

Organic geochemistry
 Marine chemistry
 Particulate organic carbon
 Particulates
 Géochimie organique
 Chimie marine
 Carbone particulaire
 Suspensions

Organic chemistry of sea water particulates Concepts and developments

G. Cauwet
 Centre de Recherches de Sédimentologie Marine,
 Centre Universitaire, avenue de Villeneuve, 66025 Perpignan, France.

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ABSTRACT

A review of present knowledge concerning the organic chemistry of sea water particulates. The distribution and chemical composition of particulate organic matter are considered, in order to establish whether knowledge in this field is sufficiently advanced or whether it must be extended. The processes of aggregate formation are described and the importance of colloidal matter, generally considered as dissolved material, is underlined. The article contains a number of recommendations concerning future studies.

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Chimie organique des particules en suspension dans l'eau de mer

RÉSUMÉ

Cet article est une revue des connaissances acquises dans le domaine de l'étude des substances organiques non dissoutes. Les résultats quant à la composition chimique des suspensions étudiées montrent qu'il reste beaucoup à faire dans ce domaine. L'étude des processus de formation d'agrégats nous amène à considérer l'importance de certaines grosses molécules que l'on considère généralement comme dissoutes mais dont la plupart sont à l'état colloïdal. Quelques recommandations pour les travaux futurs sont données en conclusion.

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INTRODUCTION

Particulate matter in the oceans may be considered to be of two main types: living organisms and detrital material. The latter is generally composed of organic fragments, clays and carbonates, on which organic substances, colloids and metals may be fixed or adsorbed.

Living organisms are chiefly present in surface water, to a depth of 100-300 m. A great number of biochemical reactions occur in this zone and the organic material undergoes considerable transformation, resulting in the creation of particles which together with mineral particles provide the sea floor with sediment.

Many extensive studies have been made of the particles in the euphotic layer (Zeitschel, 1970; Sutcliffe *et al.*, 1970; Flemer, Biggs, 1971; Wada, Hattori, 1976), but only a few deal with the organic geochemistry of deep sea suspensions. This is a consequence of two facts:

a) particulate organic carbon concentration amounts to only 5-30 $\mu\text{g/l}$ in the deep sea, while it sometimes reaches ten times these values in the upper layer (Copin-Montegut, Copin-Montegut, 1973; Hobson, Menzel, 1969; Jacobs, Ewing, 1969; Menzel, Ryther, 1968; Williams, 1972); b) the results of elemental analysis of deep sea particles show nearly constant values of organic carbon. This result was for a time interpreted as indicative of the stability of organic matter. Further studies of organic matter in suspensions and in sediments suggest that evolution and degradation occur below the euphotic layer (Eadie, Jeffrey, 1973).

The average concentration of particulate organic carbon (Wangersky, 1974 and 1976) in a water column measuring 4 000 m from the surface to the bottom amounts to 100 g/m^2 , and POC in the world oceans must be about 2×10^{16} g. The so-called dissolved organic carbon exists in concentration of about 0.5 mg/l , so that

the total quantity in a water column of 1 m² amounts to some 3 kg, which is two orders of magnitude greater than the amount present in living organisms (Fig. 1 a). The stock of organic substances is large, but some of them are resistant to assimilation, while simple assimilable molecules are too widely dispersed to provide subsistence for organisms such as filter feeding animals.

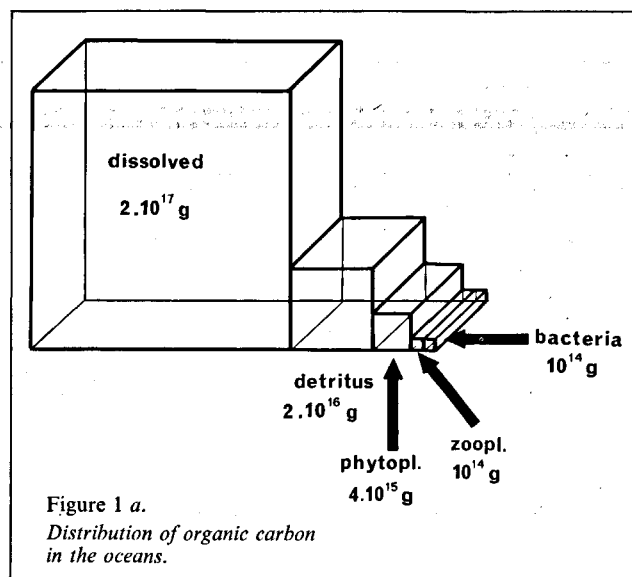
It would appear important to obtain more detailed information concerning this enormous quantity of organic matter, the relative stability of which suggests that it might sometimes be used as a geochemical tracer and thus provide information about the dynamics of the oceans. It is the purpose of this paper to determine the state of knowledge in this area, how it may be extended and what may be expected from new studies.

METHODS

Particulate matter may be recovered by filtration or centrifugation. The latter technique has not been applied extensively enough to determine whether or not it is preferable to the former, although Breck (1976), comparing filtration through a 0.45 µm filter with centrifugation, found a 30% better recovery by centrifugation.

Filtration is widely employed, but both the porosity and the nature of the filters vary from one experiment to another. Millipore or equivalent filters, made of cellulose nitrate or acetate, are commonly used, but while suitable for microscopic studies, they cannot be used for further extraction or for carbon analysis. Various pore sizes have been used, ranging from 0.22 to 5 µm; 0.45 µm is now generally accepted as a theoretical limit between dissolved and particulate matter. Glass fibre filters have been utilized to collect material for organic analyses and carbon determination. These contain some carbon which cannot be removed by baking at 400°C but they appear to be satisfactory for most purposes. Silver filters, which have also been used in various pore sizes (Gordon, 1970 a; Gordon, Sutcliffe, 1974), contain less carbon than the others and can be used without pretreatment.

Irrespective of the differences in pore sizes and filter type, some experiments show that filters can retain a considerable amount of smaller particles (Sheldon, Sutcliffe, 1969) or dissolved substances. Saliot (1975) has shown that they can retain as much as 22% of a fatty acid solution. He corroborated the results of Quinn and Meyers (1971), who found up to 80% retention of heptadecanoic acid on a 0.45 µm filter, but from small volumes of water (0.5 l). This could perhaps suggest that



centrifugation would be a better alternative. We shall see later that the problem of the separation of dissolved and particulate carbon has yet to be resolved.

The major constraint in carrying out chemical analyses of particulates is that such small quantities are involved. Enormous volumes of water must be filtered in order to obtain enough material for analysis. Handa (1972), in an extensive study, filtered several tons of water for each sample. Recent methods, with an immersed pump, allow great quantities of water to be filtered without the necessity of handling large volumes.

DISTRIBUTION

The distribution of particulate organic carbon shows regional variations, especially in surface waters, and a vertical gradient. Seasonal variations are relatively important in surface waters and sometimes also occur to a certain extent in deeper layers. All the data reported for surface waters include both living and non-living particles, so that the high values recorded are not limited to detritus and aggregates, while the seasonal variations are difficult to interpret.

Particles may be classified as mineral, organic or organo-mineral. Some authors (Lascazatos, 1974) have tried to separate organic and mineral particles, and have obtained interesting results concerning size distribution.

Surface water values have been reported for tropical waters in the Atlantic Ocean (Wangersky, Gordon, 1965); particulate carbon is more important in the surface film (20-120 µg/l) than in the few underlying metres (14-58 µg C/l). These values are higher in the productive area of the Guinea Current (200-800 and 50-200 µg C/l). In other areas of the Atlantic Ocean, values averaged 60-100 µg C/l, with higher values in April for the 0-100 m layer (Menzel, Ryther, 1964; Riley *et al.*, 1965; Gordon, 1970 b). More curious was the observation by Szekiolda (1967) of parallel bands of high and low carbon content, along the coast of Somalia. He attributed this phenomenon to a local upwelling.

Below the immediate surface layer, there is a decrease in particulate carbon. The gradient may be sharp, and is

generally of limited vertical extent to a depth of 200-300 m, at which point the deep water situation is reached, with a quite constant carbon concentration disrupted only by pronounced increases associated with particular water masses.

In deep water, particulate organic carbon is less abundant, but a large proportion of this matter is non-living, and no direct correlation can be made with surface values.

Few data are available which allow regional comparison. Riley (1970) compiled data obtained in deep water, and with the exception of one station with a high content of $75 \mu\text{g C/l}$ (Menzel, Ryther, 1964), values ranged between 20 and $50 \mu\text{g C/l}$. In the Pacific Ocean, values appear to be slightly higher, amounting to about $50 \mu\text{g C/l}$ (Parsons, Strickland, 1962); higher contents are associated with particular water masses (Dalpont, Newell, 1963; Hobson, 1967).

From all the data, it appears that the Pacific Ocean is probably more layered than the Atlantic Ocean; the study of particulate matter could provide information concerning the origin of these water masses.

SIZE AND MORPHOLOGY OF PARTICLES

Particles are generally recovered by filtration on $0.45 \mu\text{m}$ pore size filters. This is obviously a theoretical limit, and smaller particles are present in sea water. Gordon (1970 *a*) made an important study of particles greater than $5 \mu\text{m}$, which he examined for their morphology and by staining for carbohydrates and proteins. He found four types of particles: 1) aggregates composed of a variety of organic and inorganic sub-units, exhibiting an intense coloration by carbohydrate staining (Schiff reagent) and a lighter one by protein staining (bromophenol blue reagent); 2) flakes, composed of thin, more or less circular particles, exhibiting intense protein staining and less carbohydrate; 3) fragments, resembling pieces of organized tissue, showing intense carbohydrate but no protein staining; 4) unclassifiable particles. He noted that aggregates were more abundant in surface waters. This higher content in surface water may be explained if we bear in mind that bubbling can be responsible for aggregate formation from smaller particles. In this investigation, Gordon examined only particles greater than $5 \mu\text{m}$ but smaller particles are numerically more abundant and can spontaneously form larger particles by aggregation (Sheldon *et al.*, 1967; Sheldon *et al.*, 1972).

The dialysis of sea water has resulted in the recovery of nondialysable material amounting to about six times the quantity of particles recovered by filtration (Breck, 1976). While we have to take into account the existence of soluble high molecular substances, it seems possible that a great part of them are in a colloidal state.

If one accepts the idea that "dissolved" organic matter in deep sea is half composed of colloids, this will give a somewhat different distribution of organic carbon (Fig. 1 *b*).

If we except biological processes, most of the chemical reactions occurring in the sea must be in this colloidal

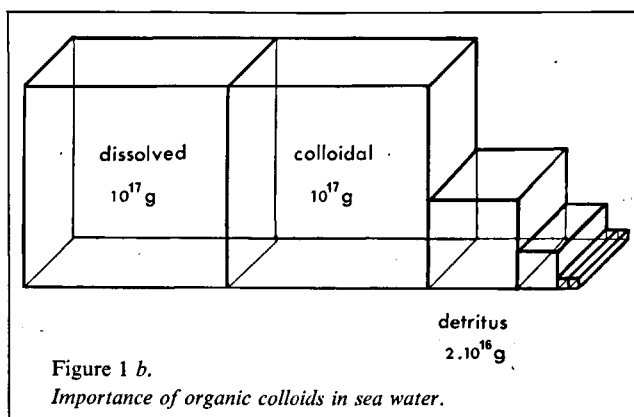
fraction. The detritus are for the most part too inert to play an important role in chemical reactions, while the strictly dissolved compounds are rapidly degraded by organisms. The colloidal fraction is thus responsible for the fixation of metals, for aggregation and for some sedimentation processes. It has been proved that it plays a very important role in the fixation of pesticides and hydrocarbons and must be considered in all studies dealing with pollution (Boehm, Quinn, 1973; Pierce *et al.*, 1974).

Thus the small particles are probably of diverse origin and composition, even if they have the same appearance, and cannot be readily classified by visual observation. The identification of non-living particles is not easy and requires further investigation.

CHEMICAL COMPOSITION

The elementary composition of particulates has been widely reported (Menzel, Ryther, 1964; Holm-Hansen, 1966; Parsons, Strickland, 1968). The C/N ratio, the order of 5/8 in surface waters, increases to 10/12 with depth, indicating that proteins are more readily utilized than are carbohydrates. Handa (1968, 1972) has confirmed this result, showing that a great part of the carbohydrate content is present as a polysaccharide which might be expected to be refractory.

The biochemical analysis of suspensions is less advanced and we have only scanty information. This is because of the large quantity of material required for such studies. With the exception of the work of Degens (1968) on nitrogenous compounds, especially amino acids, all the biochemical studies of particulate matter deal mainly with carbohydrates. The diversity of some results (Parsons, Strickland, 1962; Holm-Hansen *et al.*, 1966;



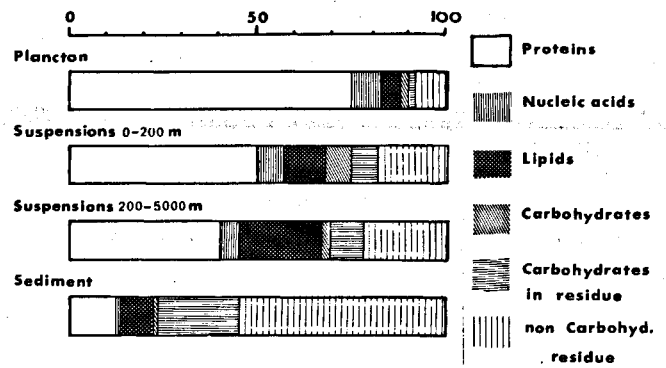


Figure 2
Biochemical composition of plankton, suspensions and sediment (from Agatova and Bogdanov, 1972).

Hobson, 1968) concerning the proportion of carbohydrates or the ratio to protein-like material, points to the need for further studies in this field.

Handa (1968, 1969, 1972) made a very complete study on this subject, and demonstrated the existence of a polysaccharide which he found to be a D-glucan, a water-insoluble fraction yielding glucose, galactose, mannose, xylose and glucuronic acid on hydrolysis. But these results concern only samples from the Western Pacific off Japan, and Handa appears to be convinced that the carbohydrate composition varies from one area to another.

Agatova and Bogdanov (1972) found a different distribution of materials, with a percentage of lipids which increased with depth (10 to 20%) and few carbohydrates (15%) (Fig. 2). The results of Handa (1968, 1969, 1972) and Hobson (1967), suggest that carbohydrates may have been underestimated in their studies.

As may be seen, virtually nothing is known of the molecular composition of organic matter in particulates. The opinion of Handa concerning the non-degradability of certain polysaccharides in deep water is not universally shared. In fact, the stability of these compounds is somewhat relative. As we now know, probably no substance can be considered definitively nondegradable; it is merely a question of degradation rate.

Some results (Parsons, Strickland, 1962) are relatively difficult to interpret: for deep samples, they found 41 $\mu\text{g/l}$ of glucose equivalent carbohydrate, 87 $\mu\text{g/l}$ protein and only 50 $\mu\text{g/l}$ carbon, equivalent to about 100 $\mu\text{g/l}$ of organic material. If we exclude an experimental error, this numerical discrepancy raises questions about the nature of deep suspended organic matter. With the exception of the water soluble fraction the carbohydrates are detected by hydrolysis, but we have no information about the remaining noncarbohydrate materials. As an example, the hydrolysis of humic acids extracted from marine sediments yields amino acids in quantity, but also lipids and carbohydrates; this does not mean that humic acids are proteins or polysaccharides, but that some heteropolycondensed molecules are present. It is highly probable that most organic matter in the deep sea is in the form of heteropolycondensed molecules, containing important carbohydrate and protein chains. These molecules are in a colloidal state in the supposedly dissolved material, which can be adsorbed on, or aggregated with particles, as a result of various physical or biological processes.

ORIGIN OF ORGANIC SUSPENSIONS

If we keep aside the atmospheric inputs, the origin of non living particulate matter in sea water can be of two kinds: an inheritance from the land mass as a result of coastal weathering or river inputs, or formed *in situ* from organisms or dissolved organic matter. The first group of inputs, important only in the land-influenced areas, consists of mineral particles (clays, carbonates, very fine sand...), together with detritus originating from terrestrial plants. These are rapidly dispersed or settled along the beaches. The second group consists mainly of a mineral part, composed of the skeletons of organisms, and an organic part consisting of detritus and faecal pellets derived from marine organisms or of aggregates formed *in situ*. We shall attempt to explain the mechanisms responsible for this aggregation.

Baylor *et al.* (1962) and Sutcliffe *et al.* (1963) have shown that organic matter is adsorbed on bubbles in sea water. Baylor (1962) found that phosphate was strongly adsorbed on bubbles and concentrated in the surface layer. These authors demonstrated that organic matter was associated with the adsorption process and suggested that it may serve as an anion binder. Further experiments by Sutcliffe *et al.* (1963) have shown that phosphates are bound to these organic molecules with a molecular weight higher than 300. They suggest that such large organic active molecules adsorb on to bubbles and produce monomolecular films which may be aggregated into insoluble organic particles. The agitation of foaming produces repeated collisions and results in a semi-stable colloidal suspension of organic materials. Further aggregation allows the particles to settle out (Menzel, 1966; Kane, 1967). Experiments on bubbling in filtered sea water by Riley *et al.* (1965) revealed the formation of particles; up to 70 $\mu\text{g/l}$ of particulate carbon can be recovered.

From the bubbling experiments it appears that particle formation is rapidly inhibited unless they are removed from the water. The decreasing yield after filtration on 0.22 μm filters would suggest the importance of bacteria, but the formation of particulates remains important even after sterilization procedures. The part played by bacteria in the process is probably important but it is not the sole factor. Large organic molecules can play a significant role in these phenomena.

Table
Sinking rate in metres by day of various sizes and kinds of particles (from Riley, 1970).

			Range	Mean
Inshore	Aggregates	> 60 μm		2.9
		30-60	0.78-1.4	1.1
		15-30	0.31-0.93	0.70
		6-15	0.31-0.57	0.50
	Misc. partic.	2-6	-	0.10
Surface	Flakes	-	-	0.17
	Aggregates	> 30 μm	0.24-2.6	1.0
		15-30	0.24-1.6	0.44
		6-15	-	0.19
	Misc. partic.	2-6	0.10-0.97	0.15
Waters	Flakes	-	-	0.18
	Aggregates	> 60 μm	0.97-2.1	1.8
		30-60	-	0.54
		15-30	0.32-0.54	0.45
		6-15	0.22-0.54	0.31
Offshore	Surface	> 60 μm		1.1
		30-60		0.83
		15-30		0.32
		6-15		0.26
		2-6		0.27
Waters	500 m	30-60		0.48
		15-30		0.29
		6-15		0.19
		2-6		0.12
		1 000 m	30-60	
15-30			0.38	
6-15			0.26	
2-6			0.25	
3 000 m	60			0.43
	30-60		0.34	
	15-30		0.29	
	6-15		0.38	
	2-6		0.22	

Experimental studies concerning the surface charges of particles in sea water provide some information on the importance of organic polymeric material in these processes. Neihof and Loeb (1972, 1974), measuring the surface charge of a variety of particulate matter in sea water, UV treated sea water and artificial sea water, demonstrated that all particles exhibit comparable negative charges in natural sea water, whereas they show different, positive or negative charges in artificial or UV treated sea water. The authors concluded that all types of particles are more or less coated with substances of high molecular weight; the nature of the suspended material determines the nature of the bond: hydrogen bonding, Van der Waals forces, electrostatic adsorption. Those results provide further reasons for the planning of studies of the polymeric material in sea water, the greater part of which is in a colloidal state.

Thus, a certain amount of information is available concerning the formation of particles by aggregation or adsorption on to air bubbles at the air-water interface; but it would be of great interest to determine the part played by biological processes and the role of physical phenomena in this connexion.

As far as the organic content of sediments is concerned, it should be recognized that the greater part of organic material undergoes recycling before it settles out. Riley

(1970) has suggested that a dynamic balance must exist between the utilization by bacteria, filter feeders and other biological processes, and renewal as a result of adsorption from the dissolved fraction. The consumption of organic particulate matter depends on the residence time in sea water, and the examination of the sinking rate is of importance. From the calculations of Riley *et al.* (1965) or the counts by Hobson (1967), we may presume a sinking rate of about 1-2 m/day. This rate obviously depends on the size and the nature of the particles, and Riley (1970) has reported varying values for aggregates and flakes (Table). The values obtained by Hobson (1967) and Riley (1965) are valid only for particles greater than 30 μm , but these represent the major part of the total volume of suspensions.

GENERAL DISCUSSION

Two important questions may be asked: firstly, concerning the manner in which organic matter may be present in particles; and secondly, concerning the chemical nature of this material.

The works of Handa (1968, 1969, 1972), Degens (1968), Saliot (1975) and others suggest some answers to the second question, but their data concern only a few hundred samples from the world ocean and there is no evidence for a constant composition of particles. Furthermore, many classes of compounds have not been investigated in detail: phenols, pigments, hydrocarbons, alcohols, organosulfur compounds... These studies would, however, be of a great interest in the determination of the origin and the evolution of organic compounds.

More important, probably, would be a knowledge of the quantity and nature of the condensed molecules which sometimes account for about 80% of the organic matter in sea water and particles. The nature and origin of this material must be related: the elucidation of some features of its structure would consequently enable us to determine whether it was formed *in situ* or inherited from the land mass. The existence of lignin-like compounds could be a good index of terrestrial origin (Pocklington, MacGregor, 1973), and the nature of the carbon-nitrogen bonding could also suggest a terrestrial humic type of material or a marine protein-like matter. Apart from the importance of elucidating the structure and origin of this polymeric material, it would also be of interest to estimate, on the basis of the structure, its degradability by organisms.

Adsorption capacities as far as metals or minor organic compounds (hydrocarbons, pesticides...) are concerned are also partly dependent on the structure of these large molecules. Breger (1968) suggested that this material has a composition related to polymerized fatty acids. This is probably true for some particular cases, when the complex organic matter has originated from one kind of organism, but not for the colloidal molecules dispersed in the ocean. The nature of the latter material is probably more complex, as its hydrolysis yields carbohydrates, aminoacids and fatty acids. The interaction of such molecules with organic compounds or metals dissolved in sea water results either in removal of the flocculate to the sediment or in an apparent change in the properties of each compound, involving changes in their behaviour. Association of humic acids with sugars and aminoacids have been noted by several authors and discussed by Degens and Reuter (1964). In brief, it may be assumed that almost all the chemical properties of the suspended matter are comparable with that of the organic substances coated on the particles.

To the question concerning the mechanisms by which the organic matter may be incorporated in suspensions, many answers may be provided. What is important is to know how equilibrium is maintained by a dynamic process involving consumption by organisms and adsorption from dissolved organic matter.

Particles originate, for the most part, with organisms: faecal pellets, skeletons, mineral particles, previously ingested and subsequently excreted. After further coating by, or aggregation with, organic molecules, they may re-enter the biological cycle. This could explain the constant values of particulate organic carbon below the euphotic layer.

Only a small number of these particles can reach the sea floor with a constant sinking rate; this accounts for the discrepancies between the calculated and measured rates. Some settling models (Brun-Cottan, 1976) based on Stokes' law can be applied only to particles greater than 5 μm .

If we consider the quantity of organic carbon contained in suspensions, it would seem not to be essential in the organic carbon cycle, but if the previous hypothesis is true, the quantity of carbon concerned can be two or three times more important. As far as mineral particles are concerned, it is possible to consider a residence time, but this is meaningless in the case of organic compounds which may be recycled more than once. We can only

consider a mean residence time for carbon, in relation to the flux through a given area (MacCave, 1975).

We are concerned here only with particles greater than 0.45 μm , but it appears that the greater part of organic material in sea water, considered as dissolved, is in fact in a colloidal state, i. e. incapable of passing through a dialysis membrane. This material, mainly composed of large molecules, can coat mineral particles very easily, and completely transform their properties. The adsorption of hydrocarbons (Boehm, Quinn, 1973), fatty acids (Meyers, Quinn, 1973) or pesticides (Pierce *et al.*, 1974) by humic matter can seriously affect their solubility in sea water. The nature and properties of that fraction of the organic matter are virtually unknown, but seem to play an important part in the chemical reactions which occur between dissolved and particulate matter in sea water.

CONCLUSION

This short review of present knowledge concerning the organic chemistry of suspensions suggests a number of conclusions:

1. the so-called "suspended matter" accounts for only a part of the non-soluble material;
2. very little is known about the chemical composition of particulates in the world ocean;
3. most interactions occur through organic polymers like proteins, polysaccharides and humic acids;
4. these reactions have yet to be more fully understood.

It is obvious that the organic chemistry of particulates and colloids should be further studied without delay. Two main ways may be envisaged: the development of experimental studies concerning aggregation and adsorption processes; and the organization of international research programmes centered on the organic chemistry of suspended matter.

If we offer a recommendation for future work, it is that the greatest effort should be in the field of co-ordination of studies and the improvement of techniques for the recovery and analysis of particulates.

More attention should be paid to the standardization of methods (pore size of filters, carbon analysis...) to render the results comparable and to the development of studies dealing with the chemistry of colloids in sea water, the interaction processes, and their influence on the cycling of organic carbon.

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