

**Sea surface microlayer:
a field evaluation of
teflon plate, glass
plate and screen
sampling techniques.
Part 1. Thickness of
microlayer samples and
relation to wind speed**

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Abstract

Surface microlayer samples were collected in the open sea with the simultaneous use of three different techniques. The thinnest water layer, 10 μm on average was collected with a teflon plate (TPM), 90 μm thick samples were collected with a glass plate (GPM) and 250 μm samples with a screen (SM). The sampling was performed under variable weather conditions. The microlayer thickness was found to increase with increasing wind speed. Glass plate and screen samples were influenced by the sea state. The intensification of turbulence in the surface layer was responsible for increased advective transport of organic matter and its accumulation near the sea surface and the greater thickness of the microlayer. When the wind speed exceeded 8 m s^{-1} (5°B), the microlayer thickness was observed to decrease gradually. The thickness of a microlayer collected by teflon plate was found to be inversely proportional to the wind speed. The classic screen method turned out to be the most useful of the techniques examined because of its relatively short sampling time and large sample volume. This technique is also applicable in inclement weather, when mechanical samplers are useless.

1. Introduction

The specific properties of the sea surface microlayer have been well understood for a number of years; even so, certain difficulties continue to be encountered as regards sample collection from this layer. The fact that all the sampling techniques yield samples of different thickness means that

the chemical and biological compositions of the samples will necessarily be different. Consequently, the results obtained by the various techniques are hardly comparable. The differences in thickness of the microlayer sampled by various techniques can span over 6 orders of magnitude, from 0.03 to 1000 μm . (Garrett 1965, Harvey 1966, Baier 1972, Szekiolda *et al.* 1972, Barger *et al.* 1974, Larsson *et al.* 1974, van Vleet & Williams 1980, Carlson *et al.* 1988, Liss & Duce 1997).

The modern experience concerning the chemical and biological structure of the sea microlayer is based on *ex situ* measurements (Falkowska 1996, Liss & Duce 1997). The microlayer sample, adhering to or filling up the collecting sampler, is removed above the sea surface and the water is poured into bottles for further analysis in the laboratory. Until non-intrusive *in situ* measurement techniques are developed, questions regarding the impact of the sampling technique or the dispensation effect of subsurface material in the microlayer sample on the results will continue to be of major importance. However, even if optical *in situ* methods, like reflected second harmonic generation, reflected sum frequency generation or reflected four-wave mixing spectroscopy, do have application in studies of the sea surface microlayer, some *ex situ* separation and analysis may always be necessary to characterise surfactant substances (Shen 1989, Frew & Nelson 1992, Korenowski *et al.* 1993, Gasparović *et al.* 1998).

The main objective of the present project was to examine the relation between hydrometeorological conditions and the thickness of samples collected from the sea microlayer.

2. Material and methods

Water samples from the surface layer were collected at the usual measurement station located in the Gdańsk Deep region ($\phi = 55^{\circ}22'\text{N}$; $\lambda = 19^{\circ}10'\text{E}$) (Fig. 1). Samples were collected in the period 1992–1998, in spring (May, June), from on board the naval vessel ORP ‘Kopernik’ and in October 1998 from on board r/v ‘Oceania’.

The samples were collected in 4- to 9-day cycles. The sea surface microlayer was sampled with a 40×50 cm polyethylene screen (mesh 24). On average, 22 such samplings were required to obtain 1 dm^3 of microlayer water. The following sampling procedure was established. First, the screen was immersed at an angle of 45° . Then, once totally immersed, the screen was left under the water until the microlayer had stabilised. Finally, it was carefully raised to the surface in a horizontal position at a speed of *ca* $5\text{--}6 \text{ cm s}^{-1}$ (Carlson 1982). Water was poured from the screen into a polyethylene bottle using a special slit in the screen frame. The water volume was determined directly after sampling so as to calculate the

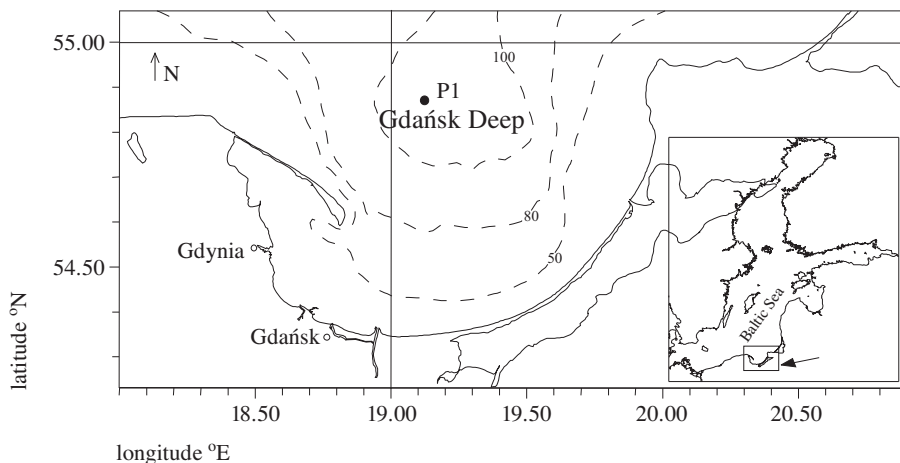


Fig. 1. Location of sampling station P1 – Gdańsk Deep

microlayer thickness. This procedure of microlayer collection using a Garrett screen from under the water was an improvement on sample collection in the ‘above-the-water’ manner as this avoided the formation of an air bubble, which often happened when using the latter technique. The same sampling procedure was applied by Carlson (1982) in a project on the Gulf of Maine, by Daumas *et al.* (1976) in the Gulf of Brusc, by Marty *et al.* (1988) and Gasparović *et al.* (1998) in the Adriatic.

The other microlayer sampling techniques involved a glass plate and a teflon plate, each with 30×30 cm of active surface. In both cases the plates were immersed into the sea vertically, all the way down to the holder, *i.e.* 30 cm deep. The plates were then hauled up from the water at a speed of about $5\text{--}6\text{ cm s}^{-1}$, and the water was drawn off to a wide-mouth bottle from both surfaces using a neoprene wiper. To obtain 1 dm^3 of microlayer water, some 60 samplings with the glass plate and around 500 with the teflon plate were required. Both screen and plates were raised from the sea at the same rate to avoid differences in sample thickness. Altogether, 60 samples were collected by teflon plate (TPM), 150 by glass plate (GPM) and 302 by screen (SM). 5 to $15\text{ }\mu\text{m}$ thick microlayer samples prevailed in the teflon plate samplings, $80\text{--}110\text{ }\mu\text{m}$ was the most frequent thickness among the glass plate samples and 200 to $300\text{ }\mu\text{m}$ in the screen samples (Fig. 2).

3. Results and discussion

The different in physical rules governing the methods of sampling are a significant source of differences in the concentrations of substances analysed in the sea surface microlayer. It is the method of sampling that

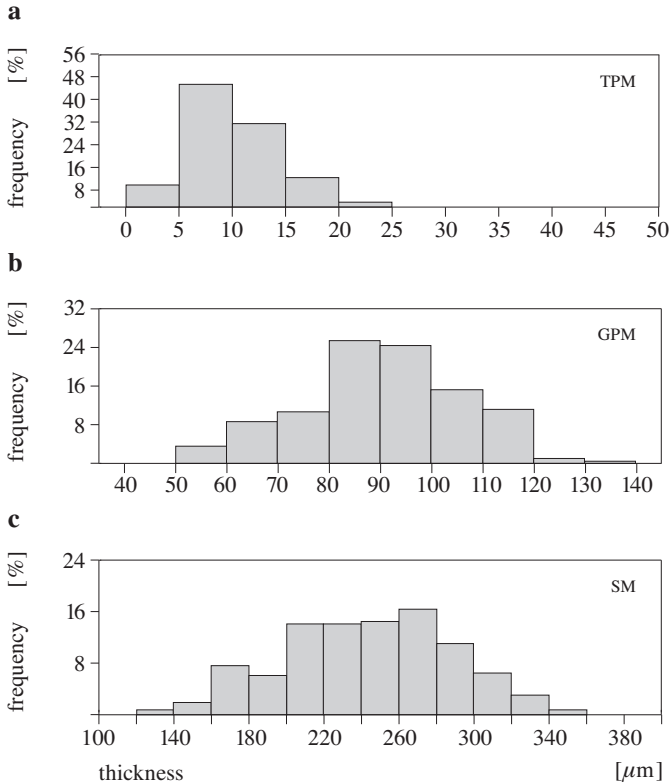


Fig. 2. Thickness of microlayer [μm] sampled by teflon plate – TPM (a), glass plate – GPM (b), and screen – SM (c)

determines the thickness of the collected microlayer. The teflon plate is strongly hydrophobic, and when raised slowly out of the sea, there remain on its surface irregularly distributed water droplets containing mainly organic substances. The glass plate does not exhibit such strong hydrophobic properties and when it is raised, a thin water layer adheres to its surface on both sides (Carlson 1982, 1983). In the screen method, the net openings form a trap in which surface water is retained by intermolecular tension forces (Garrett 1965, Daumas *et al.* 1976). Thus, each of these sampling techniques makes use of different properties of the sampling surface, hence the differences in the thickness of the microlayer collected. A sample collected with the teflon plate yields the best approximation of a surface film in which organic matter is a major constituent. By contrast, the glass plate, with its different surface properties, collects water from a thickness of about 90 μm ; consequently, this sample contains, besides non-polar substances, weakly polar compounds of hydrocarbon origin, their strongly

polar derivatives, and living organisms. The thickest microlayer is collected with the screen (Fig. 2).

The microlayer sampling was done under a variety of weather conditions. The 1992–1998 measurements showed there to be an evident relationship between the SM microlayer thickness and the wind speed (Fig. 3). A similar

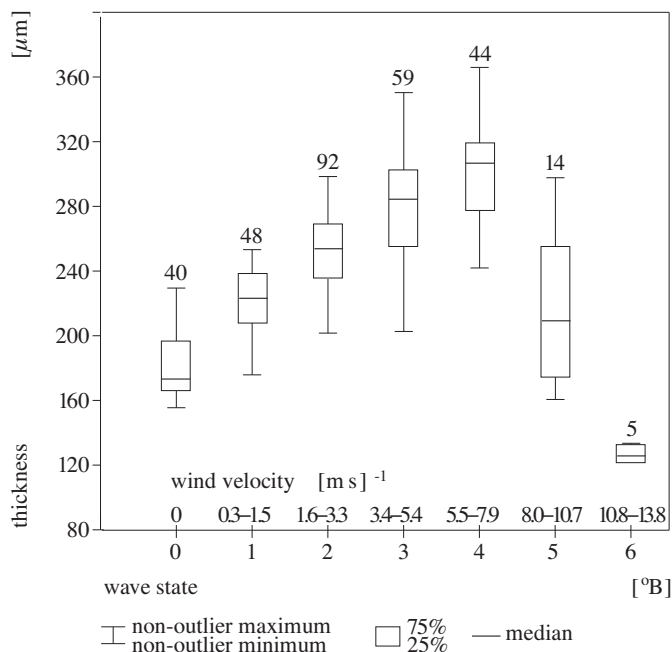


Fig. 3. Thickness of microlayer sampled by the screen technique at various wind speeds, (the digits over the box and whisker plots denote the total number of samples)

relation obtained in the case of glass plate (GPM) (Fig. 4). The microlayer thickness increased with increasing wind speed and wave height in the case of both sampling techniques. When the wind speed reached 8 m s^{-1} (5°B), the thickness of the microlayer sampled gradually diminished. Carlson (1982, 1983) studied the microlayer thickness at sea states from 0 to 4°B and obtained similar results for the glass plate, though he did not find any evident relationship in the case of screen sampling. Building up and sustaining a surface film does not require large surface tension forces; forces $< 1 \text{ dyn cm}^{-1}$ are believed sufficient (Jarvis 1967, Jarvis *et al.* 1967).

Organic substances present in seawater rise towards the air-water interface on bubbles. The studies of Jarvis (1967), later confirmed by Stramska *et al.* (1990), suggest that the number of bubbles increases when

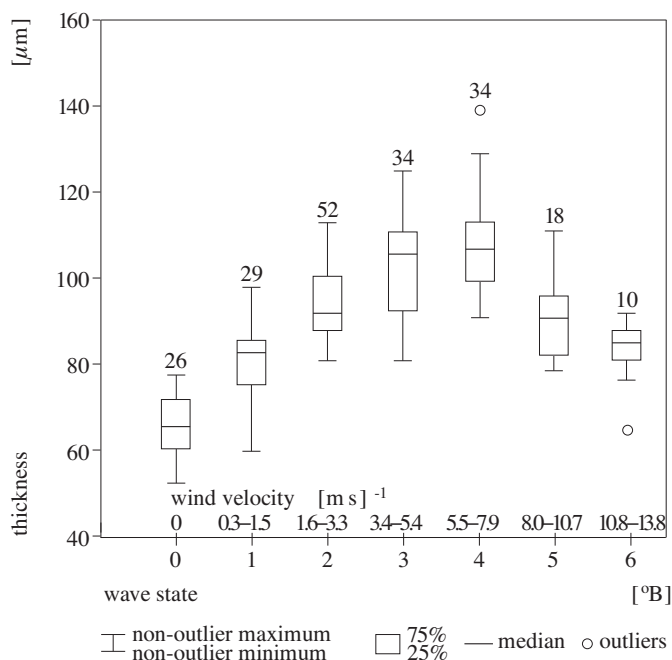


Fig. 4. Thickness of microlayer sampled by the glass plate technique at various wind speeds (the digits over the box and whisker plots denote the total number of samples)

the wind speed and wave height do so. The value of 8 m s^{-1} appears to be a critical wind speed in the study area. At wind speeds below this critical value, wave heights increase at a very low rate in response to wind. Above this speed, however, wave heights increase more rapidly. Liss *et al.* (1997) established that in coastal seawater and in areas where the concentration of water-soluble surfactant is 1 ppm, the critical wind speed is 8 m s^{-1} . Wind-generated mixing gives rise to increased advective transport of organic substances and a greater microlayer thickness. As the wind speed continues to increase, waves begin to break and whitecaps form. It is not clear, however, what happens to the soluble and insoluble components of the surfactant under these conditions. Are the processes by which organic matter is supplied and removed in approximate equilibrium? Increased wind speed and wave height exacerbate the difficulties of sampling: water droplets may be swept off the plate surface or blown off the screen net before they reach the ship's deck and are secured in the sample bottle. In either case, the end result is a diminished sample volume.

An inverse proportionality was observed between the TPM microlayer thickness and the wind speed (Fig. 5). It seems that in the case of the teflon

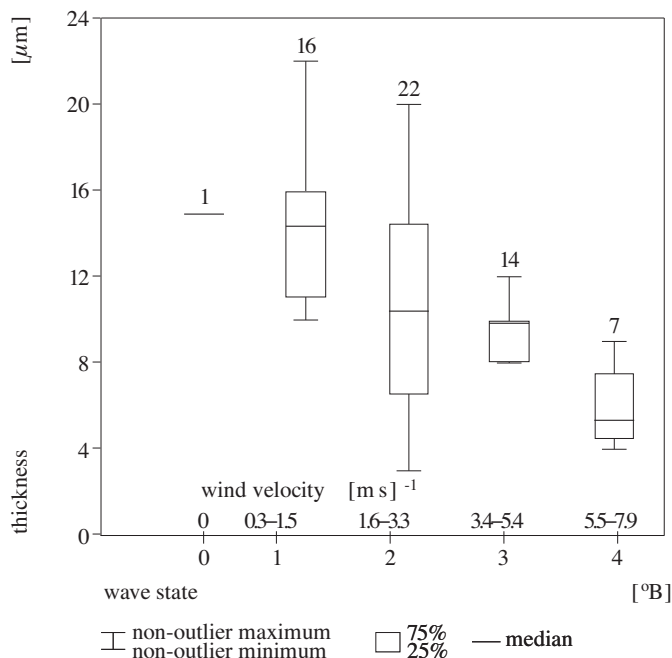


Fig. 5. Thickness of microlayer sampled by the teflon plate technique at various wind speeds, (the digits over the box and whisker plots denote the total number of samples)

plate, chemical composition and surfactant structure are decisive. It is well known that some components of the film are compounds with an asymmetric molecular structure, containing non-polar hydrophobic or weakly polar fragments with a hydrocarbon core, and strongly polar fragments. The greater the number of weakly polar groups with short-chain or water-soluble molecules (*e.g.* certain anionic detergents) at the sea surface, the more water droplets adhering to such a strongly hydrophobic adsorber as teflon (Fig. 6). In consequence, the volume of the collected sample increases. In such a case, a solid layer of water envelops the plate and the teflon plate now displays the properties of a glass plate. Active anionic surfactants disrupt the bonds between lipids and proteins and dissolve the surface film. This situation is most probable when the sea state is 0°B. But when the surface film is composed of strongly non-polar, long-chain molecules (*e.g.* lipids), water droplets then adhere to the teflon plate with only the minutest part of their surface (Fig. 6).

The glass plate generally adsorbs molecules containing hydrophilic groups, which form a solid film on the plate surface. This film can build up when the wave motion increases, owing to the factors already described,

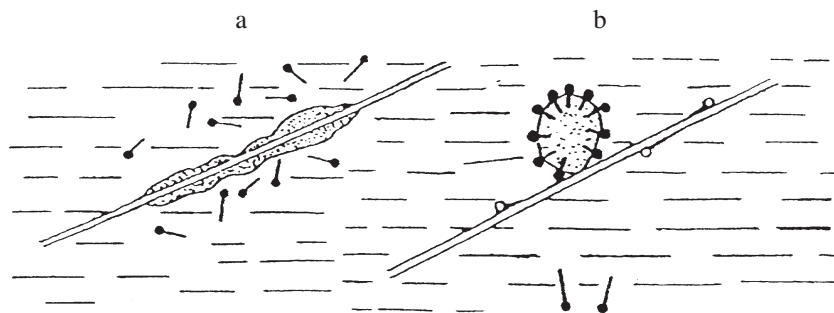


Fig. 6. Behaviour of surface-active substances on a glass plate (a), a teflon plate (b). The straight line denotes the hydrophobic group, the dot, the polar group. The asymmetric structure of the particles is responsible for their aggregation at the interface and formation of the adsorption layer

and also to the Langmuir circulation effect. However, in this case the phenomenon would be periodic in nature and would always appear in the convergence zone (Leibovich 1983). Analogous causes should be considered when SM microlayers are analysed.

Not just the wind field, but the water temperature too exerts a considerable impact on the surface microlayer thickness. Even over such a short distance as a few hundred micrometres, temperature and salinity alter with depth (Jarvis 1967, Hardy 1982). It is well known that the sea surface absorbs about 50% of the infrared radiation (Dera 1992). Surface water containing large amounts of organic matter intensively absorbs ultraviolet as well. These factors are decisive to biological development and also govern the biochemical processes in the surface microlayer, this being reflected in the vertical stratification of chemical substances. Generally speaking, salinity changes do not affect the volume of the microlayer sample, but temperature variations do alter the viscosity of molecules. Satellite observations have shown that the surface film temperature is lower than that of the water layer a few centimetres beneath ($\Delta T -0.1$ to -0.5 K) (Robinson *et al.* 1984). Many authors indicate that under certain conditions, the reverse situation obtains in the presence of a surface film of significant thickness, *e.g.* in the presence of an oil film. Differences emerged from a comparison of *ex situ* temperature measurements in the SM microlayer carried out directly after sampling in June 1992 with sample protection against solar radiation, with simultaneous *in situ* measurements in subsurface water (Fig. 7) (Falkowska 1996). Although the measurement errors were of considerable magnitude due to the measurement technique, the temperature amplitudes between the SM microlayer and water at 20 cm depth were as high as 3°C. Thus, temperature

has to be considered an additional factor influencing the thickness of the sampled microlayer (Fig. 7).

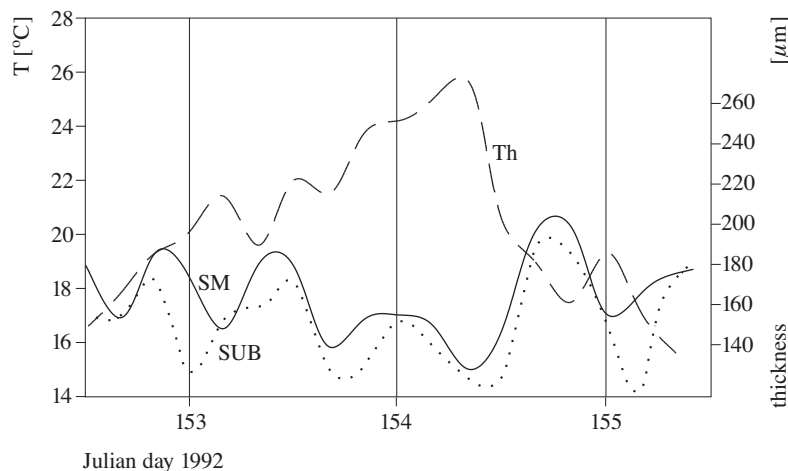


Fig. 7. Temporal changes in surface water temperature (T) and microlayer thickness (Th) in the Gdańsk Deep; SM – microlayer temperature, SUB – subsurface water temperature (ca 20 cm)

Laboratory experiments (Hatcher & Parker 1974) and also field studies (Harvey 1966, Carlson 1982) have yielded a negative correlation between microlayer thickness and subsurface water temperature. The thickness of a collected microlayer sample decreased in the 0–25°C range owing to the declining viscosity of molecules.

4. Conclusions

- Three methods – teflon plate, glass plate and screen – applied simultaneously to collect water samples from the sea surface, yielded samples of different thicknesses. The thinnest water layer, 10 μm on average, could be collected with the teflon plate; with the glass plate the thickness was 90 μm , and with the screen it was 250 μm . The difference in properties of the collecting plates was the main reason for the variation in microlayer thickness.
- Wind speed is of major importance as regards the thickness of a microlayer sampled with glass plate or screen. Any increase in wind speed and wave height intensified turbulent mixing within the sea surface layer and accelerated organic matter transport into the surface microlayer. The microlayer thickness and the wind speed were directly proportional to each other up to a critical wind speed of 8 m s^{-1} . At higher wind speeds, the thickness of the microlayer decreased.

- The chemical composition and the structure of surfactant organic matter seem to be the decisive factors as regards the thickness of a microlayer sampled with the teflon plate.
- The thickness of a microlayer sampled with the screen depended on water temperature, and the relation was inversely proportional.
- In oceanographic investigations, when a relatively large volume of sample is needed for analyses, sampling with a teflon plate is useless. However, classic microlayer sampling methods (glass plate and screen) can be used successfully even under difficult weather conditions.

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