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MACROMOLECULAR CHARACTERISATION OF BLACK SEA PARTICULATE ORGANIC MATTER (POM) BY ANALYTICAL PYROLYSIS: A COMPARISON WITH CULTURED MICROALGAE

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ABSTRACT

Suspended particulate organic matter (SPOM; 0.7-200 μm) is composed mainly of phytoplankton in the euphotic zone but the contribution of detritus, aggregates of bacteria and micro-zooplankton might be important depending on the season and the trophic status of the marine environment. Majority of the larger particles (LPOM; 200-2000 μm), collectable by tow is considered to be composed of zooplankton. Pyrolysis-GC/MS has previously been successfully applied in order to characterise the bulk macromolecular composition of SPOM in the Black and the Mediterranean Seas. In this study, spatial and vertical variations in the macromolecular composition of SPOM and LPOM (together called POM), collected at 5 stations during the cruise of *R/V* Knorr in May 2001 were determined. Such classical oceanographic parameters as POM elemental composition, *in-situ* flourescence and chl-a were compared. In addition, different species of phytoplankton cultures were pyrolysed in order to compare with, confirm and complement the findings on SPOM and to use as reference information for field studies. Centrifuged and freeze-dried cultures were pyrolysed under the same conditions used for the analyses of POM. Pyrolyses were performed at 700°C/10s and evolved products were analysed by GC-MS. Reactive pyrolysis (thermal degradation in the presence of a silylating or methylating reagent) was also applied to selected samples to obtain further information on polar compounds.

Pyrolysis products were selected as markers and the contribution of each marker to the total intensity of all the markers were calculated as a percentage and termed 'relative concentration'. These products were grouped as aromatic hydrocarbons, *n*-alk-1-enes, *n*-alkanes, cyclopentenones, furans, phytadienes, phenols and nitrogen-containing compounds and then, were classified as carbohydrate, lipid, protein, and chlorophyll markers. Aliphatic hydrocarbons (*n*-alk-1-enes and *n*-alkanes) are associated to lipids, nitrogen-containing compounds and phenols are mainly derived from proteins, furans and cyclopentanones from carbohydrates and phytadienes from chlorophyll.

The distribution of pyrolysis products released from SPOM collected in surface waters of different sites was quite similar. The relative concentrations of furans, aliphatic hydrocarbons and phytadienes changed remarkably with depth. Lipid markers increased through the oxycline while their relative concentration decreased again in the anoxic zone, at least partly because of the relative dominance of protein markers. The relative concentration of furans decreased with increasing depth. Further molecular information on carbohydrate and lipid components was obtained from reactive pyrolysis. For instance, markers of monosaccharide units not detected in conventional pyrolysis, e.g. levoglucosan, were identified in reactive pyrolysis confirming the contribution of primary carbohydrates. Vertical variation in phytadiene relative concentration was consistent with in-situ fluorescence. For example, less remarkable secondary fluorescence maximum located within the oxycline of the cyclonic station was determined by the sharp increase in the relative abundance of the phytadienes. Despite the increase in lipid markers, the ratio of lipids to phytadienes diminished as such depths.

Replicate analyses of cultured phytoplankton samples showed that the relative concentration of most of the makers was practically invariant for the examined species. This suggests that an average marker distribution could be established as representative for living algal biomass. The constituents of algal pyrolysates exhibiting the largest inter-species variations were furans, aliphatic hydrocarbons and chlorophyll markers.

Not unexpectedly, observed pyrolysis products of the phytoplankton cultures were generally similar to the euphotic zone SPOM whereas the pyrolytic pattern of LPOM was different. For all the samples the most abundant pyrolysis product of both marine SPOM and algal cultures was toluene. Though its source is still uncertain our experiments showed that the source of the high proportions of toluene observed in SPOM could derive from pyrolysis of photosynthetic organisms and not necessarily from refractory organic matter. Chloropnyll markers, namely phytadienes, found as principal products of phytoplankton pyrolysates, occured at lower relative concentrations in marine samples. This indicates the importance of the contribution of non-photosynthetic organisms having similar macromolecular composition with the photosynthetic ones to the SPOM pool in the euphotic zone of the marine environments. Alternatively, loss of chlorophyll markers during the early steps of degradation might have occurred at much faster rates than loss of protein markers.