

1. INTRODUCTION

The workshop was held at the Oceanographic Institute in Paris, from 8 to 11 December 1999. Fourteen scientists in all, originating from ten different countries, attended the meeting at the invitation of CIESM.

The meeting was opened by the Director General of CIESM, Frederic Briand, who warmly welcomed all the participants and gratefully acknowledged the hospitality of the Oceanographic Institute with which the Commission enjoys a rich, century-old, history of close cooperation. Dr Briand exposed the basic philosophy of the CIESM Workshop Series, whereby scientists and experts working at the frontier of a subject are able to engage in an intense exchange of views, aiming at a critical assessment of existing knowledge and at the identification of directions for future research. CIESM is particularly concerned that emerging issues are tackled in a multidisciplinary fashion. This is achieved by selecting topics through close concertation between the six scientific committees of the Commission, and by inviting experts from distinct horizons and disciplines.

Dr Scott Fowler, Chairman of the CIESM Committee on the Chemistry of the Marine Environment, followed by recalling the genesis of the current workshop. At a recent CIESM workshop focused on ocean-atmosphere processes, the sea surface microlayer (SML) was identified as a key interface to study in order to better understand the fate and effects of airborne contaminants and particulate inputs into the Mediterranean Sea. This interest was further strengthened by concern expressed in the scientific community that the relative importance of the SML may have been underestimated, both as a site of adverse biological effects and as a medium for the transfer of energy and material between sea water and the atmosphere. Despite scattered research activities on SML in various oceanographic fields, a general understanding of the impact of anthropogenic activities on the sea surface ecosystem is not yet available. This workshop aims to bring together a small group of active researchers to assess in multidisciplinary fashion the current state of knowledge of SML controls on the biogeochemistry of materials in the Mediterranean Sea, and to establish directions for future research. A primary goal of the workshop will be to formulate propositions towards an integrated research agenda on the SML in the Mediterranean Sea.

Topics to be reviewed and discussed included :

- distribution, transfer and fate of contaminants, trace elements, natural organic compounds and nutrients in the SML;
- trace gas exchange through the SML;
- physical nature of the SML;
- biology and primary productivity of the SML;
- toxic effects in the SML;
- photochemical processes and their role in radiation energy transfer;
- new and unique techniques for sampling the SML.

The following abbreviations are used throughout the report: SML = surface microlayer, SNAN = surface nanolayer, SSL = subsurface water.

2. NATURAL PROCESSES

The sea surface microlayer is the oceanic boundary region between the atmosphere and the ocean. As such, it plays a vital role in affecting transfers between these two major environmental reservoirs. In recent decades, the interaction between atmospheric and oceanic processes which govern most biogeochemical cycles and influence climate has become increasingly evident. For example, the idea postulated almost a century ago that iron inputs from the atmosphere affect ocean primary production has recently been supported by direct iron fertilisation of small areas of the oceans. The SML could be important in global scale processes such as the production and uptake of radiatively active gases (*e.g.* carbon dioxide and dimethyl sulphide), but this has not yet been verified.

Transformation processes of compounds in the atmosphere are largely driven by (photo-)chemical processes, and the biogeochemical flux in the ocean is largely biologically-driven. In the SML chemical and biological transformation processes interact in a complex manner. Obviously, the SML plays a crucial role in the interaction between the ocean and the atmosphere, yet our understanding of its chemical and biological properties and of its role in biogeochemical fluxes is poor. This handicaps our efforts to understand and model the global system.

The sea-surface consists of a number of adjacent compartments with transformations/transfer processes operating within and between them (Figure 1).

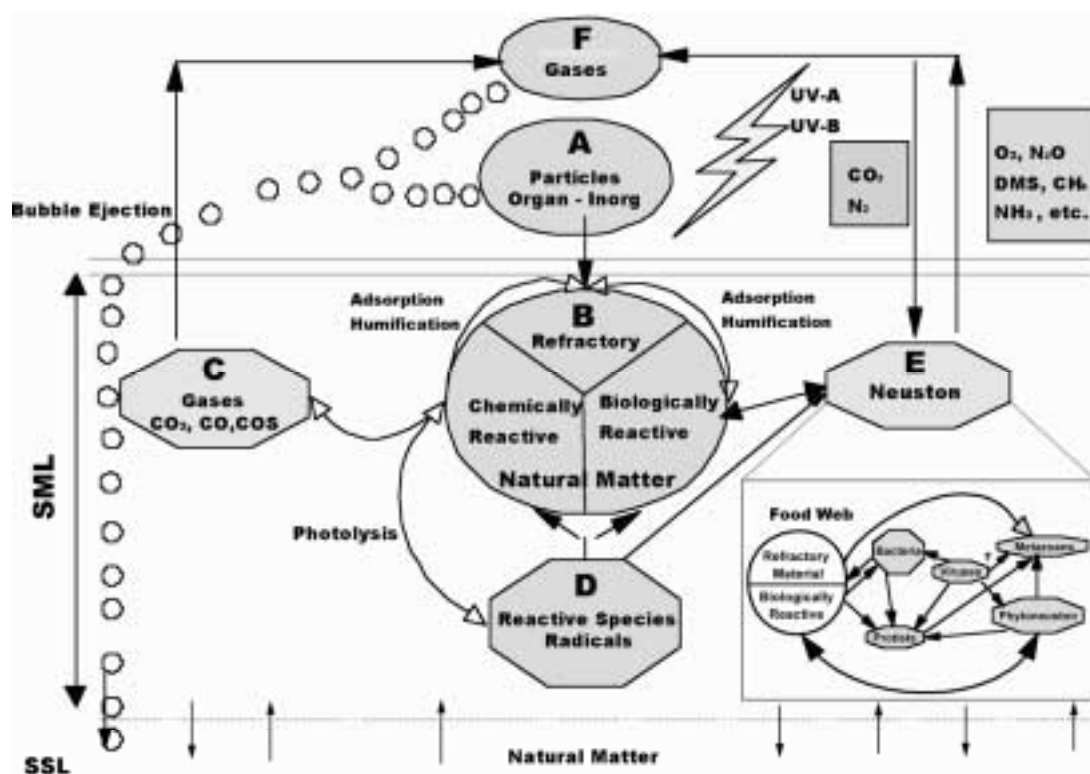


Fig. 1. The role of the sea-surface in Mediterranean Sea - atmosphere interactions : global climate.

2.1. Reservoir A : particles depositing from the atmosphere to the SML by wet (mainly rain in the Mediterranean region) and dry processes.

No distinction is made between inorganic (*e.g.* mineral dust) and organic (soil dusts, black soot carbon) since these examples represent the end-members of the spectrum of mixed inorganic-organic material, which enters the microlayer from the atmosphere. In the opposite sense, wave breaking and the resultant formation of bubbles will enhance the aggregation of organic material in the water column to form polymeric particles, and aid in dispersing microlayer organisms into the atmosphere.

Major research questions are :

QA1 – What is the reactivity of black carbon (soot) particles in the microlayer ?

Soot particles are likely to present very active sites for adsorption of trace substances *inter alia*. This input is likely to be particularly important in the northern sector of the Mediterranean due to the proximity of substantial industrial and agricultural sources of such particles from combustion processes.

QA2 – What is the importance of dust inputs in providing nutrients (P, N, and possibly Fe) for primary and bacterial production ?

Again the Mediterranean is a key area for such studies because of the large intermittent inputs of dust from the Sahara.

2.2. Reservoir B : non-living dissolved and particulate material (organic - inorganic, generally a spectrum between these two end-members).

The material in this reservoir is involved in the following types of reactions (see Carlson, 1993) :

- a) adsorption of chemically and biologically active material to refractory particles; in this process the absorbed material itself becomes refractory; humification is the conversion of chemically and biologically reactive material into refractory material;
- b) formation of trace gases (*e.g.* carbon dioxide, carbon monoxide, carbonyl sulphide) by photolysis, fueling to Reservoir C;
- c) production of free radicals and reactive species by photolysis (Reservoir D);
- d) formation by photolysis of low molecular weight labile substances such as organic acids (*e.g.* carboxylic acids and carbonyl compounds), ammonia and phosphate.

Major research questions are :

QB1 – What is the role of the SML in the formation of free radicals and other reactive species ?

Several microlayer properties favour the formation of free radicals. First, solar (particularly UVB) radiation is largely unattenuated by passage through this thin layer of seawater. At the same time, concentrations of reactive organic matter, especially lipids and proteins, and transition metals (which can act as catalysts), are often high near the sea surface.

QB2 – What is the importance of the process by which refractory polymers are formed in the microlayer ?

Such polymeric material may play an important role in stabilising the physical structure of the microlayer, and serve as an inert sink for organic material. The role of bubbles in enhancing this process has already been mentioned (Reservoir A).

2.3. Reservoir C : photochemically produced gases (carbon dioxide, carbon monoxide, carbonyl sulphide) - already mentioned under 2.2.

Major research questions are :

QC1 – Is the SML a preferred zone for the photochemical production (and destruction) of gases such as CO₂, CO and COS, as compared to the underlying seawater ?

The SML receives largely unattenuated solar radiation and generally contains abundant organic precursors, but destruction processes may be similarly enhanced, and the microlayer has a small volume compared to the subsurface water in terms of production/destruction of trace gases per unit area of water column.

QC2 – Is the input flux of CO₂ from the atmosphere controlled by the extent of photochemical destruction of organic carbon in the SML ?

This is a follow-up of the “flux capping” hypothesis (GESAMP, 1995, pp. 43-44) which remains a largely unrecognized yet important issue. Strong UVB radiation causes photomineralisation of organic carbon in the SML, leading to an increase in the concentration of dissolved inorganic carbon. Simultaneously photosynthesis is limited, which implies a decrease in the assimilation of inorganic carbon. Steady state flux of CO₂ depends on the concentration gradient: when concentration of inorganic carbon increases in the SML, then flux from the atmosphere will decrease.

2.4. Reservoir D : formation of free radicals and other reactive species – already mentioned under 2.2.

The major research question is :

QD1 – What is the reactivity and role of such reactive species in microlayer transformations ?

This is a complex and largely unexplored area of study. A way ahead may be detailed research into the formation and reactivity of hydrogen peroxide since measurement of this compound is relatively straightforward. The measured concentration of hydrogen peroxide may be low, but it may still be important since the small concentration may result from its rapid consumption due to reaction with other species/chemicals.

2.5. Reservoir E

Generally, the food web structure of the SML is not well known. Deviations from the general food web structure observed in the underlying waters will be likely due to the large fluctuations of the physical and chemical microenvironment, and to the fact that some of the planktonic and benthic species have neustonic life stages.

Major research questions are :

QE1 – Are there major differences in the species composition and diversity between the communities of the SML and the underlying water ? Is the SML enriched in bulk biomass or in particular species ? Do these species exhibit pronounced diel patterns in their activity related to the fluctuating chemical and light environment ? How stable are the SML communities spatially (vertically/horizontally) and temporally ? Is the ratio between overall production and remineralization of organic matter in the SML different from the underlying water layer ? What are the specific adaptation strategies of the populations inhabiting the SML ? Is the SML an important site for larval and species dispersal ?

More specific research questions are :

• *In relation to bacteria*

QE2 – Are there bacterial species specific to the SML ? If so, what are their physiological adaptations to this specific microenvironment ? Could these bacteria be exploited for biotechnological applications (pharmaceuticals, cosmetics, etc) ?

• *In relation to viruses*

QE3 – How does viral diversity of the SML relate to that in the underlying water and to the microbial community present in the SML ? Are these viruses exhibiting primarily a lytic or lysogenic cycle ? Is there a strong diel variability in the infection of hosts ?

Virus host systems specific for the SML should be established. The specific importance of this aspect is the potential use of such systems for biological mitigation of harmful species.

• *In relation to protists*

QE4 – Do protists control bacteria in the SML to a similar extent as in the underlying water ? Are the protists of the SML also mixotrophic in the same ratio as in the underlying zone ?

• *In relation to phytoplankton*

QE5 – What are the physiological capabilities of phytoneuston species (photosynthesis, irradiance) particularly in relation to pigmentation and release of organic matter ?

• *In relation to metazoans*

QE6 – Are there specific feeding strategies for neuston species ? Do they utilize the organic matter of the SML to a larger extent than similar species living in the underlying water ? Which groups of organisms spend part of their life cycles in the SML, what is the specific benefit for them, and what are the specific adaptation mechanisms for this particular microenvironment ?

2.6. Reservoir F

The atmospheric reservoir of trace gases both receives gases emitted from the oceans and inputs them in the reverse direction. Gases exchanging between the two reservoirs must traverse the sea

surface microlayer, and it is a long-standing research issue as to the potential importance of the SML in moderating the exchange processes. It is generally agreed that the microlayer on the open oceans is insufficiently coherent to be a direct resistance barrier to gas transfer. The situation in coastal waters is less clear-cut since under calm conditions visible slicks are sometimes apparent and they may play a role in reducing the rate of gas transfer. However, any effect is almost certainly through the damping of capillary waves, rather than through any direct resistance effect. A more open question concerns the role of soluble surfactants (the so-called “wet” surfactants) which display some degree of surface activity but also have a considerable concentration in the bulk phase. Some laboratory studies imply that these surfactants can indeed significantly reduce the gas exchange rate, although the mechanism is poorly understood. However, these results have been called into question by very recent field measurements of the exchange rate performed during the IronEx, iron fertilisation experiments conducted in situ in the equatorial Pacific; there no change in the exchange rate was observed although the level of biological activity, and presumably therefore the availability of organic surfactant material, increased by more than an order of magnitude during the course of the experiment.

The major research question is:

QF1 – Can soluble surfactants in the SML have a significant role in determining air-sea gas exchange rates and, if so, under what circumstances does the effect occur and what is its magnitude?

3. ANTHROPOGENIC INFLUENCES

There is evidence of a unique and important biological community inhabiting the sea surface. How do human activities impact this ecosystem and what is the importance of the sea surface to human populations surrounding the Mediterranean Sea? The conceptual model in Figure 2 shows the interaction between contaminants and the biological community, and traces the pathways for the fluxes between the living and non-living compartments.

3.1. Human health

3.1.1. Contamination of the sea surface with pathogenic bacteria

Q. – Do pathogens occur in the SML of the Mediterranean Sea and, if so, at what concentrations? What are their lifetimes in seawater? What are the sources and possible routes of human exposure? What is the importance of aerosols, SML deposition on beaches, bathing in contaminated water?

Some studies from other marine areas demonstrate that pathogenic viruses and bacteria exist in higher concentrations in the SML than in the SSL (Dutka and Kwan, 1978; Plusquellec *et al.*, 1999). If such enrichments are a general phenomenon in all seas, then the Mediterranean should be no exception. Yet, qualitative and quantitative data on this aspect are not presently available for Mediterranean waters. Furthermore, little is known about the lifetimes of pathogenic microorganisms in seawater, but recent evidence suggests that pathogens introduced into seawater may remain viable for much longer periods than previously believed, i.e. days to months (Joux *et al.*, 1997). Although these bacteria may be exposed to UV stress, they may also be protected within the organic matrix of the SML. Nevertheless, virtually nothing is known of their behaviour and fate in the SML.

Relatively high human population densities is a characteristics of the Mediterranean Basin, which results in high inputs of treated and untreated domestic sewage to coastal waters. This may lead to increased human exposure to pathogens in marine aerosols along beaches. Also, recent epidemiological studies indicate that sea bathing in presumably “clean” waters may pose a significant risk to human health (WHO, 1998). Common bacterial and viral infections could lead to severe illness, skin diseases and morbidity. It is thus possible that enhanced pathogen levels in the SML are the primary vector for infection of sea bathers, whereas subsurface concentrations of the same pathogens, which are routinely measured by public health authorities, may not suggest any threat to public health. This aspect needs to be evaluated for Mediterranean coastal waters, particularly in areas frequented by bathers and in the vicinity of sewage outfalls.

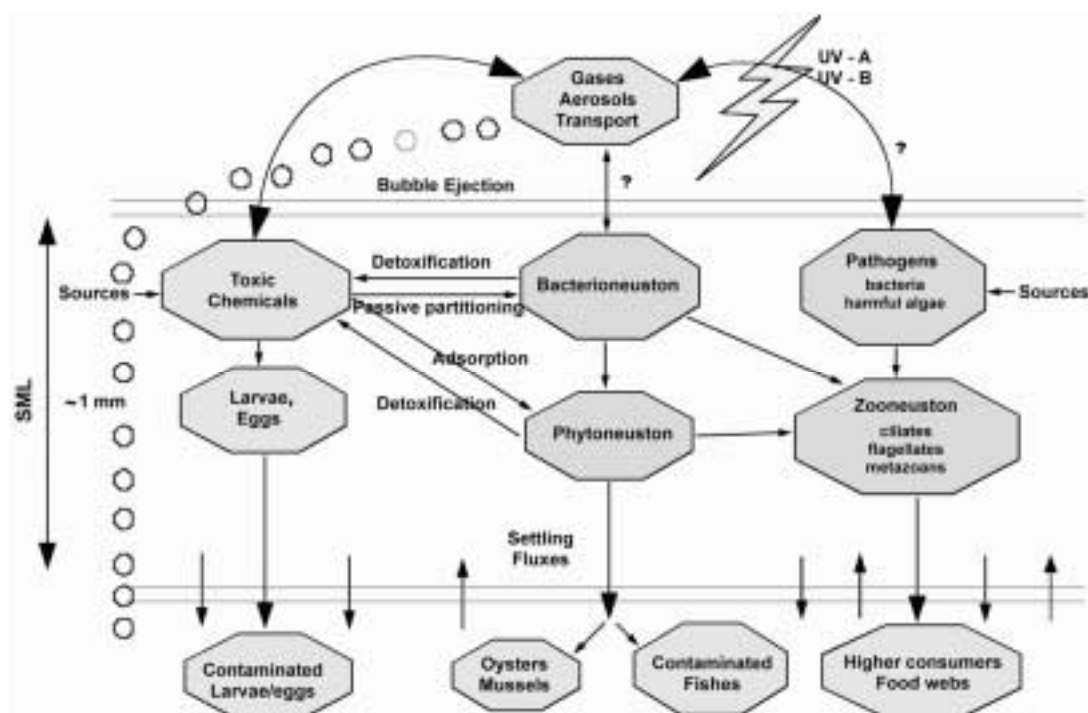


Fig. 2. The role of the sea-surface in Mediterranean Sea - atmosphere interactions : environment quality and contaminants.

A secondary route for infection of humans is through consumption of contaminated seafood. While bivalve culture is a common commercial practice around the Mediterranean, the very low amplitude of tides makes it unlikely that bivalves are significantly exposed to the SML.

3.1.2. Contamination of the sea surface with anthropogenic chemical contaminants

Q. – What is the concentration and size distribution of particles in the SML? In the Mediterranean, what is the concentration of different anthropogenic chemicals and their residence times in the microlayer? What are the sources of these chemicals?

Evidence suggests that the microlayer in many areas is highly enriched with a complex mixture of contaminants (EPA, 1990). Most of these contaminants are hydrophobic or associated with suspended particles (GESAMP, 1995; Liss and Duce, 1997). In general the data concerning this issue worldwide are scarce; for the Mediterranean they are extremely few (Cosovic *et al.*, 1977; Ho *et al.*, 1982; Cincinelli *et al.*, this volume).

To assess the composition and the concentration of anthropogenic chemical contaminants in the SML, the following methodological approach should be applied :

- a) The spatial distribution of the SML as it pertains to the chemical concentrations and chemical species composition should be studied.
- b) As temperature and solar radiations are important factors for the transformation of chemical species in SML (Falkowska *et al.*, 1999a,b), seasonal trends of the chemical concentration and species composition in the SML are important issues.
- c) Weather conditions should be also taken into consideration when the chemical composition of SML is examined, especially factors controlling the enrichment factor of chemicals in the SML.
- d) It is crucial to study the distribution of SML contaminants between the dissolved, colloidal, and particulate phases in order to understand processes in the overlying atmosphere and underlying water column (*e.g.* uptake by organisms). For comparative studies (*e.g.* in different areas), it is important that the same sampling devices are used.
- e) Simultaneous sampling of aerosol and the SML should be performed in order to precisely correlate the chemical composition of these different matrices.

f) Specific molecular markers and appropriate parameters (*e.g.* compound concentration ratios) can be used to reconcile the presence of various contaminants with their potential sources.

Some specific compounds proposed are :

- aliphatic hydrocarbons and specific tracers for oil pollution (*e.g.* n-alkanes, UCM, hopanes, steranes);
- PAHs (petrogenic, pyrogenic and retene);
- PCBs, pesticides and selected chlorinated compounds;
- phthalate;
- surfactants of domestic and industrial use;
- coprostanol (*e.g.* as a domestic sewage tracer);
- heavy metals (*e.g.* Pb, Cd, Hg, organometallic compounds, etc.).

g) Measurements of DOC and POC in the SML are useful as general parameters and for normalizing the concentration of the above mentioned tracers.

3.2. Bioaccumulation and food web transfer

Q. – At what rate are contaminants transferred from the SML to subsurface communities (plankton and nekton) ?

The SML is known to be a site of intense biological activity. Evidence indicates that a unique community exists within the sea surface, yet the food web structure and dynamics of the surface layer are poorly understood.

Neuston organisms include a wide variety of viruses, bacteria, microalgae, protists and zooplankters. Little is known about the structure and dynamics of these communities. The presence of high contaminant concentrations in the SML, such as those reported in different areas of the Mediterranean Sea (Ho *et al.*, 1982; Cincinelli *et al.*, this volume) might have a significant effect on neuston. Contamination results from passive mechanisms such as adsorption on, or diffusion across, biological membranes depending on the physical-chemical properties of the contaminant. Planktonic grazers living in and below the SML then consume these contaminated organisms. Depending upon sinking fluxes, these trophic relationships could contribute to the transfer of toxic compounds and elements through the entire food web leading to humans. One way in which this initial transfer of contaminants to deeper water food chains can occur is by the settling of fecal pellets and other forms of biodebris from neustonic grazers, as well as sinking aggregates of phytoplankton cells. For example, these particles sink out of the SML and are ingested and “re-packaged” by grazers and detritivores living in the SSL. While it is highly likely that this initial phase of the formation of particulate contaminants occurs in the SML, nothing is known of the processes involved or their rates of formation and transport out of the SML. Some insight into these processes could be obtained by deploying specially designed, floating sediment traps just beneath the sea surface to collect particles exiting the SML (Falkowska, 1999a).

Certain bacterial communities in the food web may contribute to the transformation of toxic compounds such as heavy metals and organic compounds (Ofstad and Lunde, 1978). Some previous studies have clearly demonstrated that bacteria isolated from the SML of different aquatic systems can adapt to high heavy metal concentrations by horizontal gene transfer (Lebaron *et al.*, 1993; Dahlberg *et al.*, 1997). The role of these bacteria has been extensively studied for bioremediation, but there do not appear to be any specific investigations of the role of the SML in these processes. If neuston are able to reduce the toxicity of some contaminants by biotransformation, the SML may be considered as a bioreactor, playing a key role in detoxification and in this way reducing the risk of the underlying waters and organisms becoming contaminated.

3.3. Biological effects

Q. – What species in the Mediterranean have neustonic life stages ? Are some of these commercially or ecologically important ? Are toxic effects occurring in the Mediterranean and is the species composition of the neuston community effected ?

The sea surface contains a biological community analogous to, but different from, that in the water column. That is, organisms ranging in size from viruses (nanoneuston or nanoplankton) to

large plants or fish (macroneuston or macroplankton) exist in both habitats (Hardy, 1982). The neuston community consists of a variety of species. Evidence suggests that these organisms could be important in the biogeochemical transformation and degradation of chemicals. Studies indicate that the sea surface is an important site for incubation of the reproductive and larval stages of many invertebrate (coral) and vertebrate (fish) organisms (Zaitsev, 1992). The sea surface is also a concentration point for anthropogenic contaminants coming from the atmosphere or water column. Studies indicate that biologically harmful chemicals can reach very high concentrations in the SML. Given the role of the sea surface as a biological habitat, this contamination could have important consequences for neuston.

Numerous studies demonstrate the toxic effects of collected microlayer samples on selected organisms in the laboratory (Hardy *et al.*, 1987b). Demonstrated sublethal effects include chromosome aberrations in fish embryos and delayed or abnormal development in echinoderm larvae. Acute toxicity (mortality) has also been shown in a variety of organisms. Preliminary evidence indicates toxic effects of contaminated SML on fish embryos *in situ* (Hardy *et al.*, 1987b). Studies in the New York Bight, the North Sea and Australia suggest that neustonic fish embryos, collected from contaminated nearshore sea surface areas, have greater incidences of abnormalities than those in offshore or more pristine areas (Longwell and Hughes, 1980; Cameron *et al.*, 1992). However, the overall effects of sea surface contamination on neuston or fish populations remain unknown. Furthermore, to our knowledge, studies of the biological effects of sea surface contamination in the Mediterranean Sea are critically lacking.

3.4. Photo- and bio-transformation and degradation

Q. – How important is the SML of the Mediterranean in the breakdown or transformation of anthropogenic compounds?

The microlayer receives high doses of solar radiation and also often contains high densities of microorganisms. Solar energy entering the sea surface is converted to other energy forms, *e.g.* thermal and chemical, the latter being stored in organic compounds. These compounds form the basis of initial transformations and cycling within the sea surface. Besides stimulating life processes, solar energy plays an important role in photodegradation processes. Photodegradation of these organic compounds may lead to the formation of even more toxic compounds (*e.g.* phenols). Radiation, especially UVB, is blamed for the inhibition of chemical processes including photosynthesis in the SML (Hardy and Apts, 1989) where neustonic species and DOM are likely to be affected. Recent DOC measurements and absorption spectra measured in the Baltic Sea correspond well with this hypothesis (Falkowska, 1999a,b). Whether a 12-hour cycle of organic matter transformation, caused by solar radiation, applies to the SML at Mediterranean latitudes remains to be tested.

Since DOC is an important source of carbon for bacterioplankton, future SML studies should focus on bacterial communities, and the kinetics of organic matter transformation caused by solar radiation and bacterial metabolism (see Kieber *et al.*, 1997).

3.5. Spatial and temporal structure

Q. – What is the temporal and spatial distribution of organisms and chemicals within the top meter of the Mediterranean Sea?

According to some, the sea surface consists of several distinct vertical layers with sharp gradients. To others, this description of the SML appears unrealistic and idealised. This difference of views will have to be resolved if one wishes to understand the dynamics of neuston or the distribution of organic material in the upper water column.

In addition, the biological and chemical characteristics of collected sea surface samples depend on the type of sampler used (Falkowska, 1999a,b). If there is a gradient of organic compounds according to their individual hydrophobic/hydrophilic properties, the most hydrophobic organic substances should be adsorbed in the uppermost layer. If this hypothesis is correct, certain substances of known hydrophobic/hydrophilic properties, such as saturated hydrocarbons, unsaturated lipids, PAH, refractory substances, radicals, photosensitizers, will be found along a corresponding vertical gradient.

Also, different microorganisms likely prefer different depths according to their UVB radiation tolerance, size and nutrient requirements. Bacteria that degrade highly hydrophobic anthropogenic contaminants could be highly enriched in the uppermost layer during the night when bacterial activity is known to be higher.

The SML is highly enriched in particles (Jullien *et al.*, 1982). This enrichment should be greatest in the uppermost layer of the sea surface because highly hydrophobic substances are fractionated from the water phase. Work in the Adriatic has demonstrated that the SML is enriched in natural organic matter (Zutic *et al.*, 1981; Marty *et al.*, 1988; Gasparovic *et al.*, 1998). It is highly probable that organic matter will be greatest during the daytime when photosynthetic activity is maximal. Day/night and seasonal trends of organic matter should be investigated further. As the northern Adriatic region is increasingly stressed by anthropogenic inputs of toxic chemicals and nutrients, studies of the sea surface in this region need particular attention and would greatly increase our knowledge of the initial processes of particle formation and aggregation in the SML.

3.6. The triad approach

Q. – Can sampling and analysis of the Mediterranean Sea surface be used as an effective approach to monitoring marine environmental quality ?

Our understanding of the environmental quality of the water/sediment interface has benefited greatly from application of the “triad” approach (Chapman *et al.*, 1996). This involves the simultaneous sampling of sediments for chemical analysis, toxicity testing and the evaluation of species population abundances and diversity. For monitoring the water column, a useful approach has been the adoption of the “mussel watch” concept, i.e. analyzing contaminants in the same or similar species of bivalve molluscs (*e.g.* mussels, oysters, etc.) which filter and bioaccumulate contaminants from a given location (Goldberg *et al.*, 1978; Farrington *et al.*, 1983).

Neuston inhabit the sea surface, where evidence suggests that contaminants concentrate from both the atmosphere and water column. Thus, neuston including fish eggs and larvae may be at particular risk of toxic effects. Neuston, through bioaccumulation of chemicals in the SML, may be useful indicators of the presence of contaminants. Because neuston are generally widespread, they could serve as bioindicators of recent pollutant inputs, both for nearshore sources and for atmospheric contaminants that are transported far offshore. Existing standard SML sampling techniques are relatively inexpensive and can be employed from small boats or by hand from beach areas. However, most studies to date do not provide information on contaminant levels, toxicity, or organism abundances in all surface layers at any single point and time. This renders delineating of interactions and determining time-dependent fluxes almost impossible.

The Mediterranean Sea is a very appropriate region to undertake field experiments, using the sea surface to assess marine environmental quality. Studies of the sea surface would collect, at the same time, samples of the SNAN, SML and SSL in various sites. These fractions should be analyzed for chemical concentrations, species abundances, and toxicity. Such experiments could then serve as a model for examining other oceanic regions. To maximize the scientific output from such studies, efforts should be made to sample simultaneously nearsurface atmospheric aerosols, SML chemicals, and micro- and macroneuston as well as subsurface water. In this way, the dynamics of processes occurring at the sea surface can be more precisely described.

CIESM may be a useful vehicle for launching such a project in the Mediterranean Sea. It encompasses a large and tested network of laboratories around Mediterranean shores and therefore could instruct various laboratories on how to apply the relatively straightforward techniques to sample the sea surface. Such a project would certainly contribute to establishing closer ties between the more advanced laboratories in the northwestern sector with those along the southern and eastern shores.

Photosensitized degradation of organic compounds in natural waters

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In the natural environment, organic compounds may undergo different transformations among which photochemical degradation seems to be very important. Such processes are more significant in surface waters, particularly in the sea surface microlayer which is characterized by enrichment of organic matter, and where the major part of solar light is available to promote photochemical transformations. Dissolved organic and inorganic compounds may alter the reaction rate of photochemical processes in natural waters, enabling in this way photodegradation of organic compounds which exhibit weak absorption at environmentally significant wavelengths. The absorption of sunlight (especially UV) in natural waters by dissolved organic and inorganic compounds leads to the production of a variety of transient species such as excited dissolved organic compounds, hydrogen peroxide, singlet oxygen, hydroxyl radicals, superoxide ion and organoperoxy radicals (Hoigné, 1990; Wolff *et al.*, 1981; Choudry, 1984; Haag and Hoigné, 1986; Momzikoff *et al.*, 1983). These transient species are highly reactive and can promote the photodegradation of different organic compounds (Klemenova and Wagnerova, 1990; Guiliano *et al.*, 1997; Nicodem *et al.*, 1998; Beltran *et al.*, 1993; Matuzahroh *et al.*, 1999).

The results of our study of photochemical transformations of selected organic pollutants, occurring in the waste waters of industries producing plastics, paints and adhesives in the Koper area (Slovenia) and subsequently diverted into the river Rizana and the Bay of Koper (Gulf of Trieste, northern Adriatic), are presented first. The second part of this paper presents the results of photodegradation of some polysaccharides.

Solutions of dibutyl phthalate, di(2-ethylhexyl) phthalate, acrylic acid, methyl methacrylate and acrylonitrile in distilled water, natural sea water, artificial sea water and riverine water were photolyzed using a photochemical reactor equipped with a 125 W medium pressure mercury lamp and by exposure to natural sunlight. Kinetic studies and product characterization were performed using gas chromatography, ¹H and ¹³C NMR spectroscopy.

The kinetic studies revealed different reaction rates in different reaction media. For the two phthalic acid esters the greatest reaction rate was observed in riverine water. The rate then decreased in natural and artificial sea water. From the calculated rate constants it became evident that dissolved organic matter (most probably humic substances as its major component) accelerated photodegradation, while dissolved inorganic ions produced the opposite effect. In the case

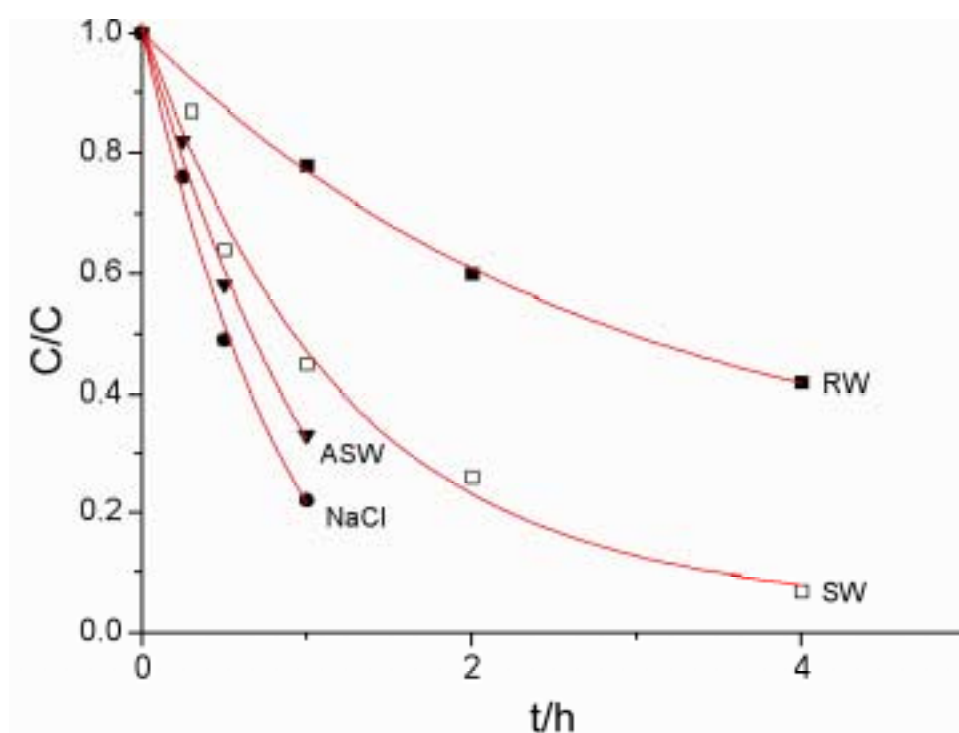


Fig. 1. Photodegradation of acrylonitrile in riverine water (RW), sea water (SW), artificial sea water (ASW) and NaCl solution

of methyl methacrylate and acrylonitrile (Fig. 1) the reverse effect was detected, i.e. the reaction rate was higher in both sea waters. The reaction rate of acrylic acid photodegradation was very similar in all reaction media.

Photodegradation of selected organic pollutants under field conditions was performed in quartz tubes exposed to natural sunlight during the summer period. About 25% of both the dialkyl phthalates degraded during 10 days exposure, while a lower photodegradation rate was observed in the case of acrylic acid and both acrylates. Hydrolysis of esteric bonds and decarboxylation of carboxylic acids are the most important reaction pathways in the initial stage of photodegradation.

Hyperproduction of mucilaginous material in the northern Adriatic has been observed for more than 250 years and recently occurred during the summers of 1988, 1989, 1991 and 1997. Mucous macroaggregates originating from phytoplankton contain various phytoplankton species and entrap zooplankton, bacteria, detrital and mineral particles (Stachowitsch *et al.*, 1990). The microscopic analyses of macroaggregates (biological composition) and NMR spectroscopic results suggest the presence of $\alpha(1,6)$ -, $\alpha(1,4)$ - and $\beta(1,3)$ - glycosidic linkages in crosslinked heteropolysaccharide structure (Kovac *et al.*, 1995). Considering the fact that carbohydrates constitute a major portion of mucous macroaggregates (Vollenweider *et al.*, 1992; Decho and Herndl, 1995) as well as particulate organic matter (POM) and dissolved organic matter (DOM) produced by phytoplankton (Biddanda and Benner, 1997), the photodegradation of the water soluble fraction of macroaggregates and selected polysaccharides (pullulan, laminarin) was studied in the second part of this work.

The study of polysaccharide photodegradation kinetics revealed an increase in monosaccharide concentrations which was followed colorimetrically (MBTH procedure, Johnson and Sieburth, 1977) in the first stage of the experiment. The prolonged irradiation resulted in decreased monomer concentration, suggesting the degradation of monomers produced after cleavage of glycosidic linkages (Kovac *et al.*, 1998). A similar reaction profile was obtained for photodegradation in natural sunlight with a lower degradation rate (Fig. 2).

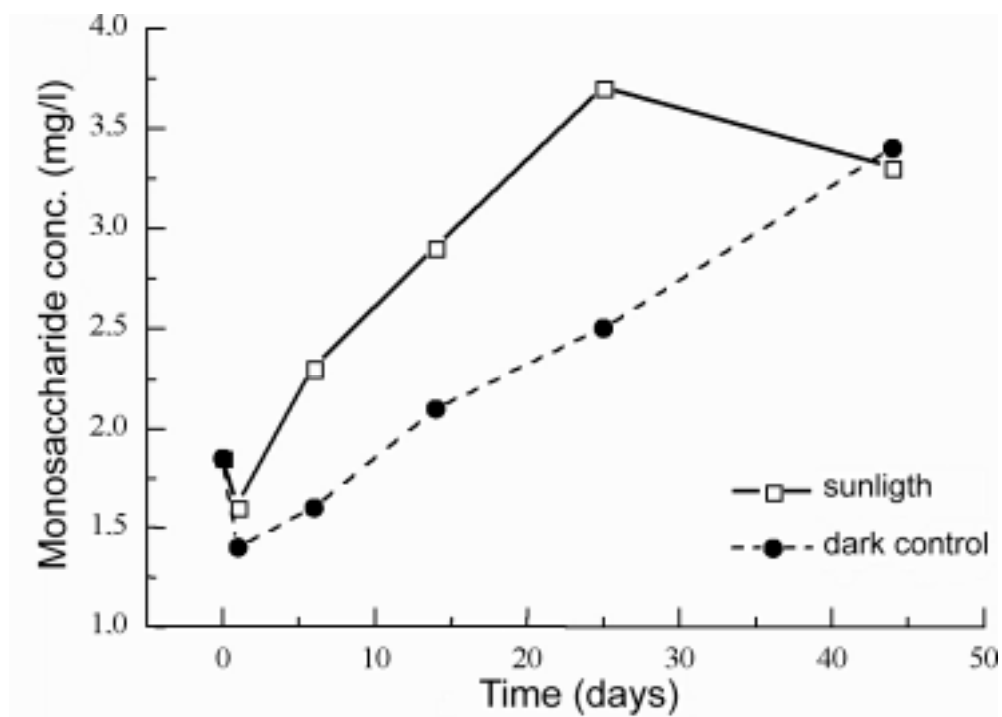


Fig. 2. Photodegradation of mucous macroaggregates in natural sunlight.

The results presented in this work indicate that photosensitized degradation of selected organic compounds in sea water should be considered as an important process. These processes are especially important in the sea surface microlayer, where the major part of incident solar radiation is absorbed.

The role of the surface microlayer in contaminant concentration and pollutant transport via marine aerosols

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Microlayer ($\cong 150\mu\text{m}$ thick) and sub-surface (-0.5 m) water samples were collected with MUMS (Multi Use Microlayer Sampler) (Hardy *et al.*, 1988; Carlson *et al.*, 1988) in the Tyrrhenian Sea off Leghorn (Tuscany, Italy) in September and October 1999. Sampling stations included both areas believed to receive low contaminant input and coastal areas closer to contaminant sources such as, in particular, the harbour of Leghorn. In the same period marine aerosol samples were collected using a high volume sampler (G 1200 PM10 Graseby Andersen, USA) arranged with a five stage Sierra-235 located at the Interuniversity Marine Biology Center (Leghorn) at about 10m above sea level and about 30m from the sea. The air flow was about $68\text{ m}^3\text{h}^{-1}$. Atmospheric particles were separated into six size fractions on glass fibre filters according to the following aerodynamic diameters: 7.2, 3, 1.5, 0.95, $0.49\mu\text{m}$. A final quartz fibre filter (Whatman) collected the particles $<0.49\mu\text{m}$. A software-driven meteorological trigger (Schiavuta *et al.*, 1992) facilitated the aerosol sampling in well-defined weather conditions (wind speed $>2\text{ms}^{-1}$ and direction $185^\circ\text{-}225^\circ$).

The main aim of this research was an evaluation of the environmental conditions of unpolluted coastal waters in some Tyrrhenian locations which have not been extensively investigated. The concentrations of organic compounds, extracted with *n*-hexane, revealed a quite good environmental situation comparable with that observed in other coastal areas (Sauer *et al.*, 1989; Hardy *et al.*, 1987a). The results of a representative sample are reported in Table 1.

Compounds	DISSOLVED			PARTICULATE		
	Microlayer	Sub-surface water	EF	Microlayer	Sub-surface water	EF
	$\mu\text{g/l}$	$\mu\text{g/l}$		$\mu\text{g/l}$	$\mu\text{g/l}$	
Total n-alkanes (C14-C34)	0.826	0.253	3.3	1.847	0.307	6.0
Squalene	0.483	0.448	1.1	0.997	0.353	2.8
Total alkylbenzenes	0.074	0.046	1.6	-	-	-
Di-iso-butylphthalate	0.314	0.144	2.2	0.148	0.142	1.0
Di-n-butylphthalate	0.237	0.064	3.7	0.359	0.205	1.8
Di-(2ethylhexyl)phthalate	1.033	0.403	2.6	0.832	0.713	1.2
Total phthalates	1.702	0.641	2.7	1.369	1.060	1.3
PAHs	5.312	0.418	12.7	9.588	2.415	4.0
MBAS	45	38	1.2	-	-	-

Table 1. Concentration of dissolved and particulate organic compounds in microlayer and subsurface water samples collected at Castel Sonnino (Leghorn) and their relative Enrichment Factors (EF).

The organic compounds and relative concentrations are the same of those found at the other stations, with the exception of the sample collected at the harbour of Leghorn. The data represent a typical condition of the Tyrrhenian Sea in this period of the year which is characterized by limited ship traffic, absence of tourism, and no algal blooms. A microlayer enrichment is observed for all the classes of compounds. The EF shown are comparable with those found in a very remote area, Baia Terra Nova (Antarctica), where similar investigations were carried out (Desideri *et al.*, 1999).

Table 1 shows the high concentration of *n*-alkanes and PAHs in particulate form which occurred in the microlayer compared with bulk-water. Moreover, we can observe that predominant phthalates are di-*n*-butylphthalate, di-*iso*-butylphthalate and di-(2ethylhexyl)phthalate. The study of the microlayer composition has allowed us to demonstrate the high concentration of organic contaminants in the harbour of Leghorn, which is enhanced in clearly visible slicks. Under these conditions the microlayer concentration was about 100 times greater than the sub-surface water concentration (Table 2).

Compounds	DISSOLVED			PARTICULATE		
	Microlayer µg/l	Sub-surface water µg/l	EF	Microlayer µg/l	Sub-surface water µg/l	EF
Total n-alkanes (C14-C34)	43.850	0.391	112.1	3674.348	10.474	350.8
Squalene	1.294	0.464	2.8	7.901	0.413	19.1
Total alkylbenzenes	1.569	0.191	8.2	-	-	-
Di- <i>iso</i> -butylphthalate	0.156	0.114	1.4	29.290	0.400	73.2
Di- <i>n</i> -butylphthalate	0.286	0.260	1.1	21.243	1.990	10.7
Di- <i>n</i> -pentylphthalate	0.152	0.123	1.2	41.615	0.365	114.0
Di-(2ethylhexyl)phthalate	33.099	0.194	170.1	41.559	0.187	222.2
Total phthalates	33.796	0.701	48.2	177.059	3.772	46.9
PAHs	133.176	1.682	79.2	225.907	0.795	284.2
MBAS	82	46	1.8	-	-	-

Table 2. Concentration of dissolved and particulate organic compounds in microlayer and subsurface water samples collected at “fishing boats quay” (Harbour of Leghorn) and their relative Enrichment Factors (EF).

The presence of slicks appears to be clearly related to the enrichment of the sea surface in hydrocarbons and MBAS. At this station the particulate alkane EF is far greater than the dissolved alkane enrichment factor (Marty and Saliot, 1976). This is true for PAHs as well. This investigation was also designed to assess size distributions of organic compounds in aerosol in order to study their transport and verify the validity of Spray Drop Adsorption Model (SDAM) (Oppo *et al.*, 1999; Lepri *et al.*, 1999). There is a direct relation between the organic compound composition of the microlayer and that found in the six different size fractions of the aerosol.

In Figure 1 is plotted the enrichment ratio of phthalates *versus* the size fraction of the particles in a representative sample of aerosol. The ratio is calculated with respect to the concentra-

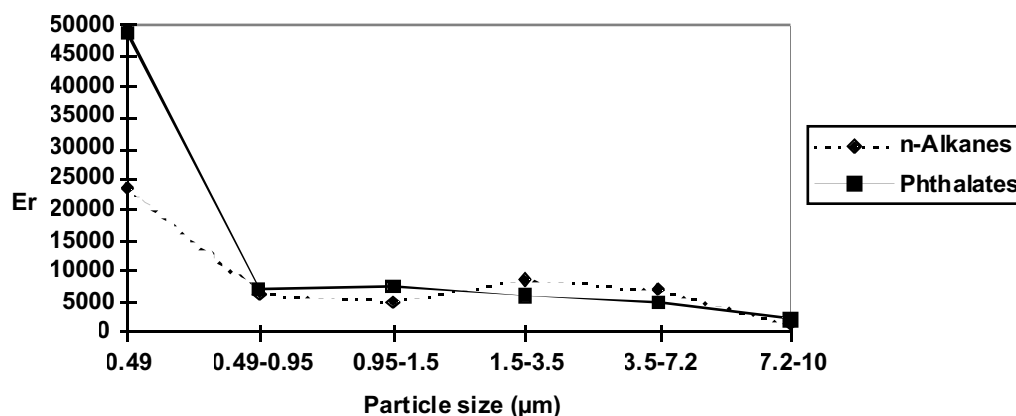


Fig. 1. Enrichment ratio (E_r) of phthalates and *n*-alkanes with respect to sodium ion as a function of particle size in a sample of aerosol.

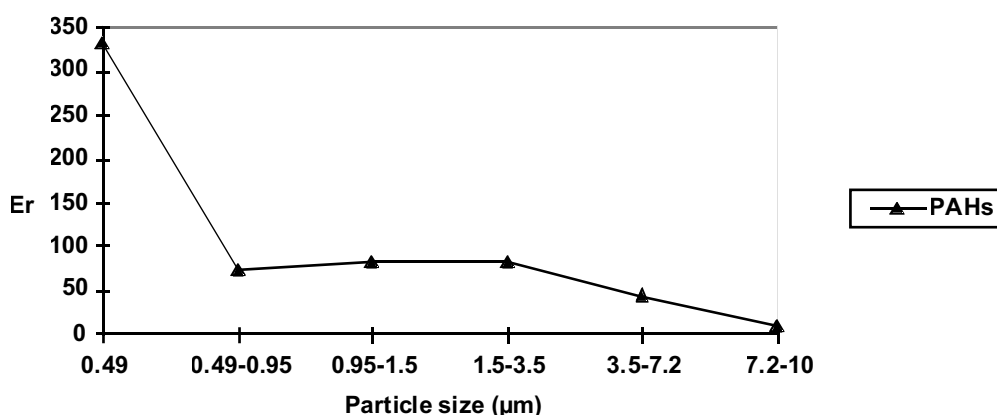


Fig. 2. Enrichment ratio (E_r) of PAHs with respect to sodium ion as a function of particle size in a sample of aerosol.

tion of the sodium ion in the same filter in order to normalize the concentrations of organic compounds with respect to a reference component which does not become enriched during the aerosolization process.

We can appreciate that relative E_r of phthalates increases as the size fraction of the aerosol particles decrease. This is in perfect agreement with the proposed SDAM which predicts quantitatively the increase in concentration and enrichment of no volatile surface active agents as the size of the aerosol particle decreases (Oppo *et al.*, 1999). According to this model a hyperbolic-like function is obtained.

It should be noted that the largest quantities of n-alkanes (Fig. 1) and polycyclic aromatic hydrocarbons (PAHs) (Fig. 2) were also associated with the smallest aerosol particles. However some values of E_r , in the range of 1.5-3.5 µm particles, appeared larger than expected; this behaviour could be due to the presence of greater amounts of humic colloidal micelles floating in this fraction, which can adsorb these compounds.

The presence of PAHs may be responsible for the mutagenic activity observed for the finest fraction of the aerosol.

Air-Sea exchange of semi-volatile organic compounds : transfer processes and the role of phytoplankton

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AIR-WATER EXCHANGE AND ITS POTENTIAL IMPORTANCE

Air-sea exchange describes the processes of addition to, transfer across and emission from the interface between the local atmosphere and water. Thus, it describes atmospheric deposition of particles and gases to the interface from rain and snow scavenging, dry deposition of particles, the exchange of gases and particles at the air-water interface, the sorption of gases at the interface, and the emission of particles and gases into the atmosphere. This work will concentrate on the exchange of gases at the air-water interface emphasizing the semi-volatile organic chemicals (SOCs) such as the chlorinated hydrocarbons (polychlorinated biphenyls-PCBs; hexachlorocyclohexanes-HCHs) and the combustion-derived polycyclic aromatic hydrocarbons (PAHs). SOCs are characterized by sub-cooled liquid vapor pressures (P°_L) less than 10^{-4} atm (~ 10 Pa) and aqueous solubilities less than 10^{-4} moles/L. These two physical-chemical parameters imply that SOCs are distributed between the gaseous and particulate phases in the urban, rural and marine atmospheres (Pankow, 1987; Bidleman, 1988) and the dissolved and particulate phases in the water column (Baker and Eisenreich, 1990; Schwarzenbach *et al.*, 1993).

Insufficient attention has been paid to the role of air-water exchange of SOCs in lakes, estuaries, and oceans. Whereas the transfer of low molecular weight, volatile and biologically-mediated gases such as O_2 , CO_2 , CH_4 , H_2S , DMS and 1 and 2 carbon halocarbons have received considerable attention for water quality, carbon cycling, global warming and other reasons (Buat-Menard, 1986; Liss and Duce, 1997), SOCs such as PCBs, DDTs, HCHs, PAHs, and toxaphene have been studied recently (Eisenreich *et al.*, 1981; Doskey and Andren, 1981; Atlas and Giam, 1986; Bopp, 1983; GESAMP, 1989; Knap and Binkley, 1991; Achman *et al.*, 1993; Iwata *et al.*, 1993; Eisenreich *et al.*, 1997). These compounds are derived from major anthropogenic emissions in urban/industrial centers and world-wide agriculture, transported globally, and often concentrated in the northern hemispheric atmosphere from $20^{\circ}N$ to $45^{\circ}N$ (Standley and Hites, 1991; Tanabe and Tatsukawa, 1986). Recent studies suggest that air-water exchange of SOCs plays an important role in the mass balancing of inputs in large aquatic systems such as the Great Lakes and the world's oceans (Eisenreich *et al.*, 1981; Strachan and Eisenreich, 1988; Hinkley *et al.*, 1991; McConnell *et al.*, 1992; Jeremiason *et al.*, 1994; Hornbuckle *et al.*, 1994). For example, the calculated volatilization flux of PCBs out of the North American Great Lakes (Strachan and Eisenreich, 1988; Jeremiason *et al.*, 1994; Hornbuckle *et al.*, 1995; Swackhamer and Armstrong, 1986; Mackay, 1989) has been estimated to be comparable to sedimentation losses and may, in fact, be substantially greater in low sedimentation ecosystems such as Lake Superior (Jeremiason

et al., 1994) and the Mediterranean Sea. There must be an appreciable cycling of SOC between air and water with the magnitude and direction of net transfer changing with season, and even with wind direction and speed. There is now convincing evidence that concentrations of SOC and their residence times in aquatic systems are influenced if not controlled by air-water exchange (Eisenreich *et al.*, 1997). Air-water exchange is also recognized as a dominant process for SOC input to the world's oceans (GESAMP, 1989; Iwata *et al.*, 1993). The direction of gas transfer is not obvious unless the air and water concentrations of the SOC are measured or accurately predicted and Henry's Law equilibrium is established, for it is the departure from equilibrium that drives the processes of gas volatilization and absorption.

Given the surface area of the world's oceans, it is not surprising that air-water exchange of organic compounds is an important interfacial problem. Large aquatic systems such as the North American Great Lakes, Chesapeake Bay, the Gulf of Mexico and the coastal and open ocean have large surface areas for transfer of chemicals in areas that are unfortunately often proximate to regions of intensified contaminant input (*e.g.* Chicago, IL-Gary, IN-Lake Michigan; Baltimore, MD - Chesapeake Bay; New York City and northern New Jersey-Long Island Sound and North Atlantic; Los Angeles/Orange County-coastal Pacific Ocean) or down the transport gradient in the open sea. Air-water transfer of SOC occurs simultaneously in both directions; whether absorption or volatilization dominates is determined by the relative fugacity ratios – $f_w/f_g >$ or < 1 . Table 1 presents some estimates of air-water exchange from marine and limnic systems which will be updated for the workshop.

Table I. Air-Water Exchange of SOC in the World's Oceans (Iwata *et al.*, 1993)

Ocean/Sea	Σ PCB	ng/m ² d	Σ HCH
Bering Sea			
With Particle	-5 to -120		-120 to -300
Without Particle	0 to -115		0 to -150
N. Atlantic			
With Particle	-10 to -90		-40 to -180
Without Particle	+20 to -60		-30 to -160
Mediterranean			
With Particle	-20 to -60		-80 to -120
Without Particle	+5 to -40		-50 to -70
N. Pacific			
With Particle	+50 to -40		-30 to -260
Without Particle	0 to -60		+40 to -250

AIR-WATER-PHYTOPLANKTON EXCHANGE

Air-water exchange and phytoplankton uptake are two of the most relevant processes affecting the fate of persistent organic pollutants (POPs) in aquatic environments (Achman *et al.*, 1993; Schwarzenbach *et al.*, 1993; Swackhamer and Skoglund, 1991). Phytoplankton uptake is the first step in the bioaccumulation of POPs in aquatic food webs, and air-water exchange is one of the main pathways for entry and loss (Iwata *et al.*, 1993; Eisenreich *et al.*, 1997). Phytoplankton also play a major role in the occurrence and biogeochemical cycles of these pollutants in the oceans. POPs uptake by phytoplankton and their removal from surface waters by settling of large particles explains observed vertical profiles in the water column (Baker *et al.*, 1991; Lipiatou *et al.*, 1993; Dachs *et al.*, 1996; Broman *et al.*, 1996; Dachs *et al.*, 1997). Furthermore, there are potential interactions between trophic status (*e.g.* biomass and growth rate dilution) and the occurrence and cycling of POP. Higher biomass results in lower concentrations of POPs in phytoplankton and high phytoplankton growth may also lead to a significant dilution of the POP concentrations (Axelman *et al.*, 1997). Increased vertical fluxes in the water column and higher PCB concentrations in benthic organisms due to eutrophication have been observed (Jeremiason *et al.*, 1999). However, the interactions between bioaccumulation dynamics and air-water exchange have not been studied even though there are a number of observations that suggest that air-water exchange

and phytoplankton uptake are coupled. Profiles of PAH and PCB concentrations observed in the dissolved and particulate phase of the water column are frequently similar to those found in the gas phase (Achman *et al.*, 1993; Jeremiason *et al.*, 1999). Furthermore, the occurrence of POPs in aquatic food webs in pristine environments suggests an air-water-phytoplankton process (Iwata *et al.*, 1993).

MODEL DESCRIPTION

Phytoplankton uptake and air water exchange: In order to compare air-water with water-phytoplankton exchange, the equations describing both processes are examined. Phytoplankton uptake of POPs may be described as (Skoglund and Swackhamer, 1994; Skoglund *et al.*, 1996):

$$\frac{dC_P}{dt} = k_u C_W - k_d C_P - k_G C_P \quad (1)$$

where C_P (ng kg^{-1}) and C_W (ng m^{-3}) are the POP concentrations in phytoplankton and water, respectively, and k_u ($\text{m}^3 \text{kg}^{-1} \text{d}^{-1}$) and k_d (d^{-1}) are uptake and depuration constants, respectively. k_G (d^{-1}) is the growth rate of the phytoplankton community or biomass (Skoglund and Swackhamer, 1994). For a self-sustained biomass k_G will have a value of zero, while for a phytoplankton community that doubles its biomass in one day, it will have a value of one.

Equation 1 describes a one compartment model but there is strong evidence from experimental work that uptake is best fit with a two compartment model, which is described by a second set of uptake and depuration constants (Skoglund *et al.*, 1996). In practice, the uptake from water into one of the compartments is sufficiently fast that it is assumed to be in equilibrium with the water phase. This is usually identified as surface adsorption or partitioning into the cell membrane (Ashizawa, 1996; Ko, 1994). For the second compartment, the concentration is obtained by integrating equation [1] assuming a constant water concentration. Therefore, the POP concentration in phytoplankton is described by

$$C_P(t) = K_{SA} C_W + C_{P,eq} (1 - e^{-(k_d + k_G)t}) \quad (2)$$

where K_{SA} ($\text{m}^3 \text{kg}^{-1}$) is the surface sorption coefficient and $C_{P,eq}$ (ng/g) is the concentration in the phytoplankton matrix in equilibrium with the water phase. Laboratory experiments of POP uptake by phytoplankton are usually carried out beginning with zero concentration in the phytoplankton and near constant concentrations in the water. In these experiments the fast first step in the uptake dynamics is used to estimate K_{SA} , while the exponential approach to equilibrium is fitted using equation 2 to obtain estimations of $C_{P,eq}$ and K_d (Ko, 1994). Finally, uptake constants are obtained considering the equilibrium conditions,

$$k_u = \frac{C_{P,eq}}{C_W} (k_d + k_G) \quad (3)$$

where the values of K_{SA} , k_u and k_d obtained are dependent on the chemical/physical properties of the POP and the phytoplankton species (Skoglund *et al.*, 1996; Ko, 1994).

The air-water exchange flux may be obtained by applying a modified two-layer model (Eisenreich *et al.*, 1997).

$$F_{A-W} = k_{ol} \left(C_W - \frac{C_A}{H'} \right) \quad (4)$$

$$\frac{1}{k_{ol}} = \frac{1}{k_w} + \frac{1}{k_A H'} \quad (5)$$

where C_A is the POP concentration in air (ng m^{-3}), H' is the dimensionless Henry's law constant corrected for temperature, k_{ol} (m d^{-1}) is the overall mass transfer rate between air and water, and k_w (m d^{-1}) and k_A (m d^{-1}) are the water side and air side transfer rates, respectively. Details on methods and correlations used for estimation of H' and k_{ol} can be found in the above references.

Water-phytoplankton fluxes for constant water concentration

When the POP concentration in water is constant, the surface of the phytoplankton is assumed to be in equilibrium with the dissolved phase. Therefore, the flux is zero between the water and the phytoplankton surface. Then, one compartment can be taken into account for the phytoplankton phase. This approach is useful in order to simplify the derivation of an adequate equation for the air-water flux. Direct comparison between water-phytoplankton and air-water exchange is accomplished by obtaining an equation for water-phytoplankton fluxes (F_{P-W}) with the same units ($\text{ng m}^{-2} \text{d}^{-1}$) as air-water exchange (equation 4). This is done by first multiplying equation [1] by phytoplankton biomass (B_P) and dividing by the surface area (S_P) of the plankton cells, thus obtaining the water-phytoplankton fluxes per square meter of phytoplankton surface per day. Secondly, in order to compare these fluxes with those of air-water exchange, we must take into account all the phytoplankton cells within the mixing depth (h_{mix} , m), which is the fraction of the water column directly influenced by air-water exchange (Fig. 1).

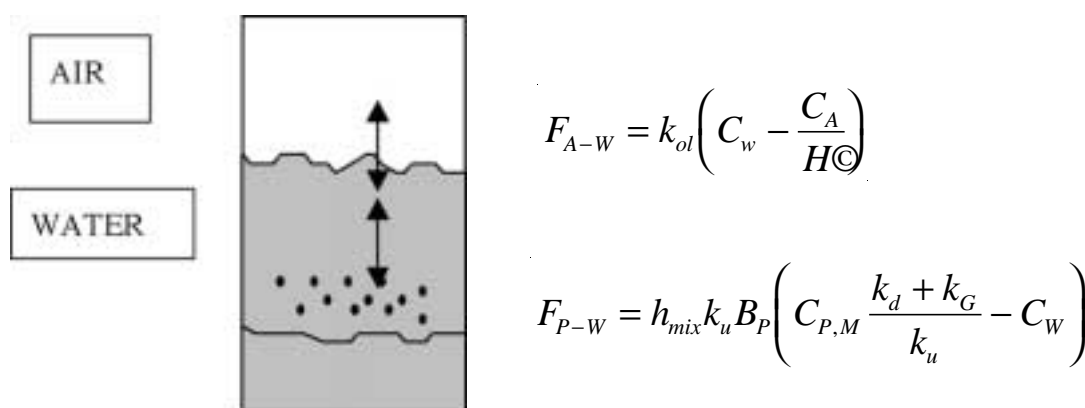


Figure 1. Model of Air-Water-Phytoplankton Exchange.

Therefore, equation [1] should also be multiplied by the ratio of phytoplankton surface area to air-water surface area, which is given by the product of h_{mix} and S_P . These modifications of equation [1] give the fluxes between phytoplankton and water per square meter of water column and day, the same units than for air-water exchange (equation 4).

$$F_{P-W} = -h_{\text{mix}} S_P \frac{B_P}{S_P} \frac{dC_P}{dt} \quad (6)$$

F_{P-W} is positive when the flux is from phytoplankton to water (deposition) and is negative during uptake. Equation [6] may be rewritten as:

$$F_{P-W} = h_{\text{mix}} k_u B_P \left(C_{P,M} \frac{k_d + k_G}{k_u} - C_w \right) \quad (7)$$

Equation [7] is analogous to that used in air-water exchange, and may in fact also be derived using a two layer model for the phytoplankton-water exchange. From equation [7], the mass transfer coefficient between phytoplankton and water (k_{P-W} , m d^{-1}) is:

$$k_{P-W} = h_{\text{mix}} k_u B_P \quad (8)$$

Water-phytoplankton fluxes for non-constant water concentration

When the POP concentration in water is not constant, the two-compartment model for phytoplankton uptake must be applied. The assumption that water and surface concentrations are always in equilibrium does not hold, since it would lead to infinite instantaneous fluxes. Therefore, dynamic sorption and desorption constants are required for the first fast sorption step. Thus, the flux between water and phytoplankton for non-constant water concentration is described as:

$$F_{P-W} = h_{mix} k_{ad} B_P \left(C_{P,S} \frac{k_{des} + k_G}{k_{ad}} - C_W \right) + h_{mix} k_u B_P \left(C_{P,M} \frac{k_d + k_G}{k_u} - C_W \right) \quad (9)$$

where k_{des} (d^{-1}) and k_{ad} ($m^3 \text{ kg}^{-1} d^{-1}$) are the desorption and adsorption rate constants, respectively.

Equation [9] describes water-phytoplankton uptake as two independent processes, one between water and phytoplankton surface and the second between water and the plankton matrix. Even though we assume implicitly that both processes are in parallel, this assumption has virtually no influence on uptake dynamics and the results reported here. The surface sorption described by the first term in equation [9] is approximately 100 times faster than partitioning into the cells (52). This means that the mathematical treatment of the second term is equivalent to considering that the phytoplankton matrix is interacting with the surface rather than with the water phase directly, which would be the case when both processes are in series. In the present work, k_u and k_d are considered as water-matrix uptake and depuration rate constants in order to treat them mathematically in a manner similar to that reported elsewhere (Thomann and Connolly, 1984). Furthermore, since the sorption described by the first term of equation [9] is two orders of magnitude faster than the sorption explained by the second term, $C_{P,S}$ will be at or near equilibrium with C_W . This means that equation [9] reduces to equation [7] when the POP water concentration is constant.

A dynamic model that couples air-water exchange and phytoplankton uptake of persistent organic pollutants has been developed and then applied to PCB data from a small experimental lake (Dachs *et al.*, 1999; Jeremiason *et al.*, 1999). A sensitivity analysis of the model, taking into account the influence of physical environmental conditions such as temperature, wind speed and mixing depth, as well as plankton related parameters such as biomass and growth rate was carried out for a number of PCBs with different physical-chemical properties. The results indicate that air-water exchange dynamics is influenced not only by physical parameters but also by phytoplankton biomass and growth rate. New phytoplankton production results in substantially longer times to reach equilibrium. Phytoplankton uptake-induced depletion of the dissolved phase concentration maintains air and water phases out of equilibrium. Furthermore, PCBs in phytoplankton also take longer times to reach equilibrium with the dissolved water phase when the latter is supported by diffusive air-water exchange. However, both model analysis and model application to the Experimental Lakes Area of north-western Ontario (Canada), suggest that the gas phase supports the concentrations of persistent organic pollutants, such as PCBs, in atmospherically driven aquatic environments.

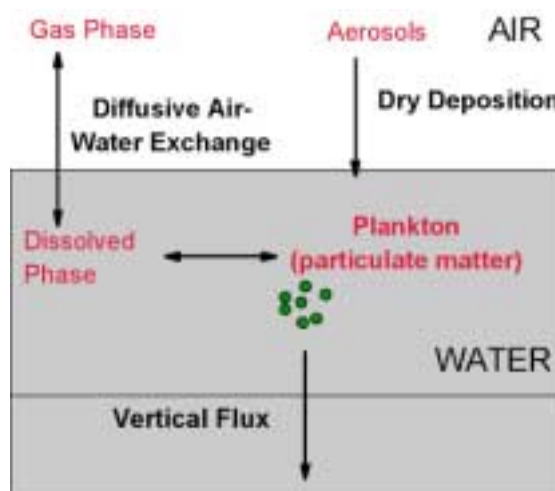


Fig. 2. Strategy for estimating air-water-phytoplankton exchanges for SOCs.

The influence of eutrophication on the biogeochemical cycles of persistent organic pollutants (POPs) such as PCBs is largely unknown. Here, the application of a dynamic air-water-phytoplankton exchange model to a large lake is used as a framework to study the influence of eutrophication on air-water exchange, vertical fluxes and phytoplankton concentrations of POPs (Dachs *et al.*, in press). The results of these simulations demonstrate that air-water exchange controls phytoplankton concentrations in remote aquatic environments with little influence from land-based sources of pollutants and supports levels in even historically-contaminated systems. Furthermore, eutrophication or high biomass leads to a disequilibrium between the gas and dissolved phase, and enhanced air-water exchange and vertical sinking fluxes of PCBs. Increasing biomass also depletes the water concentrations leading to lower than equilibrium PCB concentrations in phytoplankton. This approach will be used to estimate the role of gaseous air-water exchange of PCBs in their biogeochemical cycle in the Mediterranean Sea and presented at the workshop.

Diurnal fluctuation of nutrient and suspended organic matter concentrations in the sea surface microlayer during spring in offshore water of the Gdansk Basin

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The surface of sea water is a common interface of profound importance to both the ocean and atmospheric environments. In this interface, multiple processes of spatio-temporal variability take place, related to accumulation and exchange of biologically active substances and components detrimental in the irradiation budget. These processes seem to play the key role in supporting life in the ocean and are decisive in the global radiation balance (Prinn *et al.*, 1994; Liss and Duce, 1997). Hence, the studies concerning particular properties of the surface microlayer with the ongoing biochemical processes are of great interest to science (Falkowska and Latala 1995; Falkowska 1999 a,b).

The measurements of nutrient and DOC concentrations and suspended matter (particles, chlorophyll-*a*, phaeophytin-*a*, algae and ATP concentrations) carried out in spring in seawater layers of varying thickness (10, 90, 250 mm and under water layer) formed the basis of the discussion of the following issues:

- diurnal fluctuations of nutrient and organic suspended matter concentrations in samples collected every 1 or 2 hours from thin water layers;
- mathematical model of diurnal cycle of nutrients and organic matter.

The results obtained indicated significant differences in concentrations of the analysed determinands between the selected water layers as well as their considerable daily variability. The determined amplitudes reached considerable magnitude, *e.g.* about 40 $\mu\text{g}\cdot\text{dm}^{-3}$ in the case of chlorophyll-*a* in the layers of 10 and 90 μm thickness. Significant diurnal variations were measured also in the algae biomass and ammonia concentration (Fig. 1). The analysis of subsequent concentration maxima and minima of various substances revealed a regular pattern of daily fluctuations. Non-linear regression equation was applied to mathematical modelling of the observed diurnal fluctuations:

$$A(\tau) = a_0 + a_1 \sin(\omega\tau + \varphi_1) + a_2 \sin(2\omega\tau + \varphi_2) \quad (1)$$

where: $A(\tau)$ – concentration of the analysed substance or particles,

a_0 – the mean concentration of the analysed substance or particles,

a_1 – diurnal amplitude of concentration of the analysed substance or particles,

a_2 – half day amplitude of particle or analysed substance concentration,

φ_1 – phase displacement of the diurnal component [rd],

φ_2 – phase displacement of the half day component [rd].

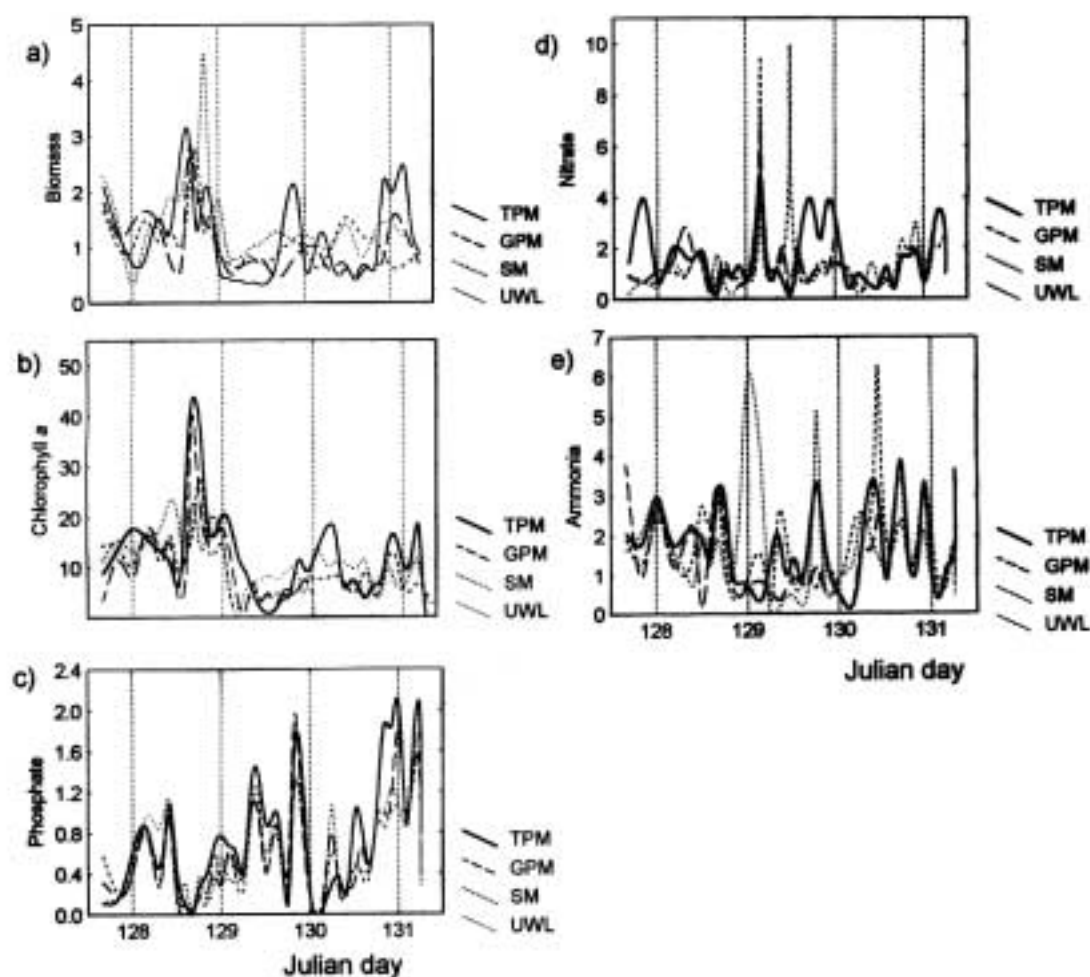


Fig.1. Examples of diurnal fluctuations in concentrations of chemical substances from selected sublayers of surface seawater (TPM - 10 μm , GPM - 90 μm , SM - 250 mm, UWL - 15 cm) from the Gdansk Basin a) biomass of *Peridiniella catenata* [mg dm⁻³], b) chlorophyll-a [mg dm⁻³], c) phosphate [mmol dm⁻³], d) nitrate [mmol dm⁻³], e) ammonia [mmol dm⁻³].

The result of summing up the diurnal and half diurnal components, following equation (1), is presented as the diurnal cycle of the studied chemical and biological parameters in the sea surface microlayer and subsurface water layer (Fig.2).

In the GPM layer (90 mm), SM layer (250 mm) and in the subsurface water layer (UWL - 15 cm depth), the concentrations of analysed substances (nitrate, phosphate, planktonic organisms the size range 2-40 μm and $N > 10 \mu\text{m}$) revealed two distinct maxima and minima displaced in time. In general, nutrients reached the maximal concentrations around noon. Simultaneously, the least number of planktonic organisms was present in these layers at that time of the day, presumably because of the plankton migration into the deeper layers when the solar radiation, inhibiting living processes, increased. The maximal number of algae was found in the mornings and in the afternoons, this resulted in nearly simultaneous or a delayed (by 1 to 2 hours) decrease in nutrient concentrations to their minimal level.

Taking into account the variations of all measured parameters, a hypothetical model was constructed concerning organic matter transformation relative to diurnal solar radiation (Fig.3).

The diagram presents the space within the sea surface, to which the greatest probability of maximal concentration of neustonic and planktonic organisms is related and moreover - the maximal concentrations of nutrients can be expected. The verification of the model was performed by additional measurements of the diurnal cycle of ATP concentrations in the sea surface

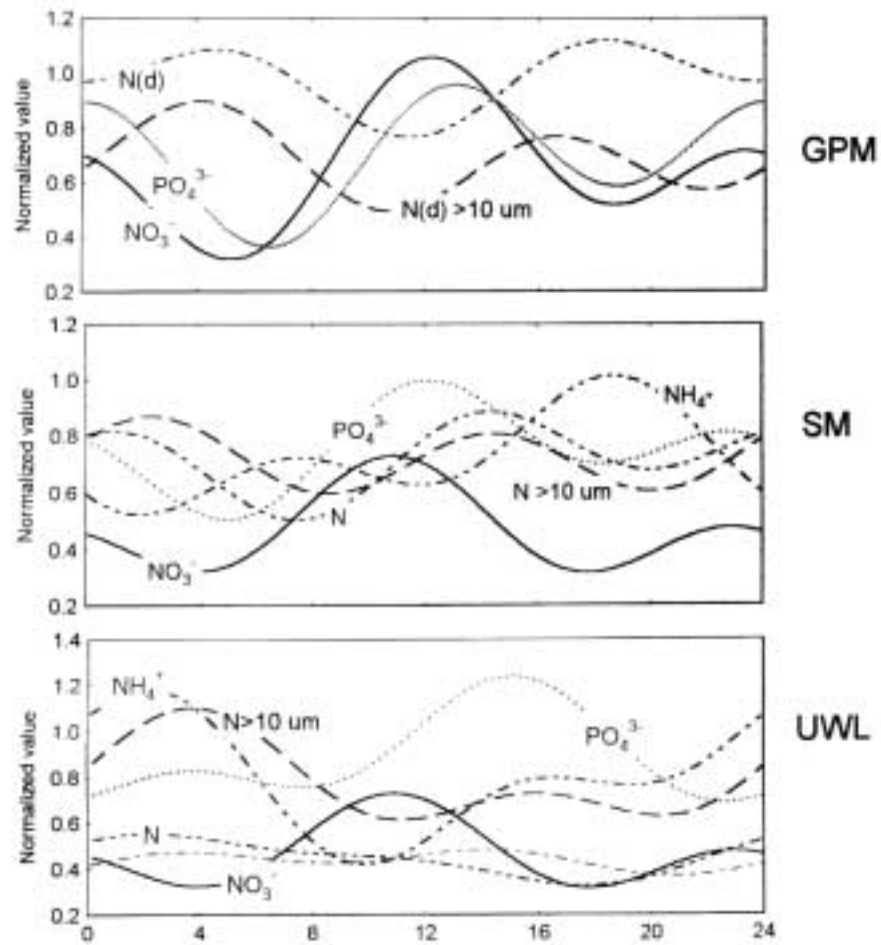


Fig. 2. Diurnal cycle of concentration variations of analysed substances in sea surface microlayer; N – total number of organic particles within the range 2 – 40 μm , N > 10 μm – number of particles with diameter larger than 10 μm .

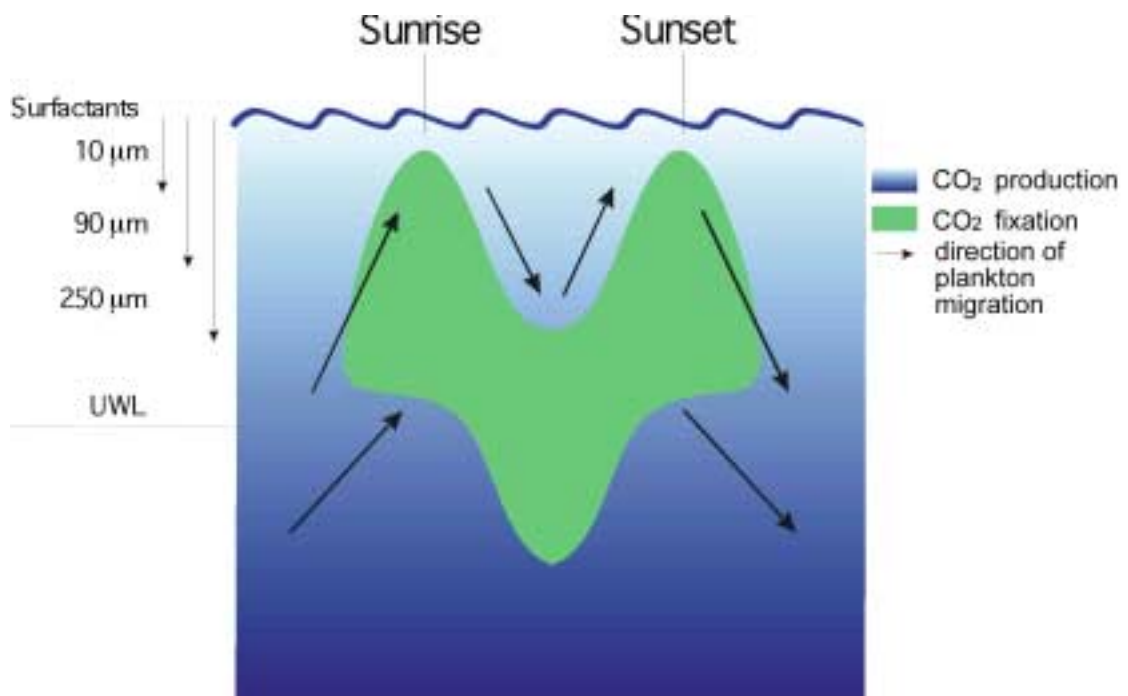


Fig.3. Hypothetical diagram of matter transformation during the solar diel cycle.

microlayer and the UV light absorption coefficient, both of which are accompanied by a synchronous measurement of radiation. These measurements demonstrated considerable phototaxia of neustonic organisms and a noticeable decline in primary production as well as intensive photodegradation processes of organic matter under severe radiation dose. The presented model of the diurnal cycle of organic matter transformations is supportive of earlier observations of primary production inhibited under solar radiation (Behrenfeld *et al.*, 1993; Herndl *et al.*, 1993; Hardy *et al.*, 1997; Neale *et al.*, 1998; Williamson *et al.*, 1999). Such results showed that biological damage increases exponentially with decreasing wavelengths within the UV radiation band, and small decreases in stratospheric ozone translate into rather large increases in biologically-damaging radiation.

The proposed model of diurnal transformations of organic matter requires further studies in other marine basins and in other seasons. The future studies should focus on bacterial population and kinetics of organic matter transformations caused by UV radiation.

Chemical characterization of the sea-surface microlayer using electrochemical methods

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As an area of exchange of matter and energy, the sea surface microlayer is an important boundary that either affects or is affected by global change (GESAMP report, 1995; Frew, 1997). The sea-surface microlayer is generally enriched in organic substances, particularly those which are surface active, metal ions, bacteria and other microorganisms relative to the subsurface water (Hunter and Liss, 1981; Marty *et al.*, 1988).

Electrochemical methods are very suitable for the study of surface-active organic matter. These methods take advantage of the fact that adsorption of surface-active molecules on a mercury electrode cause measurable changes in the electrode double layer capacity or capacity current.

Surface active substances (SAS) in seawater samples are determined by phase sensitive alternating current (a.c.) voltammetry using two approaches: (1) out-of-phase measurements based on the decrease in capacitive current in the presence of adsorbed SAS at - 0.6 V (Cosovic and Vojvodic, 1982, 1987), and (2) in-phase measurements using oxido-reduction processes of o-nitrophenol as an electrochemical probe, based on the principle that electrochemical characteristics of o-nitrophenol change in significantly different ways in the presence of adsorbed layers of SAS on the mercury electrode. These changes depend on different properties of organic substances such as hydrophobicity (shift of peak potential which is reater for more hydrophobic material) and acidity (change of prepeak height-increase for the acidic organic substances) (Gasparovic and Cosovic, 1994, 1995).

Table 1. DOC, total lipids, and surfactant activities (SA) of nonfiltered (NF) and filtered (F) samples. EF-enrichment factor.

Sample	DOC (mg/l)	EF	Lipids (μ g/l)	EF	SA(NF) (mg T-X-100/l)	EF	SA(F) (mg T-X-100/l)	EF
170								
ML	3.24	2.0	356.6	2.52	1.0		–	
ULW	1.62		141.4		–		–	
89								
ML	1.35	1.03	41.8	4.18	0.197	3.94	0.141	2.20
ULW	1.31		10.0		0.05		0.064	
93								
ML	1.39	1.08	19.0	0.84	0.073		0.076	
ULW	1.29		22.6		–		–	

General conditions: Sample 170-summer, very sunny, afternoon; sample 89-early spring, sunny, early afternoon; sample 93-rough sea after heavy rain.

Here we briefly present electrochemical results for three pairs of microlayer (ML) and underlying water (ULW) samples. Results are compared to the dissolved organic carbon (DOC) and total lipids concentrations (Gasparovic *et al.*, 1998).

Sample 170 is characterised with high DOC (3.24 mg dm^{-3}) and total lipids concentration ($356.6 \text{ } \mu\text{g dm}^{-3}$) reflected in high surfactant activity expressed as 1 mg dm^{-3} nonionic detergent T-X-100. A.c. voltammograms of o-nitrophenol probe for the microlayer and underlying water are presented in Fig. 1. A strong shift of the ONP peak potential for short and long accumulation times and disappearance of the prepeak for longer adsorption time, as well as the decrease for a shorter time, followed by an increase of the ONP peak height at longer adsorption time, indicated a dominant influence of SAS of strongly hydrophobic character in the microlayer sample, as compared with the model substance, oleic acid (Gasparovic *et al.*, 1998). In contrast, for the underlying water a small shift of peak potential as well as an increase of prepeak height indicated the presence of more hydrophilic SAS of higher acidity.

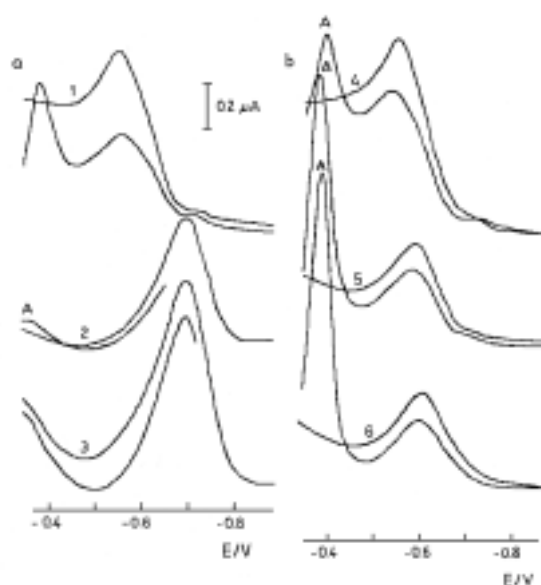


Fig. 1. A.c. voltammograms of ONP for sample 170: (a) microlayer sample and (b) underlying seawater. Accumulation times (1 and 4) 0 min, (2 and 5) 1 min, and (3 and 6) 3 min. Curves (1-6)-first scan, curves (A)-second scan in the same mercury drop, recorded immediately.

Table 2. Shift of peak potential ($\Delta E/\text{mV}$) and normalized prepeak current (i_A/i_{A0}) of o-nitrophenol for non-filtered (NF) and filtered (F) microlayer and subsurface water samples for 1 and 3 min accumulation.

Sample	$\Delta E/\text{mV}^a$		i_A/i_{A0}^c	
	1	3	1	3
170				
Microlayer NF	142	142	0.3	0d
Microlayer F	130	144	0.7	0
Subsurface NF	42	65	2.9	3.6
89				
Microlayer NF	64	108	2.0	2.4
Microlayer F	30	84	1.7	2.5
Subsurface NF	11	45	1.4	2.3
93				
Microlayer NF	9	41	1.8	3.1
Microlayer F	12	39	1.6	2.3
Subsurface NF	6	36	1.5	2.9

Despite similar DOC values (1.35 and 1.31) for the microlayer sample 89 and subsurface water, selective enrichment of SAS in the microlayer sample, confirmed by the four-fold enrichment of total lipids, is reflected in much higher surfactant activity obtained for both nonfiltered and filtered samples.

Filtered sea-surface microlayer sample 89 and fractions of different hydrophobicity, obtained by separation on the XAD-8 resin, were analysed for their DOC content and studied for SAS by electrochemical methods (Table 3). Hydrophilic organic substances were most abundant in both samples, but the highest surfactant activity was determined for the hydrophobic neutral fraction of sample 89.

Table 3. Fractionation analysis of microlayer samples 89 and 93.

Sample	DOC mg C/l	SA(NF) mg/l T-X-100	SA(F) mg/l T-X-100	Fraction (%)					
				Hydrophobic neutral & basic		Hydrophobic acid		Hydrophilic	
				SA	DOC	SA	DOC	SA	DOC
89	1.35	0.197	0.141	57.4	29.6	23.5	20.0	19.1	50.4
93	1.39	0.073	0.076	26.3	14.4	32.6	19.4	41.	66.2

SA-surfactant activity, NF-nonfiltered sample, F-filtered sample

All measurements have shown that the third microlayer sample 93 was not enriched with organic matter and SAS, as indicated by similar electrochemical behaviour of the microlayer and the underlying water samples. Fractionation analyses showed that hydrophilic organic substances are dominant both as concentration of DOC and surfactant activity. This is probably due to heavy rain dilution and subsequent scavenging in the microlayer as well as mixing of surfacial and deeper water layers by wind.

As reactivity of organic substances in natural waters is more important than concentration, the determination of surface active substances is very critical. Contrary to other specific methods used for characterization of organic matter in seawater which require isolation of the organic material before analysis, and have a very long and complicated procedure of determination, electrochemical methods are simple, direct, and fast. Electrochemical methods can serve for making rough estimations and as a good basis for the next step involving more specific methods for identification of organic substances.

Biology, contamination and toxicity of the sea surface

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THE SEA-SURFACE ENVIRONMENT

The sea surface layer (upper meter) has unique chemical and biological characteristics very different from those of deeper waters (Hardy and Word, 1986) (Fig. 1). The surface nanolayer, from the surface to a depth of several hundred nanometers, is typically enriched in lipids, carbohydrates, proteins, waxes, esters, bacteria, and viruses (Baier, 1972; Guscinski, 1986; Hardy, 1982; Hardy, 1995; Liss, 1975). The surface microlayer, to a depth of several hundred microns, is a matrix of organic and inorganic particles, bacteria, protozoans, microalgae, and detritus (Liss,

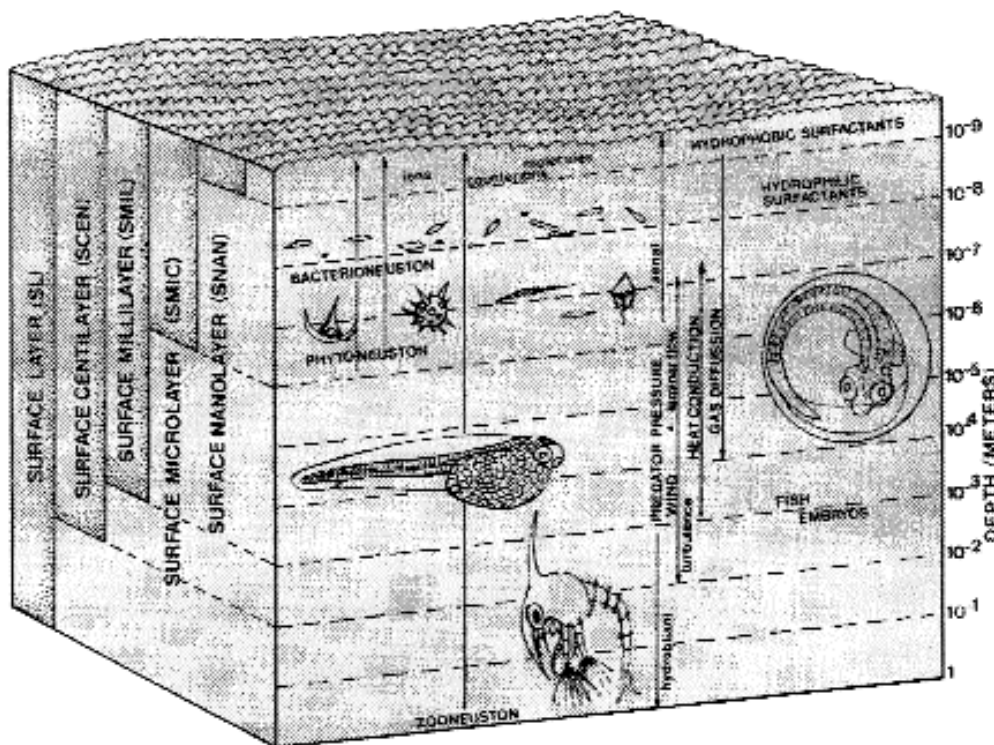


Fig. 1. Schematic diagram of the aquatic surface layer (from Hardy and Word, 1986)

1975; Word *et al.*, 1986). The surface millilayer, extending to a depth of about one millimeter, contains larger particles, small metazoan animals (>500 μm), and the eggs and larvae of numerous species of fish and shellfish (Hardy and Word, 1986).

A more general term for the organically-rich microlayer is sea-surface film. These films are formed from biogenic materials produced by plankton in the water column (complex mixtures of lipids, proteins and many other compounds) that collect at the sea surface (Williams *et al.* 1986). Physical processes such as particle floatation, bubble scavenging and surface tension enhance surface accumulation. A variety of sampling techniques allow collection of samples from different depths within the surface layer for chemical and biological analysis.

BIOLOGY

The abundance of organic matter at the sea surface provides a substrate for the growth of organisms that inhabit the sea surface microlayer: the neuston. Most studies suggest that the sea surface represents a highly productive, metabolically active interface and a vital biological habitat. Neuston range in size from a few microns to a meter. Organisms from most major divisions of the plant and animal kingdoms either live, reproduce or feed in the surface layers. Bacterioneuston, phytoneuston, zooneuston and ichthyoneuston, often reach much higher densities than similar organisms found in subsurface waters. Neuston can remain in the upper milli- or centi- layer until turbulence created by winds exceeding 10-15 m/sec disperse them (Zaitsev, 1971).

In the tropical North Atlantic Ocean the blue-green alga (cyanobacterium) *Trichodesmium* is the most important primary producer (165 mg C/m²/d) and is responsible, through nitrogen fixation, for the largest fraction of new nitrogen to the euphotic zone (30 mg/m²/d) (Carpenter and Romans, 1991). Based on a limited number of investigations, heterotrophic microneuston inhabiting the microlayer include small ciliates (Zaitsev, 1971), protozoa (Norris, 1965) and yeasts and molds (Kjelleberg and Hakansson, 1977). Tintinnids often form an important component of the marine neuston, probably feeding on the high densities of bacterioneuston (Hardy, 1971; Zaitsev, 1971). Also, the heterotrophic dinoflagellates *Noctiluca scintillans* and *Oxyrrhis marina*, are often abundant in neuston samples (Hardy, 1971; Zaitsev, 1971).

Numerous species of fish, including cod, sole, flounder, hake, menhaden, anchovy, mullet, flying fish, greenling, saury, rockfish, halibut, and many others have surface-dwelling egg and/or larval stages (Ahlstrom and Stevens, 1975; Brewer, 1981; Shenker, 1988, Zaitsev, 1971). Crab and lobster larvae in estuarine, coastal, and shelf areas concentrate in the surface film during mid-day as a result of positive phototaxis (Jacoby, 1982). In Puget Sound, English sole (*Parophrys vetulus*) and sand sole (*Psettichthys melanostictus*) spawn between January and April, releasing trillions of eggs that collect on the water surface. The embryos float until hatching occurs, generally 6 to 7 days after fertilization (Budd, 1940 and personal observation). Because of the buoyancy of their large yolk sacks, newly hatched larvae of both species often float upside-down at the surface of the water (Budd, 1940).

The larger (> 2cm) neuston organisms have been referred to as “pleuston”, although a more consistent term might be “macroneuston”. These, perhaps, 100 species or so, inhabit the surface layer (upper meter) generally by floatation or by association with floatable seaweed (Cheng, 1975). They include the jellyfish *Physalia* spp. that feed on small fish and *Verella* spp. that feed on copepods and fish and invertebrate eggs. Common gastropods in the open ocean surface layer are species of prosobranchiata and nudibranchiata. Oceanic crabs and many other organisms are found associated with the floating pelagic seaweed, *Sargassum* spp. Macroneuston undoubtedly form part of the food web linking the sea surface and subsurface layer, but the details of this food web remain unclear.

CONTAMINATION

Sea-surface films receive material input from atmospheric, terrigenous and marine sources, leading to elevated concentrations of both natural compounds and anthropogenic contaminants (Liss, 1975). Surface contamination in both coastal and offshore waters includes a wide variety

of xenobiotics. Microlayer concentrations of metals, hydrocarbons, pesticides, and PCBs often exceed EPA quality criteria for the subsurface (bulk) water (EPA, 1986; Cross *et al.*, 1987; Duce *et al.*, 1972; Hardy and Cleary 1992; Hardy *et al.* 1985, 1987b, and 1990; Harvey *et al.*, 1982; Lion *et al.*, 1979). For example, because of their lipophilic properties and high octanol:water partition coefficients organotins readily accumulate in the surface microlayer. Concentrations of TBT (tributyltin) in the North Sea microlayer exceed the UK EQS value of 2 ng TBT/L for marine waters, even at 200 km offshore (Cleary *et al.*, 1993). Secondary treated sewage effluent, containing 10 to 25% of floatable organics as well as bacteria (Word *et al.*, 1990), have been detected in U.S. and Australian surface waters (Nichols and Espey, 1991; Selleck, 1975; Word and Ebbesmeyer, 1984). Anthropogenic hydrocarbons concentrate in tissues of neustonic organisms (Butler and Sibbald, 1987; Cross *et al.*, 1987; Hardy *et al.*, 1987a and 1990; Marty *et al.*, 1979; Morris, 1974).

Many studies of nearshore areas indicate microlayer/bulkwater enrichments for heavy metals, radionuclides, PCBs, pesticides, and PAHs of 101 to 104 or more (Hardy, 1982; Hardy *et al.*, 1985, Hoffman *et al.*, 1974). However, very little data is available on the chemistry of the microlayer in offshore oceanic areas.

TOXICITY

Contaminated sea-surface films can be toxic to marine organisms. Sea-surface films contain a complex mixture of xenobiotics (Hardy *et al.*, 1987a) and synergistic effects can cause toxicity even when individual chemicals are below toxic levels (Rand and Petrocelli, 1985). Fish eggs, exposed to contaminated sea-surface films, have decreased hatching success (Hardy *et al.*, 1987b), increased mortality and chromosomal aberrations (Cross *et al.*, 1987), and increased embryonic mortalities and abnormalities (von Westernhagen *et al.*, 1987). Echinoderm larvae, exposed to sea-surface film samples from Puget Sound, the Persian Gulf following the 1991 oil spill, and offshore waters in the North Sea, all show increased mortality and abnormality (Hardy and Cleary, 1992; Hardy and Gardiner, 1991; Hardy *et al.*, 1987b). Decreased zooneuston and sole egg densities occur in urban compared to rural, Puget Sound sea-surface films (Hardy *et al.*, 1987b; Hardy and Antrim, 1988).

Higher incidences of chromosomal and/or larval abnormalities occur in neustonic fish embryos collected by neuston net tows from contaminated compared to clean areas. Malformation rates in mackerel developmental stages reached up to 100% in contaminated areas of the New York Bight (Longwell *et al.*, 1984). In the North Sea, malformation rates for flounder and dab embryos exceeded 50% in more contaminated areas compared to less than 20% in less contaminated areas (Cameron *et al.* 1992). It seems reasonable to hypothesize that these effects are due to sea surface microlayer contamination. In the Arabian Gulf, the sea surface microlayer (but not the subsurface water) was toxic to marine invertebrate larvae 1½ years after the world's largest oil spill (Hardy *et al.*, 1993). Sea surface microlayer samples from nearshore areas of south Florida proved toxic using a variety of invertebrate tests (Rumbold and Snedaker, 1997). Finally, contaminated films can be transported shoreward, potentially depositing both natural and anthropogenic constituents onto intertidal habitats (Gardiner, 1992).

Clearly microlayer contamination is a potential threat to neustonic organisms, particularly to the early life stages when organisms are most vulnerable. More *in situ* studies in microcosms and field-collected populations are needed to assess hazards to field populations.

NEUSTON WATCH

To assess the chemical hazard to neuston, a previous workshop proposed establishment of a "neuston watch", i.e. a series of selected geographic sites which would be monitored on a continuing basis at least annually (Hardy *et al.*, 1997). Information from these stations would represent a database for assessing the long-term status and trends of the sea surface. Data would be collected on: 1) the abundance and diversity of resident neuston species, 2) chemical analyses of selected anthropogenic contaminants, and 3) toxicity tests using collected microlayer samples and selected organisms.

Interactions of bacteria and dissolved organic matter at the sea surface microlayer

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The sea surface microlayer (SSM) links the marine environment to the atmosphere. In recent years, the close interaction between oceanic processes and the exchange of gases with the atmosphere has been intensively studied, particularly in relation to the role of oceanic processes influencing the global carbon budget and the climate (Andreae, 1990; Wallace and Wirrick, 1992; Kayanne *et al.*, 1995; Portielje and Lijklema, 1995). Nevertheless, there is a major gap in our understanding of the processes taking place in the SSM, due to methodological problems in sampling and studying the processes in the SSM. Below, an overview will be given on the major photochemical processes and their influence on the microbial community in the SSM.

The SSM is characterized by orders of magnitude higher concentrations of dissolved organic carbon (DOC) and microorganisms than the underlying water layers (Carlucci *et al.*, 1991; Williams *et al.*, 1986). Both, the DOC and the microorganisms are exposed to larger variations in physical parameters, i.e. primarily temperature and irradiation, than the waters underneath. Surface heating during the day leads to considerable temperature gradients within the top 10 cm of the sea surface, indicating strong diurnal stratification with an accompanied reduced mixing (Doney *et al.*, 1995). Thus the microorganisms and the DOM in the SSM are subjected to high radiation levels throughout the entire diurnal period (Herndl *et al.*, 1999). Particularly, irradiation exerts considerable stress on microorganisms, especially ultraviolet radiation (UVR).

UVR leads to photolysis of DOM and results in the formation of carbon dioxide and, to a lesser extent, of carbon monoxide (Zafiriou *et al.*, 1984; Helz *et al.*, 1994; Zepp *et al.*, 1995). Thus, a fraction of the DOC is directly converted into forms unavailable for heterotrophic bacterioplankton (Graneli *et al.*, 1996). Also, low molecular weight organic substances are formed which can be potentially taken up efficiently by bacteria (Kieber *et al.*, 1990; Mopper *et al.*, 1991; Obernosterer *et al.*, in press). Pronounced gradients of hydrogen peroxide (H₂O₂) have been detected in the superficial layers of the water column (Zafiriou *et al.*, 1984; Moffett and Zafiriou, 1990; Moffett and Zafiriou, 1993). H₂O₂ might interact with the microorganisms in the SSM leading ultimately to an inhibition of microbial activity (McFadzen and Cleary, 1994). Thus, UVR leads to the formation of both, biologically labile DOC compounds and to substances retarding microbial activity in the SSM (Obernosterer *et al.*, 1999). Despite that, recent studies have shown that originally labile DOC is photochemically transformed into refractory DOC by UVR (Obernosterer *et al.*, 1999; Pausz and Herndl, 1999). Since the concentration of labile DOC is high in the SSM (Williams *et al.*, 1986), one might assume that the formation of refractory DOC prevails over the production of labile DOC compounds. No research on this subject in the SSM has been made thus far, however.

Another important compound which has received considerable attention over the past decade is the fate of dimethyl sulfide (DMS) (Barnard *et al.*, 1982; Andreae and Barnard, 1984; Andreae *et al.*, 1985; Aneja and Cooper, 1989). DMS is photochemically altered into unknown compounds in the presence of UVR (Kieber *et al.*, 1996; Brugger *et al.*, 1998). However, only about 12% of the decrease in DMS can be attributed to the oxidation of DMS into dimethyl sulfoxid (Kieber *et al.*, 1996).

Bacterioplankton experiences severe inhibition during periods of UVR in the SSM (Kaiser and Herndl, 1997). Although it has been reported that the number of pigmented bacteria is high in the SSM (Kim, 1985; Williams *et al.*, 1986), no thorough investigation has been made thus far. We found no differences in the sensitivity of surface water bacteria as compared to deep water bacteria (Herndl *et al.*, 1993). Bacterioplankton rapidly recover from previous UV stress as indicated in lab and field experiments (Kaiser and Herndl, 1997). It has been shown, that bacteria are severely inhibited in their metabolic activity during the day in the presence of UVR and exhibit a high level of DNA damage. They are, however, also capable of efficiently repairing the UVR-induced DNA damage by using the photoenzymatic repair (Aas *et al.*, 1996; Jeffrey *et al.*, 1996; Kaiser and Herndl, 1997). After repairing the DNA damage, bacterioplankton rapidly recover from the UVR stress and exhibit higher growth rates after previous UVR exposure than bacteria constantly held in the dark (Kaiser and Herndl, 1997). This pronounced diel periodicity in bacterioplankton activity points 1) to the UVR stress during the day and 2), the utilization of the labile photoproducts formed during periods of low UVR (Herndl *et al.*, 1999). This periodicity is directly related to the diurnal stratification and its break up shortly before dusk when surface cooling causes a mixing of the superficial layer of the water column to deeper strata (Doney *et al.*, 1995).

It is still an unsolved question, whether and to what extent the bacterioplankton community differs from underlying water layers. Molecular analysis on the bacterioneuston have not been made to my best knowledge. Overall, from the microbial point of view, the SSM can be considered as a highly dynamic microenvironment with a complex structure of the DOC pool exposed to high UVR. The SSM as a microenvironment for bacterioneuston and their dynamics are likely to considerably influence the exchange processes between the oceanic and the atmospheric realm.

Investigation of the sea-surface microlayer by a complex methodological approach

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It is well known that the sea-surface microlayer plays an important role in marine environmental protection and global change (GESAMP Report, 1995; Liss and Duce, 1997). Although the physical and chemical properties of the sea-surface microlayer have been studied extensively, there is still a lack of knowledge about physico-chemical processes governing the formation and properties of the surface microlayers. Sea-surface microlayers can be studied either in an original sample without any pretreatment, or it can have been previously extracted by organic solvent and then investigated as *ex-situ* reconstructed film. Physico-chemical characteristics of natural and *ex-situ* reconstructed sea surface microlayer samples were studied using a complex methodological approach. Surface microlayer samples and the underlying water were collected in different seasons and under different weather conditions in the northern most part of the Adriatic sea, as well as in the Middle Adriatic, where samples have been taken from the sea and from the saline Lake Rogoznica. Here we present basic principles of the methods used and illustrate their application to characterization of a natural sea surface microlayer sample.

METHODOLOGY

1 – Monolayer studies

Monolayer studies, mostly measurements of surface pressure-area (π -A) and surface potential-area (ΔV -A) isotherms, as well as studies of elastic properties of sea-surface films have been performed in past years and most of them have been recently reviewed (GESAMP Report, 1995; Liss and Duce, 1997).

Monolayers can exist in a variety of states, i.e. in condensed, liquid-expanded and gaseous phases, respectively (Peterson, 1991). These states represent different degrees of molecular freedom or order resulting from the intermolecular forces in the film and with subphase, and are characterized with π -A and ΔV -A isotherms which are obtained upon compression of a monolayer and are indicative of the orientation, compressibility and surface activity of the sample.

The thermodynamic parameters describing the states of monolayers, i.e. limiting surface area A_0 , compressional modulus C_s^{-1} and compressibility, can be calculated from the π -A isotherms. The A_0 is obtained by extrapolating the linear part of the surface pressure-area (π -A) curve to zero surface pressure. The compressional modulus C_s^{-1} is determined according to the following equation:

$$C_s^{-1} = -A(d\pi / dA)$$

The higher C_s^{-1} means the more condensed (less compressible) the monolayer. The inverse value of C_s^{-1} is the compressibility of the monolayer.

2 – Brewster angle microscopy (BAM)

Brewster angle microscopy (BAM) was developed as a powerful method for optical characterization of monolayers and ultrathin films at the air/water interface (Hénon and Meunier, 1991; Hönig and Möbius, 1991). BAM is based on lateral changes of the refractive index and/or thickness of the film. P-polarized light is focussed on the clean air/water interface at the Brewster angle, which is about 53° when using visible light, and no reflection occurs. If the angle is kept constant, formation of a monolayer changes the optical situation and reflection is observed, containing information about the homogeneity of the film, existence, formation and inner structure of domains, phase transitions and adsorption of material from the aqueous subphase.

Although BAM has been used very successfully to investigate the morphology of lipid and fatty acid monolayers, as well as in studies of protein adsorption and crystallization processes at the air-water interface, to our knowledge aside from our work (Kozarac *et al.*, 1998; Gasparovic *et al.*, 1998; Kozarac *et al.*, 1999) no other study of natural sea surface microlayer samples has been reported to date. In BAM experiments we tested sea-surface microlayer samples under compression. The images derived from the film were dependent on the surface pressure. At low surface pressure, liquid condensed domains can be seen as small bright areas in the liquid expanded phase which is visualised as a dark background. Upon compression, these domains are pushed together, and at higher surface pressure only the liquid condensed phase can be seen. The observation of two phases by BAM seems to be in contrast to the interpretation of π -A isotherms characterised as being of the expanded type. This indicates that π -A isotherms alone are not sufficient for film characterization and a more complex approach is needed.

There also seems to exist a relation between the seasonal variations in the natural waters and the morphology of natural films. Samples taken in periods of high phytoplankton production gave BAM images with granular structures of liquid condensed domains in liquid expanded phase, while samples taken during a period of low primary production showed only homogeneous and continuous features in BAM images.

BAM has proved to be a very efficient analytical tool for a physico-chemical characterization of films at the air/water interface, and it can be successfully used for the investigations of interfacial layers in real aquatic systems in order to improve our understanding of the mechanisms and physicochemical processes at natural phase boundaries which play an important role in marine environmental protection and global change.

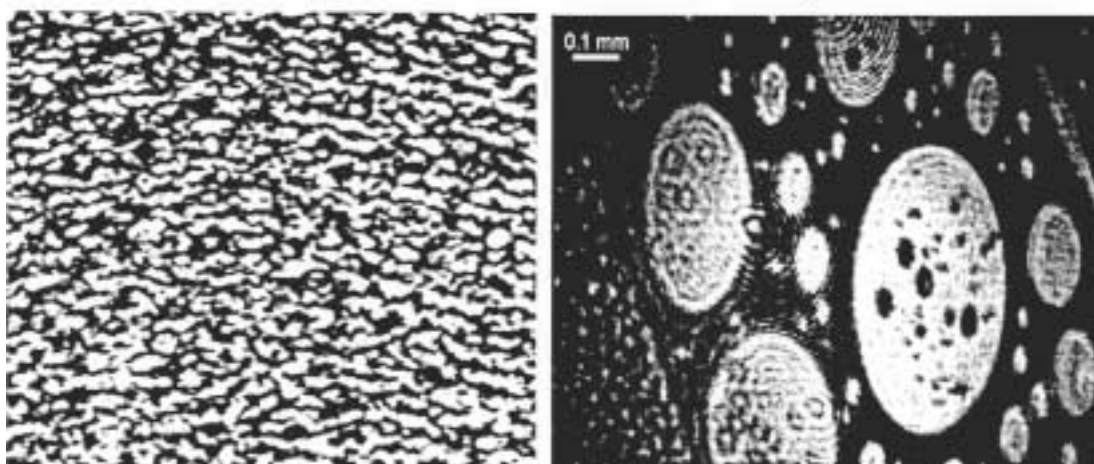
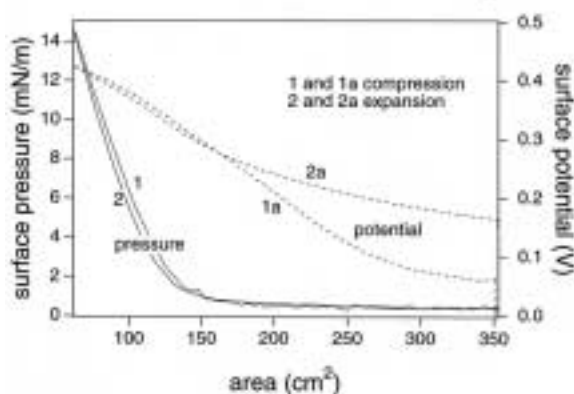
3 – Reflection spectroscopy

Enhanced reflection due to the presence of a chromophore at an air/water interface is the basis of the reflection spectroscopy method which was developed by Möbius and co-workers (Gröniger *et al.*, 1983). The incident light is split into an adsorbed part, a reflected part and a part transmitted through the interface. Reflection is dependent on the chromophore density and orientation at the interface. The chromophores present in the solution do not contribute to the enhanced signal. For the first time we applied this method to study on *ex-situ* reconstructed microlayer and measurements were performed by using a reflection spectrometer with measurement made under normal incidence of light. The preliminary results open new possibilities to study chromophoric dissolved organic matter (CDOM) present in sea-water microlayers, and its interaction with different solutes from the bulk solution which can be either of natural or anthropogenic origin.

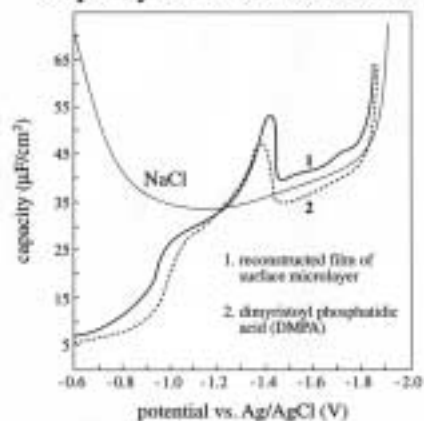
4 – Electrochemical methods

The electrochemical method, based on the measurement of adsorption effects at the mercury electrode by using phase sensitive alternating current voltammetry (out of phase signal), has been employed for the analysis of surface active substances in natural aquatic samples for many (Cosovic and Vojvodic, 1998). Electrochemical techniques (capacity measurements and polarographic maximum technique) have also been applied to microlayer studies (Cosovic *et al.*, 1977).

BAM images of different surface microlayers

 π -A and ΔV -A isotherms of microlayers

Capacity curves of transferred films



Here we applied the electrochemical method to study the *ex-situ* reconstructed natural films. The procedure is as follows : The natural surface film is first extracted by hexane and then spread onto the electrolyte solution. The layer is then transferred from the air/electrolyte interface to the mercury surface by vertical dipping of the electrode through the film. Afterwards, the capacitance of the film is determined. The method was designed and used for the studies of model lipid monolayers and their interactions with different solutes in solution (Nelson and Benton, 1986) however to our knowledge it has not been used for the characterization of natural films.

CONCLUSIONS

There is increasing evidence for the importance of studies of the nature, properties and role of the sea-surface microlayer. Monolayer techniques, Brewster angle microscopy, reflection spectroscopy and electrochemical methods can be very efficient analytical tools for making a physico-chemical characterization of natural films. These techniques can be used to give better insight into the morphology of natural films, relations between concentration and type of substances, and properties of films regarding exchange between film and subsurface. Studies of natural and reconstructed films should be carried out. Special attention should be paid to the studies of marine areas with high primary production characterized by intensive phytoplankton blooms.

The role of microorganisms at the seawater interface and potential applications

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The sea surface microlayer (SML) is a particular biotope, a barrier between atmosphere and ocean where chemicals, viruses, bacteria and phytoplanktonic cells accumulate. Some organisms are able to grow in this environment and thus, probably play a key role in the transformation and production of organic compounds. Although sampling of the SML is often difficult, mainly when large amounts of material are required, most studies indicate an enrichment or concentration of microorganisms in the SML compared to underlying waters, often by orders of magnitude (Dahlback *et al.*, 1982). Nevertheless, the diversity and the ecological role of these species remain unknown. Furthermore, species living and growing in this microlayer may have developed physiological adaptations to survive adverse environmental conditions such as UV radiation and the presence of toxic compounds.

The higher frequency of pigmented, antibiotic-resistant, and heavy metal-resistant bacterial species in the air-water interface compared to the bulk waters is likely due to the accumulation of toxic compounds in this layer (Hermansson *et al.*, 1987). Nevertheless, the role of bacterial species in the transformation of chemical contaminants is generally unknown and it is not known to what extent the SML plays a key role in detoxification processes and thus, in the protection of underlying waters. This is mainly due to our inability to physically isolate the bacterial species which are able to transform or to fix these organic compounds. The higher frequency of pigmented isolates at the surface may reflect a response to the intense solar radiation at the interface. Strains of the bacteria in the SML which maintain metabolic activity probably have a higher ability to survive UV radiation than bulk water isolates. Variations in the sensitivity of marine bacterial species to UV radiations were recently reported (Fig. 1; Joux *et al.*, 1999). Resistance mechanisms are often based on DNA repair and/or DNA protection. The isolation and the genetic and physiological characterisation of these isolates should be further investigated.

Although little is known about the structure of biological communities in the SML, neuston species could be of great interest for some biotechnological applications. Some bacterial and phytoplanktonic species are able to produce organic compounds such as fatty acids and polysaccharides which could be of great interest for pharmaceutical and dermo-cosmetic applications (anti-oxydant, antiageing effects, etc.).

The hydrophobicity of biological cells probably play a key role in the adhesion of bacteria to the surface microlayer. Most studies on the role of bacterial communities have quantified production rates and compared those with rates in the underlying waters (Carlucci *et al.*, 1985).

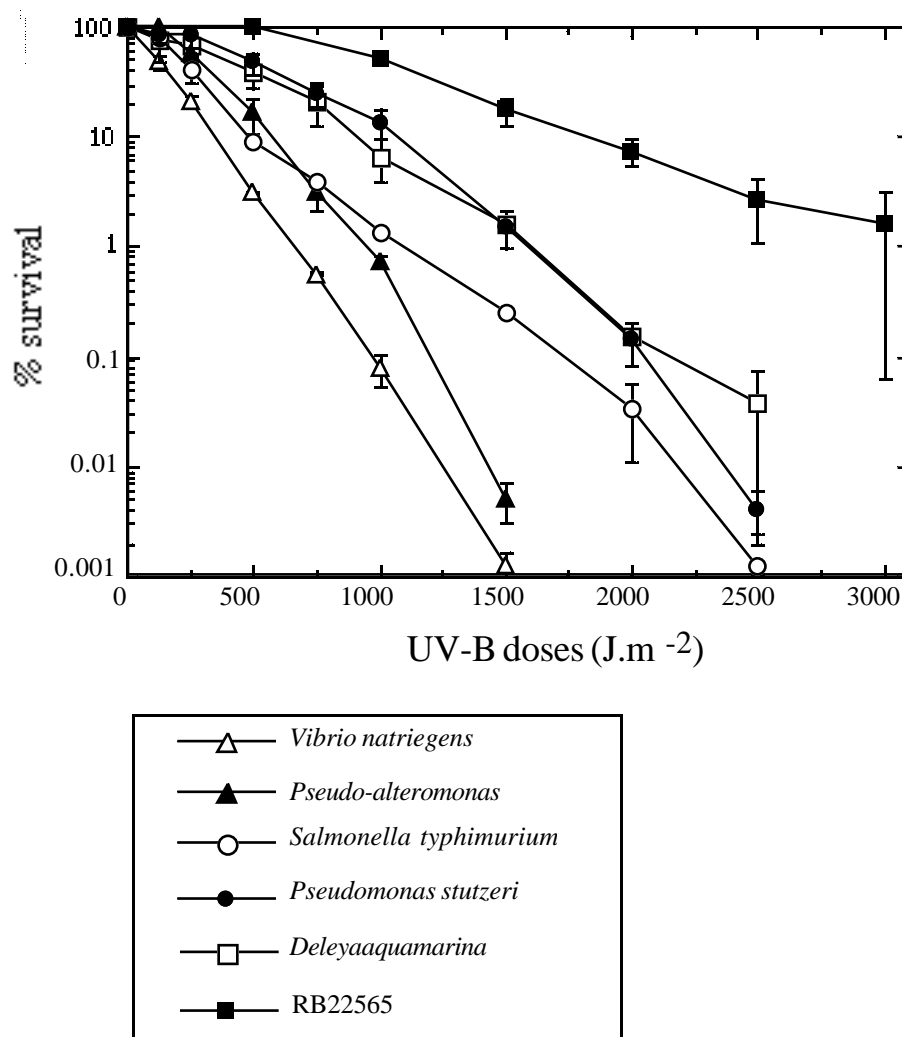


Fig. 1. Effect of UV-B exposure on the survival of different bacterial strains collected during the stationary phase. Data are presented as percentages of the initial counts (~108 CFU ml⁻¹) and represent mean values (± standard deviation) from two different experiments.

However, there is clear evidence, as is the case for bulk water communities, that surface-film microheterotrophic assemblages consist of a dormant, inhibited, or damaged population which is transported or accumulated from other environments, and a viable, physiologically-adapted population which is involved in biological processes occurring *in situ*. The understanding of biological processes occurring at the air-water interface requires new methodologies to isolate bacterial strains which are able to grow in this biotope and to investigate their functional role in the transformation of organic matter. New approaches have been recently developed in this way and applied to marine coastal bulk waters. They are based on a combination of physiological and/or taxonomic probes with cell sorting (Servais *et al.*, 1999; Lebaron *et al.*, 1999).

The role of the sea surface microlayer in air-sea gas exchange

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The exchange of gases across the sea surface is an important process in global biogeochemistry. A whole host of gases of importance for the chemistry (and physics) of atmosphere and oceans are produced in seawater and the air and subsequently transfer across the air-sea interface. For example, the oceans are the repository for about 40% of the man-made carbon dioxide emitted into the atmosphere from the burning of fossil fuels. In the opposite sense, the oceans are the largest natural source of sulphur (in the form of dimethyl sulphide (DMS)) to the atmosphere, where after oxidation to sulphate particles it plays important roles in the acidity of atmospheric aerosols and rain and also in controlling the albedo of the planet. The mechanisms by which these and many other gases cross the air-sea interface has been the subject of intense study for the last 30 years. However, the role that films at the sea surface might play in the transfer process has received relatively little attention.

The sea surface microlayer is the poorly defined region within the first few hundred microns of the water closest to the air-sea interface. Its thickness is conventionally taken as the depth of water sampled by the various devices designed to collect material from this zone. The microlayer is often found to be enriched in organic material and other substances and these certainly have the potential to affect gas transfer. It was the subject of quite intensive research about 25 years ago (see for example the reviews by Liss (1975) and MacIntyre (1974) and has been studied sporadically in the intervening quarter of a century. Much of this more recent research has been brought together in the book edited by Liss and Duce (1997).

Early attempts to assess the possible importance of the microlayer in inhibiting air-sea gas exchange concentrated on oil films, or monolayers of well ordered “dry” surfactants. As predicted by theory, any effect was much more significant for gases whose air-water transfer was controlled by processes on the air side of the interface (*e.g.* H₂O, NH₃, SO₂), as opposed to those gases for which water-side transfer processes were dominant (CO₂, DMS, organo-halogens, non-methane hydrocarbons). In the latter case the oil or surfactant was merely adding a small increment to the already substantial liquid side resistance, whereas for gases under air-side control the added resistance was substantial. However, although these differential effects could be shown in laboratory experiments (*e.g.* Liss and Martinelli, 1978), their relevance to most field situations was not clear. In the open sea, conditions are generally too rough and there is insufficient supply of surfactant (or oil, except in the case of direct spillage) for coherent films to exist, except in some calm areas where there is high biological activity.

More recently, attention have been focussed on the possible role that the so called ‘wet’ surfactants may play. These substances do not form coherent films at the sea surface but are ubiquitous since the molecules which comprise them are a fraction of the general dissolved organic

material in seawater. Some laboratory experiments have shown that they can be very effective in reducing air-water transfer for gases whose exchange is under water-side control (which group of gases contains most of the biogeochemically important ones) (Goldman *et al.*, 1988; Frew *et al.*, 1990). In addition, these workers have done laboratory experiments, but on samples collected at sea, that appear to show a very substantial effect which decreases in magnitude with distance from the coast (samples taken on a traverse from Narragansett, Rhode Island to Bermuda) (Frew, 1997). In contrast to these results, some very recent measurements made at sea using the dual tracer technique in the IronEx II iron fertilisation study show no change in air-sea gas exchange rate even though the biological activity in the water increased by at least an order of magnitude during the course of the experiment (Nightingale *et al.*, 1999). A resolution of this apparent discrepancy awaits further study.

A final aspect of this research topic is the possible role of the enzyme carbonic anhydrase in promoting air-sea gas exchange of carbon dioxide. It is known that marine organisms synthesise this enzyme in order to promote uptake of carbon dioxide dissolved in the water during photosynthesis. The question is whether it is exuded by the plankton either actively or passively (i.e. on death or on being eaten) in a form that can remain active in the water. It is known that carbonic anhydrase is surface active, and so would tend to accumulate in the microlayer. Matthews (1999) has recently reported some laboratory experiments which clearly show that photosynthesising plankton can certainly enhance the air-water exchange of carbon dioxide relative to other gases. However, it is difficult to know how to extrapolate these results to the real ocean and thus to estimate their likely role in the global cycling of natural and man-made carbon dioxide.

How chemistry of the sea surface microlayer influences biogeochemical processes at the atmosphere/ocean interface

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What do we know about the chemical composition of the sea-surface microlayer? In the 1960s the atmosphere/ocean boundary became a subject of interest or even passion for many oceanographers. Various new concepts and data were available such as methodologies for film sampling, first observations of enrichment of many mineral and organic compounds, living and non-living species in the film and controversies about the evidence of selective accumulation of different organic moieties (proteins/lipids). Many points were subjects of strong debate owing to the importance of this new frontier of the ocean (GESAMP, 1995; Liss and Duce, 1997).

One state of the art study was performed on coastal waters from the Gulf of California and Baja California by Williams *et al.* (1986) with extensive measurements of general parameters including DOC and DON, and specific organics, such as urea, proteins, carbohydrates and lipids, together with microplankton and bacteria determination. The authors reported that systematic correlations between the measured variables were few, suggesting that organic matter of films was a complex mixture of biologically-derived compounds dominated by macromolecular moieties of proteins, carbohydrates, lipids and their condensation/degradation products.

Simultaneously lipids received increased attention because of their potential tensio-active properties, reactivity with regard to photo-oxidation, and their potential use as markers to differentiate between various contributions of organic matter. Jullien *et al.* (1982) presented a comprehensive analysis of proteins, carbohydrates and lipids in particulate matter of several samples of sea-surface and overlying waters from polluted and pristine coastal Mediterranean waters. Their data showed that the microlayer was enriched in lipids with respect to the overlying water. This selective enrichment could be explained by the accumulation of tensio-active fatty acids. In contrast the macromolecular organic matter was depleted in the microlayer. The authors gave the following explanation: aggregates and flocculates can be formed in the microlayer from dissolved and colloidal material leading to large particles that can not remain at the boundary and thus settle rapidly throughout the water column. Harvey *et al.* (1983) suggested that the formation of part of marine humic substances in near surface waters in the Gulf of Mexico could result from crosslinkage and autoxidation of polyunsaturated fatty acids catalyzed by ultraviolet light and transition metals. Recent studies by Kieber *et al.* (1997) developed this concept of the formation of marine humic substances from photo-oxidation of triglycerides and fatty acids. Carlson (1993) summarized various processes occurring at the air-sea interface, underscoring the concept of a site of "early diagenesis of organic matter". Strong evidence of transformation and conversion of dissolved to particulate carbon in the surface microlayer was given, together with transformation from low to high molecular weight materials, and photochemical alterations. This later process

is a subject of great interest in examining the formation of biologically labile compounds from dissolved organic matter (Moran and Zepp, 1997) and the degradation of refractory dissolved organic matter (Miller and Moran, 1997).

The composition of surface films from the open and coastal North Adriatic Sea was described by Marty *et al.* (1988) and Gasparovic *et al.* (1998), using a multiparameter approach: screening by hydrological and biological conditions, characterizing global parameters such as surfactant activity and organic carbon, and analyzing the organic matter at the molecular level and by using lipid markers. Surfactant activity and particulate organic carbon showed a similar trend along a transect between the Croatian coast and the Pô River Estuary, with a predominant contribution of autochthonous production to the total pool of organic matter, and a substantial increase at stations under the influence of the Pô River where bacterial activity increased together with a marked contribution from allochthonous inputs. Surfactant activity measurements indicated the predominance of polar polymeric material.

From a series of samples collected at different seasons and analyzed by a combination of methods including electrochemical characterization of adsorbable organic substances using the ortho nitrophenol probe and monolayer techniques for surface pressure, surface potential and Brewster angle microscopy, Gasparovic *et al.* (1998) demonstrated that higher enrichment of organic matter in the surface microlayer occurred during the warm period of the year. This was reflected in the high surfactant activity of the organic substances present, and the formation of a more condensed layer than for the other samples collected in Spring, thus underscoring the importance of temperature and in situ production of organic substances by plankton and bacteria.

THE UNIQUENESS OF THE MEDITERRANEAN SEA

The Mediterranean is a semi-enclosed sea. It is characterized by a high anthropogenic pressure of various types (Aubert, 1995): pollution by microorganism, with a potential impact on the environment, particularly on the health of populations when the quality of coastal waters is questionable; chemical pollution such as nutrients and organic compounds often leading to eutrophication and dystrophy; inputs from various industries and human activities, heavy metals, detergents, pesticides, petroleum hydrocarbons and radionuclides. Most of these pollutants occur in coastal zones which are very sensitive to the present increase of various contaminant inputs. Dramatic events occur periodically in the Danube delta area of the Black Sea with consequences on its fisheries, and in the North Adriatic Sea with mucilage production events.

One can easily see that most of these contaminants enter the ocean through its surface (urban effluents, rivers and streams, petroleum tanker wrecks, atmospheric inputs, etc.) and thus apply high anthropogenic pressure on the ultrasurficial marine ecosystem. Moreover the Mediterranean Sea is characterized by high solar radiation during a large part of the year which provides intense conditions of ultraviolet irradiation. The sea surface temperature is also high compared to other marine areas, and this stimulates intense evaporation and probably development of microorganisms at the sea/atmosphere boundary.

Thus, the Mediterranean appears to be a unique site to study and model the impact of human pressure on the ultrasurficial ecosystem and its consequences on global change.

THE FUTURE ?

The Mediterranean Sea and particularly areas of high biological activity which lead to eutrophication during spring and summer events, are model sites to develop our knowledge of the biogeochemical processes occurring at the sea/atmosphere boundary. Potential sites for study could be, in the vicinity of a marine institute or a sea-based laboratory, i.e. the Ligurian Sea off Monaco, the Gulf of Trieste off Piran, the Gulf of Lion off Banyuls, the Ebro Delta off Barcelona, the Northern Black Sea and the Danube Delta, etc. Although since the 1960s we have obtained some snapshots of the Mediterranean ocean/atmosphere boundary, a time-series of physical, chemical and biological parameters characterizing the processes of production exchange, and recycling of matter is missing in order to draw conclusions on the potential role of the addition of anthropogenic substances at the ocean surface on a global scale.

The role of atmospheric input of natural and anthropogenic organic compounds in the biogeochemistry of the Eastern Mediterranean Sea

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The role of atmospheric input in the organic biogeochemistry of the Eastern Mediterranean was investigated. This investigation included three major compartments: i) a baseline study of biogenic and anthropogenic compounds in aerosol particles from a coastal area, ii) a baseline study of biogenic organic compounds in the water column (dissolved and suspended particles) of the same area, and iii) the study of dry and wet atmospheric deposition of anthropogenic and biogenic organic compounds. Specific source indicators (molecular markers) such as n-alkanes, steranes, triterpanes, PAHs, n-alkanols, fatty acids and photo-oxidation products of PAHs, and unsaturated fatty acids were examined.

The origin of air masses

Five day back trajectories were calculated by using a 3-D atmospheric transport model (Ramonet *et al.*, 1995). An analysis of all the back trajectories of air masses arriving at our sampling station over the years of the experiment (1993-1995) showed that air masses from N/NW represent 40-80%, from S/SW 0-40% and from W ~ 20% of the total throughout the entire year.

The marine aerosol chemical composition

Aerosol samples from air masses with the most frequent origin (N/NW) have been fully analysed in order to determine their chemical composition. An average of 83 % of the total aerosol concentration could be identified as follows: cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+) 9.3 %; anions (Cl^- , NO_3^- , SO_4^{2-}) 49.5 %; elements (Al, Si, P, Fe) 4.4 %; organic C, 15.7 %; black C, 4.2 %. The remaining 17 % was attributed to SiO_2 and Al_2O_3 . Air masses originating from Africa were characterised with non sea salt sulphate (nss- SO_4^{2-}) mean concentrations substantially lower ($90 \pm 12 \text{ neq/m}^3$) than the mean concentration (187.9 neq/m^3) of the all samples, while air masses originating from western and central Europe had the highest nss- SO_4^{2-} concentrations ($206.7 \pm 94.3 \text{ neq/m}^3$). The same general trend was observed in regard to black C concentrations which were 2-3 times higher than those observed above the western Mediterranean.

Fine organic aerosol composition

Rural aerosols contained n-alkanes ($7.1\text{-}24.3 \text{ ng/m}^3$), hopanes (Albaiges *et al.*, 1979), n-alkanols ($2.7\text{-}16.7 \text{ ng/m}^3$), n-alkanals ($0.9\text{-}3.7 \text{ ng/m}^3$), n-alkan-2-ones ($0.4\text{-}2.1 \text{ ng/m}^3$), n-alkanoic acids ($1.0\text{-}20.1 \text{ ng/m}^3$) and PAHs ($0.2\text{-}2.0 \text{ ng/m}^3$). The aerosol composition was dependent on the ori-

gin of the air masses. Air masses of local influence contained lower amounts of biogenic, *e.g.* *n*-alkanols, *n*-alkanals and *n*-alkan-2-ones (Cranwell, 1977), and anthropogenic compounds such as unresolved complex mixture (UCM) of hydrocarbons and PAHs. On the other hand air masses originating from the N and NW contained higher amounts of *n*-alkanols and *n*-alkanals and were characterised by specific molecular markers of marine origin such as 6,10,14-trimethylpentadecan-2-one (Cranwell, 1977) and α,ω -dicarboxylic acids with $C_n > C_{20}$. A characteristic of Eastern Mediterranean aerosols, in comparison to those from the western Mediterranean, was the very low concentration of unsaturated fatty acids and the relatively high concentration of C_8 and C_9 ω -oxo-carboxylic acids and α,ω -dicarboxylic acids, which result from the photo-oxidation of C_{16} and C_{18} unsaturated carboxylic acids. PAH aerosol fractions corresponding to the above air masses are characterised by a clear pyrogenic composition (4). Retene, a tracer for forest fires, was present in all rural aerosol samples.

Determination of dry and wet deposition.

Dry and wet deposition composition and rates were measured i) by applying the Holsen and Noll (dry deposition), and Ligocki (wet deposition) models on cascade impactor data (Prahl *et al.*, 1984), and ii) by analysing wet and dry deposition samples (for the first time in the entire Mediterranean area). Model calculations gave a total atmospheric flux of $2,195 \mu\text{g m}^{-2} \text{yr}^{-1}$ for *n*-alkanes and $50 \mu\text{g m}^{-2} \text{yr}^{-1}$ for PAHs, both of which are comparable with those obtained in the Western Mediterranean using the same approach. Field measurements (samples collected during the years 1997 and 1998) gave a total flux (through dry and wet deposition) of $7,800 \mu\text{g m}^{-2} \text{yr}^{-1}$ for *n*-alkanes and $90 \mu\text{g m}^{-2} \text{yr}^{-1}$ for PAHs.

Sea water column organic compound composition

Samples have been collected along two transects in the Cretan Sea and from two depths of 10 and 150 meters. Suspended particles were separated from the dissolved phase of the sea water. *n*-Alkanes in the particulate phase were found in low concentrations (19.11-48.41 ng/L) and were mainly of marine biogenic origin. These low concentrations are corroborated by the low concentrations of total suspended particulates (4.00-5.42 mg/L) and chlorophyll (0.048-0.205 $\mu\text{g/L}$) measured in the same area. The petrogenic component was also present. A very good correlation ($r^2 = 0.95$) was established in sea water between the ratios UCM/[Total Resolvable *n*-Alkanes] (UCM/TRA) and methyl phenanthrene/phenanthrene (MP/P), further demonstrating the presence of petrogenic hydrocarbons. The concentrations of PAHs in the dissolved (383.30-1353.54 $\mu\text{g/L}$) and particulate phase (341.14-1354.78 $\mu\text{g/L}$) were low, and the diagnostic concentration ratios indicated a more pronounced petrogenic than pyrogenic origin. Biogenic lipids such as *n*-alkanols (24.80-56.58 ng/L in particulate and 18.79-98.31 ng/L in the dissolved) and sterols (27.35-207.60 ng/L in particulate and 7.26-24.39 ng/L in the dissolved) determined in these samples were of marine and marine bacterial origin, and their presence could be explained by the phytoplankton species present in this area. The same was observed for the class of fatty acids (107.08-324.87 ng/L in the particulate and 191.56-410.15 ng/L in the dissolved). The above-mentioned class of lipids with a terrestrial origin was also present, but in lower amounts than the autochthonous fraction. The determination of long chain alkenones ($C_{37:2}$, $C_{37:3}$, climatic indicators) in the water column is also noteworthy.

The above results demonstrate that:

- higher terrestrial plants and microbiota, marine organisms, forest fires, fossil-fuel combustion, unburned oil residues, and atmospheric chemistry (photo-oxidation) have been identified as major sources of organic compounds for the Eastern Mediterranean aerosol;
- the occurrence of anthropogenic and biogenic lipids is strongly influenced by both seasonal and spatial variations, being highest in aerosols coming from N/NW. Compounds of marine origin such as low molecular weight *n*-alkanes (C_{15} , C_{17} and C_{19}), phytane and pristane are present in aerosols (Fig. 1A) during spring (phytoplankton bloom). Unsaturated fatty acids (related to the phytoplankton bloom) are also present in the aerosol during the same period (Fig. 1B). On the other hand their photo-oxidation products (oxo- and dicarboxylic acids C_8 and C_9) dominate (i.e. over the unsaturated fatty acids) under intensive photo-oxidation conditions (late spring and summer, Fig. 1B);

Eastern Mediterranean aerosol: marine contributions

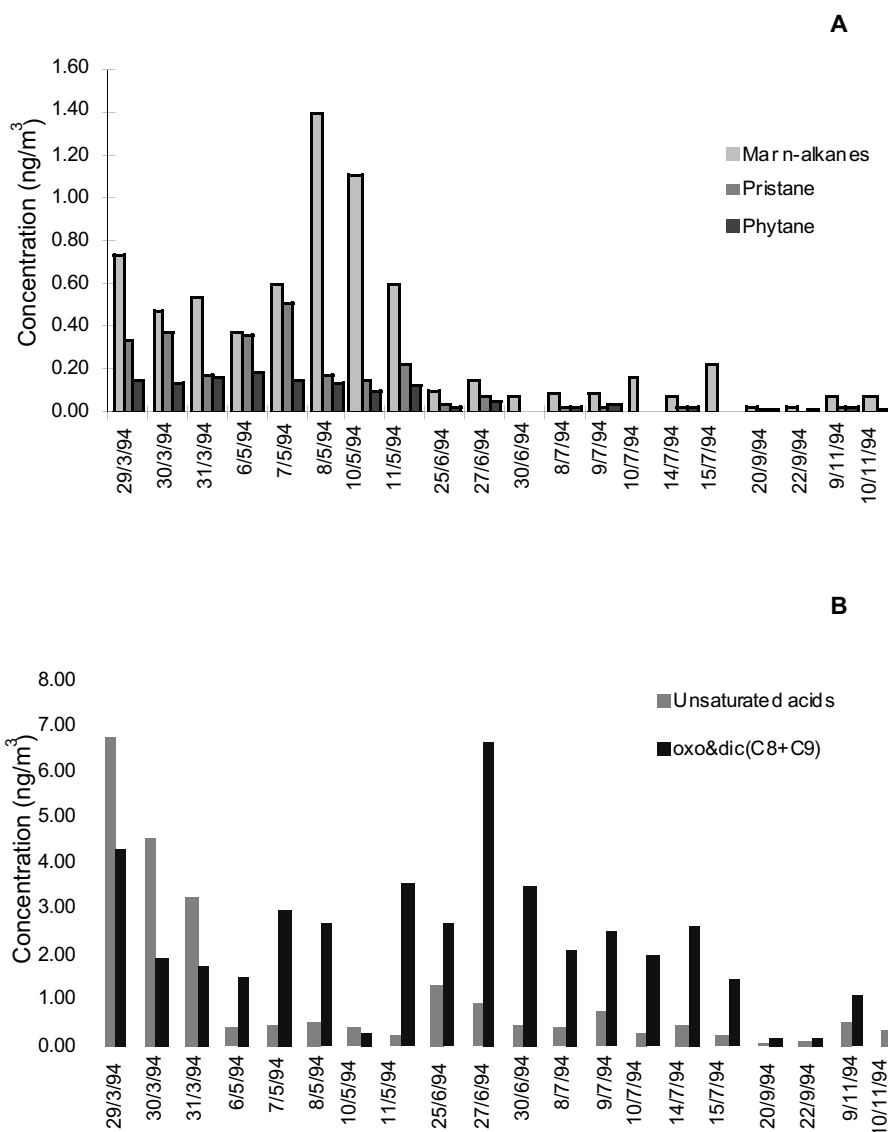


Fig. 1. Eastern Mediterranean aerosol contributions. (A) Compounds of marine origin, (B) Unsaturated fatty acids and photo-oxidation products.

- the natural compounds are preferentially deposited to the sea surface over the anthropogenic compounds;
- atmospheric deposition accounts as the most important input of allochthonous organic matter into the eastern Mediterranean Sea. This observation is in agreement with previous findings in the NW Mediterranean (Lipiatou *et al.*, 1994) and North Pacific (Gagosian *et al.*, 1986).