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High Molecular Weight Material in Baltic Waters

by

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ABSTRACT

The concentration of high molecular weight material (> 10,000) in Baltic water was determined by Amicon membrane ultra filtration, followed by transmission spectroscopy of the concentrate. Most northern Baltic samples contain only about 1 % of the amount of macromolecular material that would be expected by a simple dilution model, based on data from a typical humic stream. A rapid precipitation of the material under saline conditions is indicated.

INTRODUCTION

The problem of defining and measuring the naturally occurring humus components in natural waters has been brought nearer solution by the use of sephadex gel filtration for determination of molecular weight distributions. As shown by Gjessing (1965), Pennanen (1972) and many others, the humus behaves in many cases as a two component system, a small molecule (< 5000) and a large, colloidal fraction (> 50,000). Khaylov and Finenko (1968) observed this same pattern in humus concentrated from Baltic waters.

Recently Gjessing (1970) has confirmed that Amicon ultra-filtration membranes give virtually the same results as sephadex, for weight distributions of humus materials. The ultra-filtration process enjoys the advantage that the separation is chiefly physical, and the ambiguities introduced by adsorption tendencies to the sephadex resin are avoided. In most experiments involving highly colored waters, however, a small part of the retained material is visibly adsorbed to the face of the membrane, even with vigorous stirring. He also notes that considerably small weight material is retained by the filters unless several volumes of fresh water are washed through. The Amicon catalog (1.) specifies a 95 % removal of

of "microsolutes" after three volumes wash. Aside from these restrictions, the ultrafiltration method appears to be well suited to analytical determinations with natural waters, where tedious preconcentration is unacceptable.

Sharp (1973b) employed the Millipore VS membrane filter (0.025 µm) and the Amicon XM-50 (ca. 0.003 µm) in order to size-class the organics in sea water of the central North Atlantic. He found that approximately 8 % of the total organic carbon falls in the range 0.025-0.8 µm, and 16 % is in the range 0.003-0.8 µm. Assuming the same definition as Vold and Vold (1966) for the colloidal range (1 µm - 10^{-3} µm), he estimates that the particulate material (> 1 µm) amounts to only 10 % of the total colloids.

The Baltic system constitutes a somewhat different situation from the open sea. Many hundreds of streams, rich in humus from pine forests and boggy areas, feed this sea, causing organic carbon values to be about five times the value for the North Atlantic (see, for comparison: Sharp 1973a; Carlberg, 1973). The color of the Baltic ranges from a greenish-blue in the Danish Sound to a rich coffee-brown in the northern extreme of the Bothnian Bay. As the humus, which constitutes the bulk of organic material in the streams, is known to contain a large amount of high molecular or colloidal material, it was considered important to know what became of this material after entry into the marine environment.

MATERIALS AND METHOD

500-ml aliquots of samples taken in all-plastic Hydro-Bios samplers were placed in home-made PVC reservoirs. Under two atmospheres pressure, the water was forced through a Millipore HA filter (0.45 µm) in an in-line holder and thence into a 50-ml Amicon ultra-filtration cell.

A PM-10 membrane was used, primarily for reasons of flow velocity (500 ml in ca. 2-3 hours) and since this seemed to bracket the smaller and larger fractions of natural humus, as estimated from many published determinations on sephadex.

A series of preliminary studies showed that two washings were sufficient to remove 90 % of the absorbance at 280 nm from the effluent. Without these washings the absorbance of the retained volume, and presumably the organic solution concentration, was two to three times greater than the final value after washing. Sharp's (1973b) failure to do this is perhaps a significant point.

The 500-ml was concentrated to 10-ml, washed twice with 50 ml of distilled water, and the absorbance (-log % T) at 280 nm was read in a 2-cm cell, with distilled water as reference. The absorption spectrum of the concentrate is similar to the spectrum of glass-fibre filtered Baltic water, with a broad shoulder near 280 nm, and strong end-rise below 250 nm. Samples were taken from stations and depths corresponding to a broad cross section of the Baltic waters, including the Gulf of Finland and the Bothnian Sea and Bay.

In addition to these marine samples, an identical determination was made using freshly collected water from Hellerudmyra stream A, a typical Nordic humic water source, well-studied by Gjessing (1970b). Dissolved organic content was monitored by absorption measurements on filtered samples at 280 nm.

The data show that the relative proportion of high molecular weight material drastically increases toward the nearly fresh water zone of the far northern Bothnian Bay. Even the highest marine value, however, falls far below that of the humic stream.

SUMMARY

It is evident that, for the more saline samples, the decrease in high molecular weight material with decreasing total organics, is a dilution process.

When the data for I-3, 0 meters, and for the stream are considered, however, a very different picture emerges. The relative concentration of high molecular weight material increases about one and two orders of magnitude, respectively, for these waters. This can be explained on the basis of colloidal flocculation and precipitation of the high weight material as it enters the marine environment. Station I-3 represents the northernmost extreme of the Baltic, lying within a few kilometers of the shore. The salinity is a minimum here, as a large river, the Kemi Älv enters nearby. The humus in these waters has only recently entered the saline conditions of the sea and flocculation or adsorption to existing particles has not proceeded to a great extent.

It should be noted that Gjessing (1970a) gets much higher relative values for the high weight fraction from Hellerudmyra than the present experiment. This could be due to the fact that he performs an initial preconcentration in a vacuum evaporator.

CONCLUSIONS

The loss of high molecular weight humus material from limnic waters entering the Baltic Sea is implied by comparison of data from the stations of the present study. As colloid flocculation under saline conditions is a well-known phenomenon, this mechanism suggests itself. Jerlov has observed particle formation in admixtures of sea water and humic Swedish pond water; therefore, the present data might reflect this same process.

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