

# Nitrogen and phosphorus exchange in the contact zone between the sea and the atmosphere\*

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Air-sea exchange  
Surface film  
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## Abstract

The paper describes a method of collecting samples of sea surface film. The enrichment factors of the microlayer towards nitrogen (0.37-4.92) and phosphorus (0.45-1.48) compounds have been calculated. Factors of aerosol enrichment in the sea surface film have been presented, and the magnitudes of the effective nitrogen and phosphorus fluxes from the atmosphere to sea water have been estimated to be equal to 35.7 and 1.15  $\mu\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ , respectively.

## 1. Introduction

The search for methods of description of the exchange between the sea and the atmosphere has been the topic of numerous investigations. Attempts to evaluate the magnitude of emissions of various substances have been presented in many papers (Bezborodov and Yeremeyev, 1984; Duce and Hoffman, 1976; Garbalewski, 1977; Graham *et al.*, 1979; Wallace *et al.*, 1972). Detailed investigations on aerosol exchange between the sea and the atmosphere with regard to the dynamic conditions in both these media were reported by Garbalewski (1977).

The magnitude of emission of nitrogen and phosphorus compounds from the sea to the atmosphere is little recognized in the literature investigating

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the circulation of these compounds in the Baltic. Falkowska (1988a) presented an approximate method of evaluating the emission of nitrogen and phosphorus compounds from the sea to the atmosphere, based on experimentally determined coefficients of the decline of these compounds in the near-surface sea layer.

Numerous authors prove in their papers that the flux of particles emitted from the sea surface on breaking of gas bubbles evolving from water is the main supply source of the atmosphere with marigenous aerosols (Duce and Hoffman, 1976; Garbalewski, 1977; Graham *et al.*, Lemlich, 1972; MacIntyre, 1972). When escaping from the sea surface, they sweep away a very thin surface water film from the sea-air interface. Hence, an escaping droplet contains the material from the sea surface film of *ca.* 0.05  $\mu\text{m}$  thickness. The chemical composition of sea surface film differs very much from the composition of surface water at 10–20 cm depth (Duce and Hoffman, 1976; Garrett, 1965; Graham *et al.*, 1979; Harvey, 1966; Jarvis, 1967). Because of this, the previous evaluations of the emission flux magnitude, based on measurements of the concentration of chemical substances in near-surface water, seem to be underestimates.

This paper aims to verify the previous methods of emission evaluation by using a method regarding the sea surface film as the main emitting layer.

## 2. Materials and method

The investigations were carried out in May 1989 aboard the naval ship ORP 'Arctowski' on the waters of the Gdańsk Deep and in June 1989 aboard a vessel of the Institute of Oceanography k/h 'Oceanograf 1' in Puck Bay. The following samples were collected:

- surface film,
- sub-surface water from a depth of 15 cm,
- sub-surface water from a depth of 1 m.

Additionally, samples of marine aerosols were collected in May. The aerosols have been collected on glass fiber Whatman GF/F of 0.7  $\mu\text{m}$  pore diameter.

Aerosol samples were collected at 10 m a.s.l. on a stand located in the forebody of the anchored ship. The filters were changed once a day, after 5–10  $\text{m}^3$  of air had passed through them. The filters were roasted at 450°C and weighed prior to expose.

Surface film samples were collected with nets at a distance of 1 Mm from the windward side of the anchored ship. Sub-surface water samples from the depth of 15 cm were collected by hand in polyethylene containers, while those from 1 m were collected using a bathometer. Samples of sea water were collected at the sea state of 0–1°B.

Garrett's nets were used for collecting sea surface film samples. The 40 × 50 cm nets were made of polyethylene (23 mesh) stretched over polyamide frames. The nets were washed with alcohol and bidistilled water before each use.

Surface water film samples were collected using the following technique. The net was immersed in water at an angle of 45°; after a complete submersion it was kept under water until a continuous surface film formed again. Then the net was raised horizontally to the surface at a rate of 5–6 cm · s<sup>-1</sup> (Garrett, 1965). Ten seconds after taking the net out the collected water was poured through a groove made specially in the frame into a polyethylene container. On average, eight surface film samples were collected in each container. The volume of the samples was measured directly after collecting and chemical analyses with methods described by Grasshoff (1976) were then performed.

Aerosol samples were analyzed in the land laboratory after drying and weighing the filters in order to determine the weight of the collected aerosols. Preparation of the filters for analysis and the applied chemical methods have been described in papers by Falkowska (1985) and Falkowska and Korzeniowski (1988).

Basic meteorological measurements were carried out on the ships during the investigations.

### 3. Results and discussion

Concentration of nitrogen and phosphorus compounds in the surface film and the sub-surface layer differed. In both cases the concentrations in the surface film were higher than in the deeper layers (Tabls. 1 and 2). The greatest concentration differences between the microlayer and the surface water occurred in the Gdańsk Deep for nitrogen compounds. Moreover, surface film was characterized by greater variability of nitrogen compound concentrations compared to the deeper water layers.

Total phosphorus concentration in aerosols above the Gdańsk Deep fell within the 11.5–72.1 ng · m<sup>-3</sup> range (Tabl. 3), while those of total nitrogen – from 250 to 923 ng · m<sup>-3</sup>. Inorganic forms constituted almost 50% of the nitrogen mass. Ammonia nitrogen concentration in aerosols showed the smallest variations (Tabl. 3).

Microsurface enrichment factors (*E*) for nitrogen compounds ranged from 0.32 to 9.92 (Tabl. 2), the smallest values occurring for inorganic nitrogen compounds, with the largest values being for its organic forms. An opposite tendency was observed for phosphorus compounds (Tabl. 1). Enrichment factors of the 15 cm layer were approximately ten times lower than those of the 1 m layer. (Puck Bay, Tabls. 1 and 2).

Table 1. Phosphorus compounds ( $\mu\text{mole} \cdot \text{dm}^{-3}$ ) in surface sea water

Component	Gdańsk Deep, May 1989				Puck Bay, June 1989				Narragansett Bay				The North Sea	
	$\bar{x}$	$\sigma$	$\Delta$	$E$	$\bar{x}$	$\sigma$	$\Delta$	$E$	$\bar{x}$	$\sigma$	$\Delta$	$E$	$E$	$\Delta E$
PO <sub>4</sub> -P	Film	0.87	0.64	0.24-1.91	1.48	0.67	0.15	0.46-0.93	1.23	0.02-0.27	0.09	0.09	-0.40-1.80	
	.15 cm	0.35	0.37	0.05-1.08		0.30	0.04	0.25-0.35	0.20					
	1 m					0.25	0.06	0.15-0.35						
P <sub>Tot</sub>	Film	2.03	0.35	1.56-2.61	0.77	1.67	0.28	1.26-2.04	0.86					
	15 cm	1.15	0.23	0.76-1.52		0.90	0.33	0.34-1.32	0.07					
	1 m					0.84	0.33	0.18-1.14						
P <sub>Org</sub>	Film	1.16	0.63	0.30-2.10	0.45	1.00	0.17	0.70-1.25	0.67	0.18-0.37				
	15 cm	0.80	0.35	0.42-1.20		0.60	0.34	0.00-1.02	0.02					
	1 m			0.59	0.28	0.03-0.89								

n - number of data,

h - surface film thickness,

 $\bar{x}$  - mean concentration, $\sigma$  - standard deviation, $\Delta$  - variability range,E - surface film enrichment factor =  $\frac{x_{\text{microlayer}}}{x_{\text{below surface}}} - 1$  (Graham et al., 1979).

Table 2. Nitrogen compounds ( $\mu\text{mole} \cdot \text{dm}^{-3}$ ) in surface sea water

Component	Gdańsk Deep, May 1989				Puck Bay, June 1989				The North Sea 1975-1976		
	$\bar{x}$	$\sigma$	$\Delta$	$E$	$\bar{x}$	$\sigma$	$\Delta$	$E$	$E$	$\Delta E$	
$(\text{NO}_3 + \text{NO}_2)\text{-N}$	Film	1.88	0.43	1.20-2.58	0.32	1.50	0.45	0.85-2.40	0.70	0.47	-0.53-2.49
	15 cm	1.42	0.24	1.12-1.80		0.88	0.38	0.42-1.47			
	1 m					0.75	0.29	0.50-1.31			0.17
$\text{NH}_4\text{-N}$	Film	1.34	0.65	0.86-2.76	0.38	1.17	0.35	0.66-1.82	0.44	0.22	-0.49-3.00
	15 cm	0.97	0.28	0.74-1.58		0.48	0.23	0.20-0.89			
	1 m					0.50	0.22	0.13-0.74			-0.04
$\text{N}_{\text{Tot}}$	Film	6.71	0.98	5.38-8.33	1.25	5.76	1.29	4.42-8.24	0.68		
	15 cm	2.98	0.56	2.25-3.82		3.42	0.84	2.34-4.51			
	1 m					3.14	0.95	1.64-4.26			0.09
$\text{N}_{\text{Org}}$	Film	3.49	1.39	2.09-5.88	4.92	2.95	1.21	1.23-4.56	0.45		
	15 cm	0.39	0.26	0.11-0.85		2.04	1.11	0.35-3.84			
	1 m					1.82	1.26	0.36-3.56			0.12

Legend as in Table 1.

Similar values of the microlayer enrichment factors have been obtained by Graham *et al.* (1979) for the Narragansett Bay and by Chapman and Liss (1981) for the North Sea. The results of Chapman and Liss (1981) were obtained between 1975–1976 and prove that microlayer enrichment factors are subject to seasonal changes. In the case of phosphates no enrichment (negative value of  $E$ ) was established in 7 out of 32 collected surface film samples. For nitrates the microlayer enrichment factors were negative in 13, while for ammonia – in 7 out of 30 collected surface film samples. The prevailing number of cases with negative microlayer enrichment factors was observed by Chapman and Liss in April, as well as October and December; this concerned mainly phosphates and nitrates.

Graham *et al.* (1979) report a directly proportional dependence of microlayer enrichment factors on wind velocity. De Souza Lima (1985) does not confirm this correlation. It follows from the investigations carried out in the Gulf of Marseille that enrichment in phosphates was high when the sea surface was calm, and decreased as wind velocity increased. De Souza Lima believes that large dispersion of the values of  $E$  at small wind velocities ( $2 \text{ m} \cdot \text{s}^{-1}$ ) allows us to deduce that processes other than the state of the sea affect accumulation of phosphates in the microlayer. Apart from the seasonal dependencies indicated by Chapman and Liss (1981), De Souza Lima (1985) indicates distinct diurnal variations of the  $E$  coefficient, the changes being not equal for all the nutrients. It should also be emphasized that river inflows and atmospheric precipitation can influence the accumulation of substances in sea surface film, thus causing the value and variability of the  $E$  coefficient.

On the basis of the dependence given by Duce *et al.* (1972) the factor of enrichment of aerosols by sea surface layer was calculated:

$$EF = \frac{[C/Na]_{\text{aerosol}}}{[C/Na]_{\text{water}}}, \quad (1)$$

where:

C – concentration of the determined compound,

Na – sodium concentration.

Sodium concentration in aerosols equal to  $1747 \text{ ng} \cdot \text{m}^{-3}$  (Bolalek and Kręzlewicz, 1987) has been adopted for calculations, while sodium concentration in sea water has been determined from the dependence:

$$\begin{aligned} \text{Na/Cl} &= 0.5530 \quad (\text{Trzosińska, 1977}), \\ \text{Na} &= 2.29 \text{ g} \cdot \text{dm}^{-3}. \end{aligned} \quad (2)$$

Calculation of  $EF$  for nitrogen and phosphorus were carried out using the mean concentrations of the elements given in Tables 1 and 3.

Table 3. Nitrogen and phosphorus compounds in aerosols ( $\text{ng} \cdot \text{m}^{-3}$ ) over the Southern Baltic

Region		$P_{\text{Tot}}$	$(\text{NO}_3 + \text{NO}_2) - \text{N}$	$\text{NH}_4 - \text{N}$	$N_{\text{Tot}}$	$N_{\text{Org}}$
Gdańsk Deep, May 1989	n	5	5	5	5	5
	$\bar{x}$	35.9	233.0	-70.8	597.2	295.3
	$\sigma$	22.6	69.0	18.4	220.1	148.4
	$\Delta$	11.5-72.1	155.3-339.4	35.4-89.0	249.7-922.7	59.0-494.2
Coastal zone, 1981-1985 (warm half-year, Falkowska, 1988b)	n	20	20	20	20	20
	$\bar{x}$	150.0	530.0	360.0	1190.0	280.0
	$\sigma$	120.0	380.0	320.0	860.0	270.0
	$\Delta$	20.0-390.0	30.0-1710.0	20.0-1340.0	70.0-3310.0	20.0-960.0
Open sea zone, 1981-1985 (warm half-year, Falkowska, 1988b)	n	32	32	32	32	32
	$\bar{x}$	90.0	340.0	210.0	720.0	150.0
	$\sigma$	80.0	370.0	270.0	670.0	200.0
	$\Delta$	0.8-320.0	0.3-1340.0	0.8-119.0	4.0-2335.0	4.0-890.0

$EF_{P_{tot}}$	-	580 - 1200
$EF_{NO_3+NO_2}$	-	7700 - 16900
$EF_{NH_4^+}$	-	2400 - 6200
$EF_{N_{tot}}$	-	3400 - 12800
$EF_{N_{org}}$	-	3480 - 12800

Graham *et al.* (1979) determined the enrichment factors for phosphorus in the Narragansett Bay, ranging from 6 to 114. Piotrowicz *et al.* (1979) obtained  $EF$  values of the same order of magnitude for copper, iron and zinc. Bezborodov and Yeremeyev (1984) report  $EF$  values of 1600 for inorganic phosphorus.

Due to their very large variability, the two components of equation (1), *viz.* the concentration of the examined substance in aerosols and in the microlayer, exert the greatest effect on the final value of the  $EF$  coefficient, the seasonal and regional factors, as well as the direction of air masses advection, determining the character of the changes. Surface film sampling technique is also important. Samples of microlayer of 280  $\mu\text{m}$  thickness have been collected at the Gdańsk Deep and Puck Bay (Tabl. 1). Numerous investigators suggest that the true thickness of the surface layer is much smaller. As a result this the values of the enrichment factors can vary significantly depending on the sampling technique.

Nitrogen and phosphorus emission fluxes from the sea to the atmosphere have been calculated on the basis of the results listed in Tables 1 and 3 according to the dependence given by Duce *et al.* (1972):

$$F = EF \cdot F_{Na} [C/Na]_{\text{water}}, \quad (3)$$

where:

$$F_{Na} = 46.4 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \quad (\text{Bolalek, 1987}),$$

thus:

$$F_P = 0.92 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1},$$

$$F_N = 15.86 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}.$$

Emission fluxes in the Southern Baltic have been estimated to fall within the ranges:

$$0.93 - 17.41 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \quad \text{for nitrogen,}$$

$$0.13 - 2.82 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \quad \text{for phosphorus (Falkowska, 1988a).}$$

The estimation presented here of nitrogen and phosphorus emission fluxes is very close to previous calculations of Falkowska (1988a) despite the use of different measuring techniques and estimation methods.

Emission fluxes of aerosols containing nitrogen and phosphorus from the atmosphere to the were calculated on the basis of mean precipitation rate ( $V[\text{cm} \cdot \text{s}^{-1}]$ ) and concentration of the elements in aerosols of the near water atmosphere layer ( $C_{\text{aerosol}}$ ) listed in Table 3 according to the equation:

$$F = C_{\text{aerosol}} \cdot V. \quad (4)$$

The following mean aerosol precipitation rates were adopted for the calculations:

$$\begin{aligned} V_P &= 1.6 \text{ cm} \cdot \text{s}^{-1}, \\ V_N &= 2.4 \text{ cm} \cdot \text{s}^{-1} \quad (\text{Falkowska, 1988b}). \end{aligned}$$

Emission flux magnitudes estimated on the basis of equation (4) are equal to:

$$\begin{aligned} F_P &= 2.07 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \quad \text{for phosphorus,} \\ F_N &= 51.58 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \quad \text{for nitrogen.} \end{aligned}$$

The effective flux of nitrogen and phosphorus in the aerosol exchange between the sea and the atmosphere is the difference between the emission and imission fluxes. In May 1989 it was directed to the sea and was equal to:

$$\begin{aligned} F_E &= 1.15 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \quad \text{for phosphorus,} \\ F_E &= 35.7 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \quad \text{for nitrogen.} \end{aligned}$$

#### 4. Conclusions

Investigations carried out at the Gdańsk Deep and Puck Bay revealed a great variability of nitrogen and phosphorus compound concentration in the sea surface film and aerosols of the near water atmosphere layer. Such a situation can result from variable environmental conditions. As evidenced by the results of other researchers, the concentrations of nitrogen and phosphorus compounds vary in diurnal and seasonal cycles, depending on the biological activity of living organisms. Changes of nitrogen and phosphorus compound concentration in the aerosols result mainly from the variability of the anemobaric situation.

Emission fluxes from the sea to the atmosphere over the Gdańsk Deep were estimated to be  $0.92 \mu\text{g} \cdot \text{P} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$  and  $15.86 \mu\text{g} \cdot \text{N} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ .

The effective nitrogen and phosphorus influx is directed from the atmosphere to the sea surface and is equal  $35.7 \mu\text{g} \cdot \text{N} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$  and  $1.15 \mu\text{g} \cdot \text{P} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ .

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