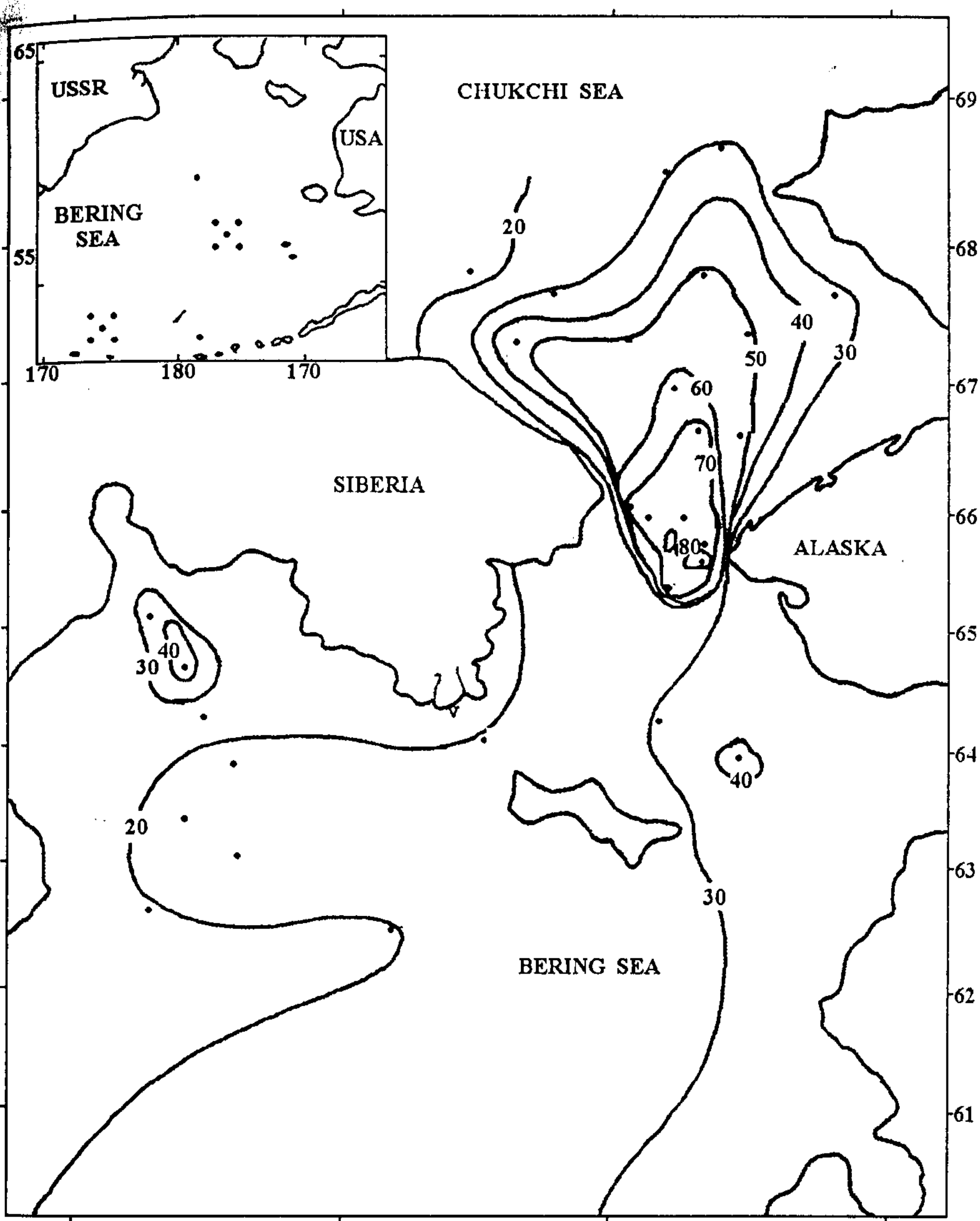

Figure 1. Depth-integrated distribution of humic acids (g/m²).

production (at times > 10 g C m^2/day), seemed to be greatly contributed to the intense humification processes, providing maximum HA accrual in the region under consideration (Figure1).

It should be pointed out that the axes of westward and northward HA concentration gradient coincide very well with the western and eastern fronts, respectively exhibiting strong coupling to hydrographic as well as biological conditions in the area. However, despite a good agreement with the general features of a primary productivity distribution pattern, direct comparison manifests a lack of correspondence between values of primary production and HA content in the same water parcel (Pershina, 1991; Zeeman, 1991). This finding appears to be explained by considering the great differences in the residence time of HA (600-6000 years) (Skopintsev, 1981; Druffel et al., 1989) versus the ephemeral state of algae populations that produce them. As a result of such longevity, the content of humic compounds could serve as a quasi-conservative characteristic of the water parcel, whereas the HA distribution pattern could be interpreted as an indicator of long-term physical-biological coupling in sea ecosystems.

CONCLUSIONS

The data presented show that carbon cycling in the Bering/Chukchi Seas has a global significance. Through northward transport to the Arctic Ocean of ~50 Mt C/yr of POC and DOC, respiration can account for nearly 50% of the polar basin AOU demands. Of the total carbon input, an estimated 30% of the refractory pool is derived from humic substances. Humic acid distribution is coupled to the major physical-biological processes of the Bering/Chukchi ecosystem and is a quasi-conservative parameter reflecting long-term production and decomposition coupling. We can speculate that the HA biopolymer precursors pool (termed earlier as DOC_{HTC}, or biodegradable DOC) may have a direct correlation with the seasonal changes in the primary productivity regime, being dependent on the phytoplankton biomass, which contained its chemical precursors. In other words, this DOC pool could be traceable to the short-term variations in primary productivity. If so, precise determination of both of these DOC pools is of great importance, providing means for further understanding the mechanisms of diagenetic transformations of biological material during humification processes. For this approach to be useful, highly reliable analytical methods of determination of the total DOC pool and its constituents should be used. Studying the DOC pool on the molecular level with a use of modern physical-chemical techniques is a next important problem to be solved here.

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