

TRANSFER OF CHEMICAL SUBSTANCES THROUGH THE MARINE WATER – ATMOSPHERE BOUNDARY LAYER

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TRANSFER SUBSTANCJI CHEMICZNYCH PRZEZ WARSTWĘ GRANICZNĄ WODA MORSKA – ATMOSFERA

Praca prezentuje wyniki badań i główne hipotezy naukowe skupione wokół procesów występujących na granicy wody i atmosfery. Główny nacisk położono na określenie roli mikrowarstwy powierzchniowej morza w przeniesieniu substancji chemicznych w postaci gazów i aerozoli pomiędzy oboma ośrodkami. W wyniku badań pojawiły się fundamentalne pytania o zachowaną równowagę pomiędzy absorpcją i desorpcją CO₂ na granicy warstw oraz re-emisję rtęci Hg(0) z wody do atmosfery. Eksperymenty laboratoryjne nad absorpcją CO₂ z atmosfery i desorpcją CO₂ z wody morskiej stały się ważną przesłanką do szerokiej dyskusji naukowej o globalnym budżecie węgla. Re-emisja rtęci do atmosfery to problem przejawiający się silnym oddziaływaniem radiacji słonecznej i zdolności materii organicznej do redukcji jonów Hg(II). Problem efektywnej re-emisji rtęci do atmosfery został zaprezentowany jako złożony zespół uwarunkowań dynamicznych, fotochemicznych i biologicznych w transformacji Hg(II) do Hg(0). Rola żelaza atmosferycznego rozpatrywana jest na tle eutrofizacji wód powierzchniowych południowego Bałtyku. Depozycja tego elementu w aerozolach i w opadach deszczy jest prawdopodobnie zbyt mała, aby stymulować rozwój fitoplanktonu i wzmacniać poziom troficzności morza.

Summary

The processes occurring at the marine water – atmosphere boundary layer and involving selected important components of our environment are discussed. Special attention is focused on the specific role of the marine water surface microlayer in transfer of those components, properties of aerosols, fundamental question of CO₂ absorption/desorption balance and environmental conditions enabling re-emission of mercury from marine water into the atmosphere. Simple laboratory experiments on CO₂ absorption from atmosphere and desorption of CO₂ from marine water are shown as an initial point for any wider discussion on the global carbon budget. The emission of mercury to the atmosphere is considered to be promoted by the solar radiation. Under strong solar radiation the ability of organic matter to reduce these ions is enhanced thus making the emission more effective. The phenomenon observed seems to be confirmed by the analysis of the data for months of low and high radiation intensity. A significant role of atmospheric iron in eutrophication of southern Baltic is emphasized. Concentration of this element in dry and wet deposition is, however, too low to prevent limitation of phytoplankton growth in marine water.

THE EXCHANGE OF GASES AND AEROSOLS BETWEEN MARINE WATER AND ATMOSPHERE

An interaction between the sea and the atmosphere involves processes occurring in the two opposing directions; the one from the atmosphere towards the sea and the other one from the sea towards the atmosphere. At the boundary layer of the two phases one can distinguish the sea-surface microlayer of unique properties conditioned by the abrupt change in several physical parameters. The microlayer plays a double function: firstly, it is a source of substances being transferred from the sea to the atmosphere and constitutes a surface adsorbing and absorbing substances which fall out of the atmosphere. This implies that the exchange of both natural and anthropogenic substances must occur through the sea water – atmosphere boundary layer [8].

The atmospheric input is being accomplished via the dry and wet deposition. Over the marine coastal zone and over the open sea, aerosols drop gravitationally while gases are under the influence of several phenomena including diffusion and entropic effects modified strongly by the wind action. Further processes are conditioned by turbulent or molecular diffusion, inertial settlement and/or reaction with components of the water. Among the above processes, gravitational sedimentation is particularly effective for relatively large aerosol particles and rain droplets. Small particles undergo the Brown motions and due to the adhesion processes enlarge their size. Whether they will be transferred to higher parts of the atmosphere or removed from it depends on actual physical parameters of the atmosphere (pressure, temperature, humidity, velocity and direction of the advection). It has been evaluated that in mid latitudes 70–80% of the total mass of aerosols is being removed from the atmosphere through various forms of wet depositions [10, 19]. The opposite process – emission of aerosols from the sea surface occurs mainly due to bursting of gaseous bubbles which rise out of the bulk water. Surface tension forces of the bubble membrane are the major factor which causes welling up process of aerosols. The total flux of particles blown up from the sea surface is directly proportional to the square of the wind velocity. In a general mass of atmospheric aerosols dominate those being of marine origin their composition and size being dependent on the distance from the land. The establishment of sources of all components of gases and aerosols in the coastal zone is a difficult task since in this both marine and terrestrial masses of wind mixed here come from various directions [19].

THE TRANSFER OF CARBON DIOXIDE

The basis for constructing global carbon budget is the assumption that CO_2 fluxes in processes of absorption by oceanic waters and desorption from those waters are nearly the same [11, 20] and are of the order of $100 \cdot 10^{12}$ kg at the prevalence of absorption by only $1\text{--}4 \cdot 10^{12}$ kg. The alkaline pH of the marine water should constitute a strong driving force for the absorption of atmospheric CO_2 and simultaneously it should constitute a strong barrier for the desorption of CO_2 from the marine water [16, 17]. The repeated laboratory experiments involving forced CO_2 desorption from marine water confirmed, what was quite obvious from the physical and chemical point of view that the phenomenon occurs with the greater intensity when pH is lower. What was, however, not compatible with the widely accepted

view of global CO_2 fluxes, the desorption of this gas appeared to be hardly detectable not only at very high $\text{pH} = 9.0$ but also at $\text{pH} = 8.0$ and despite dramatic decrease in CO_2 partial pressure over the marine water samples. This decrease was accomplished in two independent experiments carried out with the use of closed chambers; in the first experiment by the use of vacuum generated by water jet pump [16] and in the second one by effective removal of this gas with the aid of aqueous solution of KOH [17] (Fig. 1).

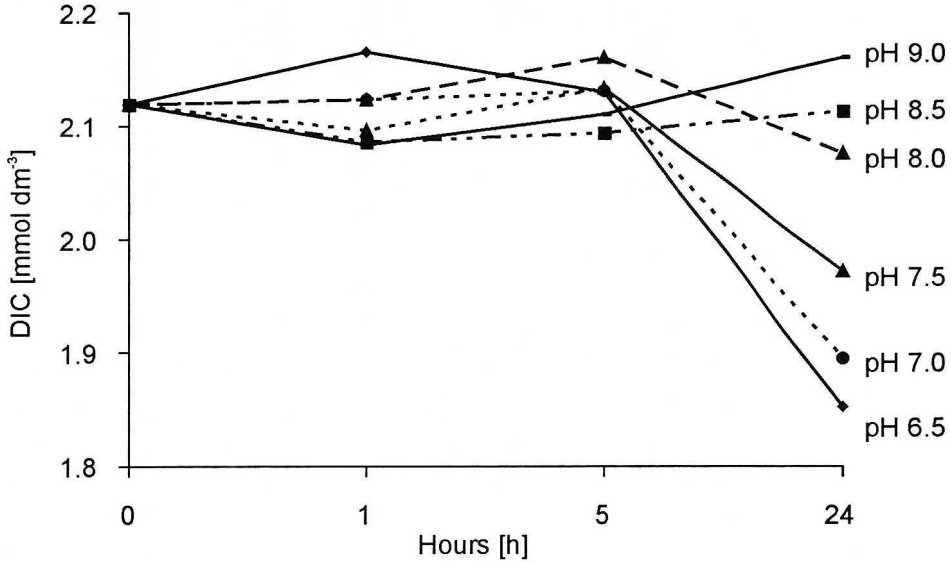


Fig. 1. Dissolved Inorganic Carbon (DIC) in marine water samples of different pH as a function of the CO_2 desorption time; the CO_2 desorption was forced by the reaction with KOH solution placed above the sea water in the tightly closed chamber

If the CO_2 desorption practically did not proceed under so drastic decrease in partial pressure of this gas over the marine water, then it seems almost unlikely that in natural environmental conditions it proceeds to such a degree as to almost balance the reverse process (atmospheric CO_2 absorption) which is easily detectable even at $\text{pH} = 6.0$.

Another interesting but rather surprising result dealt with the most advantageous marine water pH which could enable the fastest CO_2 absorption. From the general chemical point of view it seemed obvious that water samples of higher pH should be more effective in this respect. Such a result could also be expected from the analysis of the Fig. 1 if periods longer than 24 hrs were considered. From the same figure one could also conclude that in a short-term scale the problem may appear to be more complex. To recognize the problem, marine water samples of $\text{pH} = 6.5, 7.0, 7.5, 8.0, 8.5$ and 9.0 were placed in a 20 dm^3 chamber and treated with 1 dm^3 of CO_2 (measured at room temperature and atmospheric pressure). After 5 hours, total dissolved inorganic carbon (DIC) was determined and compared to the initial value. The greatest DIC increase occurred indeed at $\text{pH} 8.0$ (Fig. 2) as was indicated by relative positions of curves in Fig. 1 and not at $\text{pH} 9.0$ as one could have expected from general chemical point of view.

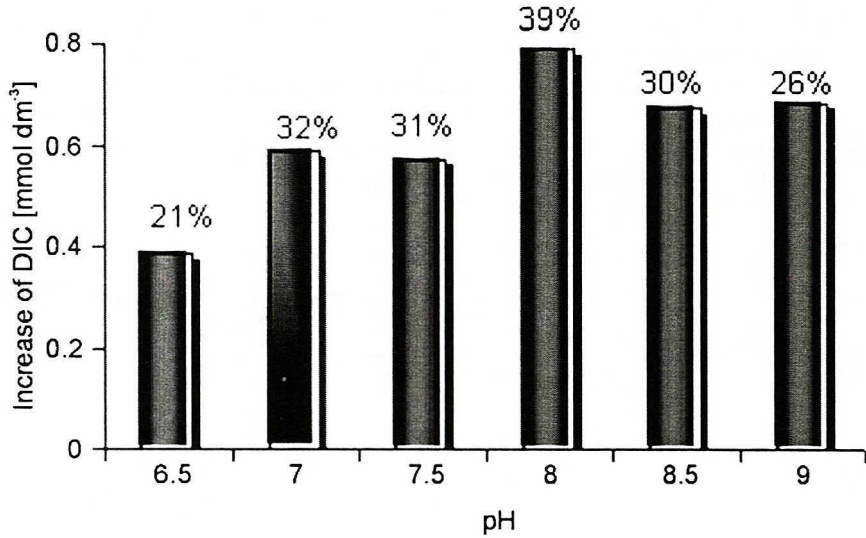


Fig. 2. Increments of dissolved inorganic carbon (DIC) in seawater samples of different pH after 5-hour contact with atmosphere, enriched with 1 dm³ of CO₂ per chamber of total volume 20 dm³

Among several factors causing such a rather surprising result the following two major effects were considered: the effect of some substance (occurring at optimum high concentration at pH close to 8.0) catalyzing absorption of CO₂ and the role of the biotic factor. This very intriguing question is currently the subject of a complementary study involving the possible role of HPO₄²⁻, Fe²⁺ and Zn²⁺ ions; the last one being an active center of the metalloenzyme carbonic anhydrase.

Studies on the absorption-desorption phenomena at the marine water atmosphere boundary layer are being continued in semilaboratory conditions taking into account variable meteorological conditions (pressure, air humidity, temperature, radiation, turbulent mixing) and species of phytoplankton characteristic for a given season of the year. The biochemical state of the organic matter accumulated in the marine water surface microlayer is considered

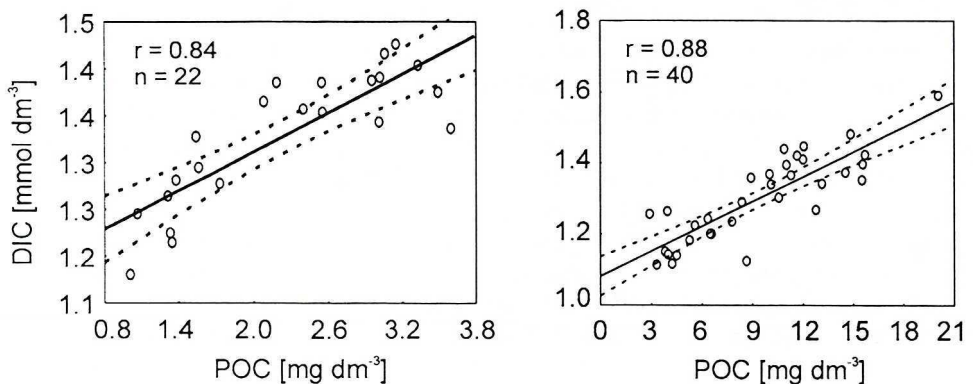


Fig. 3. Dependence between concentrations of dissolved inorganic carbon (DIC) and particulate organic carbon (POC) in the two semilaboratory experiments involving diatoms (a) and blue-green algae (b); confidence level = 95%

as crucial for both the magnitude and the direction of the net CO_2 exchange. The presence of phytoplankton at the stage of intense growth enhances the CO_2 absorption from the atmosphere. On the other hand, a pronounced increase of DIC may constitute a significant barrier for the CO_2 absorption. This may be concluded from Fig. 3 which reflects the fact that the transformation of organic carbon (released by algae) to inorganic carbon is a relatively fast process. If the respiratory break-down process was slow then the DIC vs. POC dependence would not be linear. The greater the increase in the phytoplankton biomass (POC) the more inorganic carbon (DIC) is being released, thus contributing to a higher partial pressure of CO_2 and consequently to lowered capability of marine water for absorption of this gas from the atmosphere. The turbulent mixing of the surface water undoubtedly affects both absorption and desorption of CO_2 , however, not to the same extent and finding the corresponding explanation for the net effect in this respect is another interesting goal.

The results obtained in the aforementioned experiments seem to impair the commonly recognized opinion that the global processes of CO_2 absorption and desorption at the ocean – atmosphere are nearly balanced.

THE TRANSFER OF MERCURY

Because of high toxicity and bioaccumulation, mercury is regarded by Environmental Protection Agency (EPA) as a very hazardous component of the natural environment. Also in the strategic goals elaborated by GESAMP [8] much attention is drawn to the effects of mercury on the marine and terrestrial ecosystems.

The evaporation of mercury from the earth's crust and water reservoirs are besides of volcanic emissions major sources of mercury in the atmosphere. It must be stressed that the contribution of anthropogenic emission is significant compared to the natural one. This in particular takes place in the case of the Baltic Sea making it one of the most polluted with mercury water reservoirs. The pollution of the coastal zone of the Baltic Sea occurs with the participation of rivers and the atmosphere. Processes of mercury exchange between the sea and the atmosphere are therefore of great importance to the mankind. Their recognition requires that both biotic and abiotic factors on the corresponding exchange fluxes are taken into account.

For several years it has been commonly thought that mercury introduced to the aquatic reservoir will settle on the bottom and will remain there in a non-mobile state (mainly in the form of practically insoluble mercury sulfide). Quite recently the evidence has been presented that mercury introduced by man for a century to the environment is being reemitted [14, 15]. In comparison to the pre-industrial period, the level of pollution of the Baltic sediments increased several times reaching the concentration as high as 40 ng per 1 g of the dry mass [13]. The latest studies of mercury level in sandy sediments of the coastal zone of the Gulf of Gdansk have shown that the concentration of total mercury ranges from 41 to 109 ng per 1 g of the dry mass. Much higher concentrations in the range 246–422 ng per 1 g of the dry mass were reported for loamy sediments [3]. This almost 100-fold increase in mercury concentration (in relation to regions being far from anthropogenic sources) occurred due to the sewage in the Puck Bay in the Mechelinki region. The above data indicate unequivocally that sediments are deposits of mercury that earlier entered the sea water. Although the emission of mercury was significantly limited in the past century, in several regions its

concentration still remains very high [14]. This is confirmed by the results of measurements carried out in the coastal zone of the Gulf of Gdansk with the aid of AAS GARDIS 3 since 1977 [9]. According to Bełdowska [2], in the late autumn and winter season the Gdańsk Basin becomes a reservoir of atmospheric mercury. Apparently both the low radiation level and low temperature were advantageous for the absorption of mercury by marine water during that season. Another possible factor were slower (than average during the whole year) living processes in the late autumn and winter. In that time mercury deposition fluxes ranged from a few to almost $200 \text{ ng}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ [2]. For comparison, the global mercury emission from ocean to atmosphere is evaluated as ca. $2000 \text{ Mg}\cdot\text{year}^{-1}$ [18]. During storms the emission may increase even 25-fold [1] which is particularly characteristic of the coastal zone. The measurements carried out in the region of the Gulf of Gdańsk have shown that this zone is a mercury source for most of the year. The fluxes of mercury transferred from the surface seawater microlayer ranged from 12 to $6000 \text{ ng Hg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ while at stations located far away from the coast and at open sea they ranged from 19 to $171 \text{ ng Hg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ [2]. The escape of mercury to the near-water layer of the atmosphere occurred very intensively when the solar radiation enabled reduction of ionic to gaseous mercury by dissolved organic matter. In such exceptional conditions, oversaturation with gaseous mercury occurred giving rise to its intense re-emission to the atmosphere. The turbulent mixing of water enhanced the exchange of gaseous mercury between seawater and atmosphere and hence accelerated mercury transformation processes such as accumulation by biofilm, accumulation by phytoplankton, reduction of Hg(II) to Hg(0) , detoxification of algae [4]. The results of semilaboratory experiments constitute the basis for the hypothesis that detoxification of *Cyclotella meueghlainiana* diatoms causes exceptionally strong mercury re-emission from seawater to the atmosphere [5]. The marine sources indicated here supply the air over the coastal zone of the Gulf of Gdańsk with mercury (Fig. 4).

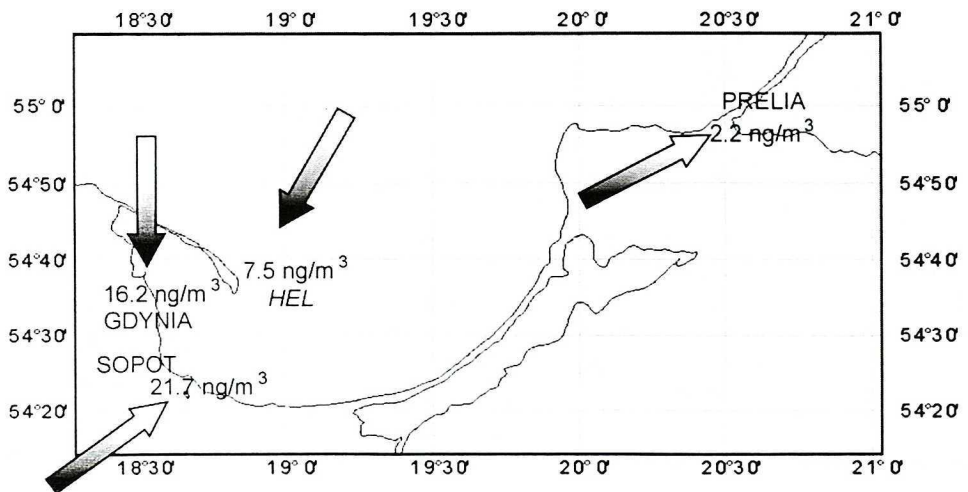


Fig. 4. Maximal value of gaseous mercury concentration in the air over the coastal station in the Gdańsk Basin; advection of air under which the maximal Hg concentrations occurred are pointed out by arrows

Statistical analysis of the data for the gaseous mercury collected in years 1997–2003 showed no linear dependence between $\text{Hg}(0)$ and air temperature [2]. Only in a few cases (June, and July) when the ambient temperature exceeded 10°C a statistically important positive linear correlation ($r=0.75$) was determined. Presumably, the high temperature was at that time the parameter determining oversaturation of seawater with gaseous mercury its emission to the atmosphere and enhanced evaporation from land soil. During the remaining months the effects of various factors, e.g. air temperature, air pressure, humidity, wind speed, wind direction were overlapping with variable intensity giving no clear picture of the dependence on any strictly defined parameter.

THE ROLE OF ATMOSPHERIC IRON IN EUTROPHICATION OF THE SOUTHERN BALTIC

The atmosphere is a significant source for dissolved and particulate iron, especially in relation to coastal surface waters. From the atmosphere iron is being removed via the wet and/or dry deposition. The wet deposition of particles is thought to be a major iron source for oceans and constitutes ca. 80% of the total atmospheric input [6]. The mineral iron present in aerosols is not directly bioavailable. The acidic components of rain and aerosols and photochemical processes transform it to soluble $\text{Fe}(\text{II})$ and $\text{Fe}(\text{III})$ compounds, however, after the contact with marine water with alkaline pH most of the iron is again converted into insoluble forms. The remaining part of iron entering surface waters becomes a stimulator of the phytoplankton growth.

The coastal zone of the Gulf of Gdańsk is under a strong influence of the Vistula river waters rich in iron and, on the other hand, under the influence of atmospheric depositions. During measurements carried out over the southern Gulf of Gdańsk the average fluxes of total iron (Fe_{tot}) in rain depositions were the greatest in winter (4.14 mg m^{-2}) and spring (3.34 mg m^{-2}), at the highest amplitude in spring and in summer. A wide range of variability

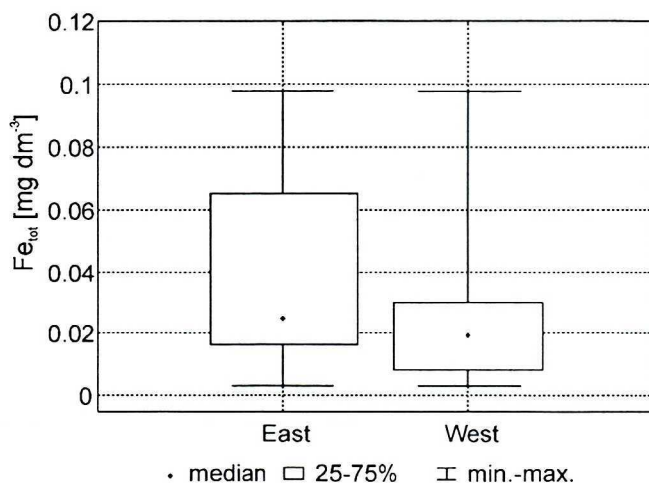


Fig. 5. Changes of iron concentration in the wet deposition caused by East and West advection

of iron concentrations over the Gulf of Gdańsk was indicative of not only complexity of processes preceding the deposition, but also of flushing out of aerosols from the atmosphere. The effectiveness of iron flushing increased with the decrease of pH which undoubtedly has strong relevance to the solubility of particular iron compounds in water. The presence of Fe(III)-hydroxycompounds, being typical rain components was, in turn, revealed in samples collected at low air temperatures ($< 10^{\circ}\text{C}$) [7]. The fact that iron concentrations in wet deposition are low suggests that the atmosphere as an ineffective source of this metal is unable to prevent limiting phytoplankton growth in marine water.

Fig. 5 shows that among analyzed meteorological factors affecting iron concentrations in depositions the most significant were eastern winds i.e. those entering from the Gulf of Gdańsk. A particular role must be attributed to the swash zone which stimulates emission of iron containing aerosols, however, terygenic sources are also of some significance.

CONCLUSIONS

Independent, specially designed experiments on CO_2 absorption and desorption processes indicate that in environmental conditions global absorption flux is much greater than the global desorption flux.

At pH close to 8.0 particularly advantageous conditions for absorption of CO_2 occur suggesting that we may be dealing with the very specific reaction which so far, has not been recognized well enough.

Transformations of mercury in marine water and its escape to the atmosphere are conditioned by various biotic and abiotic factors. Among abiotic factors the most important ones are: the temperature of the water and air, wind mixing and solar radiation which stimulates photochemical processes. Among biotic factors affecting mercury transformation the most essential is phytoplankton concentration as well as concentrations of auto- and allochthonic dissolved organic matter.

The effectiveness of iron wash out depends on various parameters of which the most important seem to be pH and height of wet deposition. Despite of large variability of iron concentration in rain, this kind of input appears to be less significant for phytoplankton compared to river outflow of this element.

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