

## Executive Summary

The integration of global economics and a great advance in the development of information technologies during recent decade motivated the emergence of various international organizations, which objective is the evaluation and monitoring of global processes in the natural environment. The monitoring of persistent organic pollutant (POP) dispersion in the atmosphere, soil, water on the global scale is one of the directions of these organization activities.

The availability of modern powerful computers allow to devise models of POP global dynamics with a high degree of detalization in space and time. Within the framework of the EMEP, Meteorological Synthesizing Centre-East has developed a three-dimensional model of POP dynamics in the atmosphere, soil, vegetation and marine environment within the geographical scope of Europe, the North Atlantic and European Arctic with horizontal resolution about 150x150 km<sup>2</sup>. This model is under operation.

Main task of this work is to improve the model description of POP distribution in the marine environment.

The transport of pollutants in the sea basin of the EMEP region as well as POP fluxes through the sea surface are described by the sea module of the model. The marine environment in POP transport problems is characterized by the capability to accumulate a large share of a pollutant with its subsequent transfer to other media [Wania, 1998]. The characteristic time of POP degradation in sea water can be as much as decades.

The sea module considers processes of POP three-dimensional turbulent diffusion, advection with dynamic fields of sea currents,

POP degradation and a pollutant flux through the sea surface.

Model calculations with the sea module [Strukov *et al.*, 2000] qualitatively correctly describe POP concentration field in the marine environment and are in reasonable agreement (within an order of magnitude) with measurement data. In the module, however, it is assumed phase an organic pollutant is in the dissolved state. It should be mentioned that in the marine environment more than 90% of POPs can be associated with particulate matter and aggregated to dissolved organic compounds [Schultz-Bull *et al.*, 1998]. Between POP bound molecules and POP in the solution the dynamic redistribution takes place. As a first approximation it may be assumed that this distribution is in equilibrium, i.e. POP concentration associated with particulate matter and dissolved organic compounds is proportional to POP concentration in the dissolved phase.

At a sufficiently large share of POPs associated with sinking particles the export of a pollutant out of the grid together with particles can essentially affect the mass balance in the water medium. POP molecules associated with particles and dissolved organic compounds of a large molecular mass do not take part in the exchange process of the water-air surface thereby altering the parameters of POP flux through the sea surface.

Particle suspension in sea water consists of micro-organisms (phytoplankton, bacterio-plankton, micro-zooplankton), organic (products of plankton vital activity), inorganic particles connected with organic material

(particles deposited from the atmosphere, products of denudation processes).

The highest concentration of particles and, consequently, the largest POP share on organic carriers are characteristic of the upper oceanic layers, shelf and productive zones, i.e. of zones essentially affecting POP concentration dynamics in the model (oceanic upper layers). In regions with high particle concentrations and intensive POP fluxes from the atmosphere to the ocean together with particles, a great quantity of pollutants reaches the oceanic bottom, that may appreciably affect vital activity of benthos organisms.

Concentrations of micro-organisms, organic particles and dissolved organic compounds in sea water are determined by a scheme of plankton evolution in a biotope. Their adequate description at different meteorological and ecological conditions is possible by mathematical models for marine biogeocenosis.

The model developed consists of two parts: the first describing the dynamics of POP carriers and the second simulating on this basis the transport of POPs themselves.

The first submodel operates with a simplified system of plankton evolution in a biotope. It describes the dynamics of primary producer - phytoplankton, which concentration depends on fields of biogens and solar radiation intensity. In its turn phytoplankton evolution affects the concentration dynamics of bacterioplankton, detritus and dissolved organic compounds. Zooplankton dynamics is not considered since it is less important for POP transport. Concentration of all the fields considered are calculated with allowance made for three-dimensional advection and three-dimensional turbulent diffusion. Organic particle distributions also depend upon source

intensities located in shelf zones and lower oceanic layers, when the lower boundary of the mixed layer reaches the bottom.

The field of inorganic particles incoming from the atmosphere, shelf zones and bottom sources (if mixing is acting throughout the water depth) is determined by advection, turbulent diffusion and sedimentation.

Tentative calculations show that the introduction of mechanisms of pollutant partitioning with the dissolved phase and the phase associated with particles and dissolved organic compounds can inflict an appreciable impact on pollutant concentration dynamics. With the availability of particles sedimented to the bottom there appears an additional mechanism of POP downward transport. Spatial distribution of POP concentrations vary due to a considerable difference in degradation rates of pollutants associated with carriers in comparison with that of a dissolved substance.

Seasonal variations of POP concentrations in sea water also undergo appreciable changes. In the majority of regions phytoplankton concentration is essentially increased during spring months ("spring blossom"). It leads to the increase of bacterioplankton, detritus and dissolved organic matter. These changes define annual concentration variations of POPs associated with carriers and POP dissolved phase.

For further refinement of the description of POP concentration fields in the marine environment within the considered domain the emphasis should be placed on the following:

- refinement of dynamic models, parametric coefficients for phytoplankton and bacterioplankton in the calculation region,

- description of biogen field dynamics,
- integration of microzooplankton to the dynamics model for better description of biogeocenosis in the considered biotope,
- parametrization of POP fluxes on the bottom of the water basin,
- more detailed description of particle and dissolved organic compound sources such as riverine runoff and tidal events,
- refinement of the content of suspended particles and dissolved organic compounds considered in redistribution of POP between dissolved and bounded states.

After refinement the model should be used both for more detailed investigation of POP cycling in the marine environment and for preparing fields of POP carriers (particulates and dissolved organics) to be used in operational POP models.



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## Problem formulation

Following the recommendations of scientific workshops [WMO 1997, 2000] Meteorological Synthesizing Centre-East (MSC-E) is being developed a multicompartment model for calculating the transport and accumulation of persistent organic pollutants (POP) in the atmosphere, sea water, soil and vegetation. This report describes the continuation of works presented in [Strukov *et al.*, 2000], in particular, the development of the module of processes taking place with POPs in the marine environment (transport, diffusion, redistribution between phases, sedimentation). As it was pointed out earlier the marine environment can be the principal accumulator of a number of POPs. To describe adequately POP distribution over sea basins it is necessary to take into account many factors such as: the transport by horizontal and vertical currents, vertical and horizontal turbulent diffusion; dynamic redistribution between POP phases; dynamics of suspension particle concentration; POP exchange at the water-air interface and on the oceanic bottom. At the previous stage efforts were concentrated on the processes of POP exchange on the interface water-air and POP transport in sea water. This report describes further development of the sea module for POP long-range transport within European domain. In particular, we introduced to the model the dynamics of sea particles of different types, POP partitioning between different phases (dissolved, bound with different types of particles and dissolved organic matter), phase-dependent processes of POP degradation and sedimentation.

In nature POPs in sea and oceanic waters occur in a free (dissolved) state and bound with suspension particles and with dissolved

organic substances (organic polymers, colloid materials etc.) [Wania *et al.*, 1998]. While describing POP global transport from their sources to high latitudes the transport with suspension particles in the ocean may be of a greater importance than airborne transport [Schulz-Bull *et al.*, 1998]. In our work particles are divided into three types: particles with density close to that of water (phytoplankton, bacteria); particles with density slightly exceeding water density (detritus) and particles with density essentially exceeding the density of water (particles with inorganic nucleus). The particles of the second and third type are subjected to gravitational sedimentation. For phytoplankton and bacteria sedimentation processes are not considered since their density is slightly different from that of water and due to their capability to vertical migration impeding their gravitational sedimentation. Deposited particles export associated with them POPs outside the calculation reservoir. The role of the particles of the first type (phytoplankton, bacteria) is particularly important while describing POP gas-phase transport through the water-air surface. In the system atmosphere-soil-ocean POPs enter the ocean mainly from the atmosphere [Pavlova *et al.*, 1998]. The highest concentration of phytoplankton and bacteria is observed near the water-air surface [Semina, 1977] and consequently the most pronounced partitioning of gaseous and other phases of POPs. The particles of the third type (with inorganic nucleus) enter the water from the atmosphere with riverine run off, sea shore erosion and as a result of resuspension processes in the near bottom layer. In the marine environment inorganic particles have a tendency to be associated with organic substances [Kullenberg, 1982].

The developed model is intended for investigations both of POP behavior in the marine environment and for the preparation of density fields of particles of different types in sea water to be used in a simplified version of the operational model.

## POP partitioning between different phases in the marine environment

### General principles of POP phase partitioning in the marine environment

Persistent organic pollutants enter the World Ocean mainly from the atmosphere with precipitation in the dissolved and particulate phase, with falling out particles in the bound phase and as a result of reversible transfer through the ocean-atmosphere surface of the free (gaseous) phase. In sea water the redistribution of pollutant phases takes place. A pollutant can occur in water in different states dissolved ("free" or "gaseous" state), associated with particles and bound with dissolved organic substances. Particles can be different in nature and in physical and chemical parameters. Bacterio-, phyto- and zooplankton, detritus and quartz etc. can act as particles in water. Dissolved organic substances associated with POPs are also diverse. In the literature, however, in the majority of papers dedicated to POP transport in sea water generalized classes of particles and dissolved organic substances are considered. Modern approach to this problem is discussed, for example in [Wania *et al.*, 1998]. In this paper POP partitioning between the dissolved phase and the phase associated with particles is described by equilibrium

partition coefficient (l/kg) (in the measurement units given by the authors):

$$K_d = C_p / C_w$$

where  $C_p$  - POP concentration on particles (mol/kg);  $C_w$  - concentration of the dissolved phase (mol/l).

The bulk of suspended particles in sea water are covered by "porous" organic matrix where POP lipophil molecules are "dissolved". The constant of equilibrium between POP concentrations on these organic matrices and in the ambient environment is called by organic carbon/water equilibrium coefficient and it is denoted as  $K_{oc}$ .  $K_{oc}$  (l/kg C) value can be represented as:

$$K_{oc} = C_{oc} / C_w$$

where  $C_{oc}$  - POP concentration in organic particle matrices (mol/kg C).

Coefficients  $K_d$  and  $K_{oc}$  are related as:

$$K_d = K_{oc} \cdot f_{oc}$$

where  $f_{oc}$  - relative content of organic carbon in a particle (g C/g).

The above relationships are true for sufficiently low concentrations of POP when organic matrices are not saturated by POP molecules. In our problem POP concentrations satisfy this condition. Dissolved organic substances can amount to 90% of the total organic matter in sea water. By analogy with particles of dissolved organic substances we consider organic carbon/water equilibrium coefficient:

$$K_{doc} = C_{doc} / C_w$$

where  $C_{doc}$  characterizes a potential quantity of chemical bonds with POPs (mol/kg).

$K_{doc}$  values for different organic compounds vary within wider limits than  $K_{oc}$  values.



Similar approaches to the consideration of POP redistribution in water are suggested, for example, in [Broman & Axelman, 1998; O'Conner, 1998; Bakker et al., 1998].

In the work [Bakker et al., 1998] POP total concentration in water is represented by the relationship (cited from the paper):

$$[X]_{tot,w} = [X]_{unc,w} + ct X_{sus} \cdot sus + ct X_{doc,w} \cdot DOC_w$$

where  $[X]_{tot,w}$  - POP total concentration in water ( $g/m^3$ );  $sus$  - suspension concentration ( $kg/m^3$ );  $DOC_w$  - concentration of dissolved organic matter ( $kg/m^3$ );  $ctX_{sus}$  - POP concentration on suspended particles ( $g/kg$ );  $[X]_{unc,w}$  - unbounded POP concentration in water ( $g/m^3$ );  $ctX_{doc,w}$  - POP concentration on dissolved organic matter ( $g/kg$ ).

For POP concentrations on particles and dissolved organic matter the following relationships are used:

$$ctX_{sus} = K_{p,sus} \cdot [X]_{unc,w}$$

$$ctX_{doc,w} = K_{p,doc} \cdot [X]_{unc,w}$$

where  $K_{p,sus}$  - coefficient of POP adsorption on particles ( $m^3/kg$ );  $[X]_{unc,w}$  - concentration of unbounded POP in water ( $g/m^3$ );  $K_{p,doc}$  - coefficient of POP adsorption on dissolved organic matter ( $m^3/kg$ ).

At the same time for the adsorption coefficient there are expressions:

$$K_{p,sus} = K_{oc} \cdot fr_{oc,sus}$$

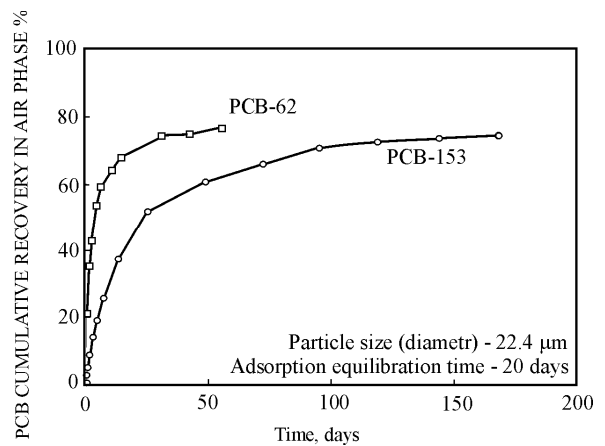
$$K_{p,doc} = K_{oc} \cdot X_{doc}$$

where  $fr_{oc,sus}$  - coefficient of organic carbon content on particles ( $kg/kg$ );  $X_{doc}$  - coefficient of the efficiency of POP binding with organic matter representing binding degree of a given dissolved substance with POP considered.

Coefficient of organic carbon-water at equilibrium is commonly represented via  $K_{ow}$  - POP partition coefficient in octanol/water system:

$$K_{oc} = 0.411 \cdot K_{ow}$$

D.J. O'Conner [1998] considers evolution equations for partitioning of POP concentrations between different phases. It is stated that the rate of phase equilibrium establishment of substances is much higher than characteristic rates of other kinetic processes such as degradation, sedimentation etc. and phase partitioning can be considered to be at equilibrium. At intensive dynamics of phytoplankton in the surface layer the equilibrium can be broken down. The time of equilibrium establishment can differ for different POPs, types and sizes of particles and other parameters. Y.Gong et al. [1998] present the results of laboratory experiments for sedimented particles of suspension. Characteristic curves of POP desorption for two PCB isomers are demonstrated in figure 1.



**Figure 1.** Dynamics of the ratio of dissolved POP concentration to their concentration of the bound phase on sediment particles for two PCB isomers [Gong et al., 1998]

Along axis y values (%) of PCB desorbed from sediment particles to air column of the laboratory device. Axis x shows time in days. The plot points out that dynamics of equilibrium establishment between the bound and free phase is of an exponential character

and the characteristic time is from several days to a month.

POP partitioning between phases is particularly important near the atmosphere - ocean surface where, first, particle and dissolved organic species concentrations are especially high, second, main sources of POP arrival in water are located. POP gas-phase flux through the surface is represented via POP concentration in the dissolved phase and the decrease of this concentration due to concentrations in other phases can essentially affect the flux value.

Laws of POP binding with cellular organisms (bacteria, phyto- and zooplankton) are of a complicated character. Molecules of pollutants can sediment on a cell external surface (to be adsorbed) and penetrate to a cell in the process of metabolism (be absorbed). For most of plankton organisms in the marine environment adsorption processes prevail over absorption processes. For smaller organisms the adsorption dominates. For example, for bacteria about 80% of POP is bound with a cell due to adsorption [Wallberg & Anderson, 1999].

### **Equations of POP phase partitioning used in the model**

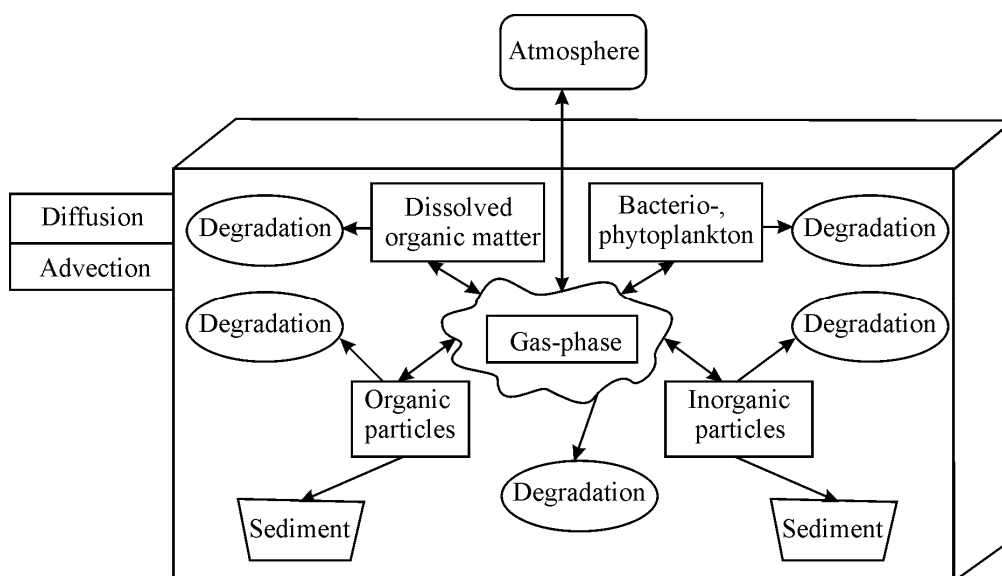
In view of said above the scheme of POP phase partitioning model for the marine environment is demonstrated in figure 2.

According to this scheme POP total concentration is expressed by the relationship:

$$C = C_g + C_{pr} + C_{ph} + C_d \quad (1)$$

where  $C$  - total pollutant concentration;  $C_g$  - concentration of the dissolved (free or "gaseous") phase;  $C_{pr}$  - concentration of the phase connected with sedimenting particles;  $C_{ph}$  - concentration of the phase connected with plankton;  $C_d$  - concentration of the phase connected with dissolved organic matter.

In the first approximation we assume that the process of phase partitioning is in equilibrium (i.e. instantaneous). Compared to characteristic time used in the model it is possible to neglect the equilibration time (fig.1). This assumption is obviously valid when we consider characteristic times of processes as long as about a year. For the equilibrated partitioning in view of low concentrations considered in the modelled problem we take a linear dependence of concentrations of the bound phases on concentrations in the dissolved phase.



**Figure 2.** Model scheme of dynamics of POP different phases in the marine environment

$$\begin{aligned}
 C_{pr} &= K_{pr} \cdot N_{pr} \cdot C_g \\
 C_{ph} &= K_{ph} \cdot N_{ph} \cdot C_g \\
 C_d &= K_d \cdot N_d \cdot C_g
 \end{aligned} \quad (2)$$

where  $N_{pr}$ ,  $N_{ph}$ ,  $N_d$  - concentrations of carriers in the bound phases (sedimenting particles, plankton and dissolved organic matter respectively). Proportionality coefficients  $K_{pr}$ ,  $K_{ph}$ ,  $K_d$  are determined, in particular, by the organic matter content (in octanol equivalent) on carriers binding pollutants and by the coefficient of binding pollutant octanol/water. Inserting (2) into (1) we obtain:

$$C = C_g \cdot (1 + N_{pr} \cdot K_{pr} + N_{ph} \cdot K_{ph} + N_d \cdot K_d) \quad (3)$$

In this case concentrations of the bound phases can be represented as:

$$\begin{aligned}
 C_{pr} &= C \cdot N_{pr} \cdot K_{pr} / (1 + N_{pr} \cdot K_{pr} + N_{ph} \cdot K_{ph} + N_d \cdot K_d) \\
 C_{ph} &= C \cdot N_{ph} \cdot K_{ph} / (1 + N_{pr} \cdot K_{pr} + N_{ph} \cdot K_{ph} + N_d \cdot K_d) \\
 C_d &= C \cdot N_d \cdot K_d / (1 + N_{pr} \cdot K_{pr} + N_{ph} \cdot K_{ph} + N_d \cdot K_d)
 \end{aligned} \quad (4)$$

All the phases in the considered approximation are subjected to three-dimensional advective transport, horizontal and vertical turbulent diffusion and

degradation (decomposition). The process of particle sedimentation inflicts an impact on  $N_{pr}$  concentration. The dissolved phase with concentration:

$$C_g = C / (1 + N_{pr} \cdot K_{pr} + N_{ph} \cdot K_{ph} + N_d \cdot K_d)$$

on the sea surface interacts with atmosphere gaseous pollutant.

Particles in the model are divided into two classes: particles with inorganic nucleus and particles consisting of organic matter only. Particles of the first type - quartz enter the ocean from the atmosphere, rivers and coastal zones in the process of continental denudation. These particles in sea water associate with organic matrix and become capable to adsorb POP molecules. Particles of the second type - mainly detritus as well as various colloid systems coagulates. In the model it is reasonable to make difference between particles of the first and second types due to their appreciable difference in densities and consequently in sedimentation rates. We also suggest to divide plankton into two groups as well: bacterioplankton and phytoplankton. Other plankton species

(zooplankton, protozoa and others) are considered as plankton with lower bioproduction in the biotope [Monin, 1977]. The first two types of plankton are divided for the following reasons: they are clearly different in the succession process and essentially different in their capability of binding POP molecules. Hence parameters  $N_{pr}$ ,  $N_{ph}$ ,  $K_{ph}$  can be considered as sets  $N_{pr} = (N_{pr}^1 \cdot N_{pr}^2)$ ,  $N_{ph} = (N_{ph}^1 \cdot N_{ph}^2)$ ,  $K_{ph} = (K_{ph}^1 \cdot K_{ph}^2)$ , where  $N_{pr}^1$  - concentration of carriers of sedimenting particles with inorganic nucleus,  $N_{pr}^2$  - concentration of carriers of sedimenting organic particles,  $N_{ph}^1$  - bacterioplankton concentration,  $N_{ph}^2$  - phytoplankton concentration,  $K_{ph}^1$  - effective coefficient of POP binding with bacterioplankton,  $K_{ph}^2$  - effective coefficient of POP binding with phytoplankton. Undeniably the number of components in such complex chemical-biological systems as biotope is much greater. Types of dissolved organic compounds are also diverse. However, the consideration of the diversity of these components is beyond the scope of this work.

## Dynamics of POP phase-carriers in the marine environment

To describe a full pattern of POP concentration dynamics in a sea basin taking into account POP molecule binding with suspension particles and dissolved organic carbon (POP phase carriers), it is necessary to describe dynamics of these components. Below we consider some models available in the literature describing the formation of organic matrices being POP carriers.

### Models of marine biogeocenosis development

Here we consider rather simplified set of components of the marine environment: water, dissolved organic compounds, bacterioplankton, phytoplankton, detritus, inorganic particles. Nevertheless even this simplified scheme is complicated enough and has multiple connections. Besides the scheme

should include the description of external parameter dynamics such as the concentration fields of biogenic elements\*, solar radiation flux, sea current velocities etc. A general scheme of the system accepted is given in figure 3.

The description of marine biotopes\*\* and their mathematical simulation can be found in many works, for example in [Sergeev *et al.*, 1979; Kullenberg, 1982; Monin, 1977].

One of classical models describing a biotope evolution is the model of Lyapunov [Monin 1977]. The scheme of Lyapunov's model is demonstrated in figure 4.

\* biogenic element are chemical elements required for an organism evolution (nitrogen, phosphorous compounds etc.)

\*\* marine biotopes - habitat of a complex of sea organisms

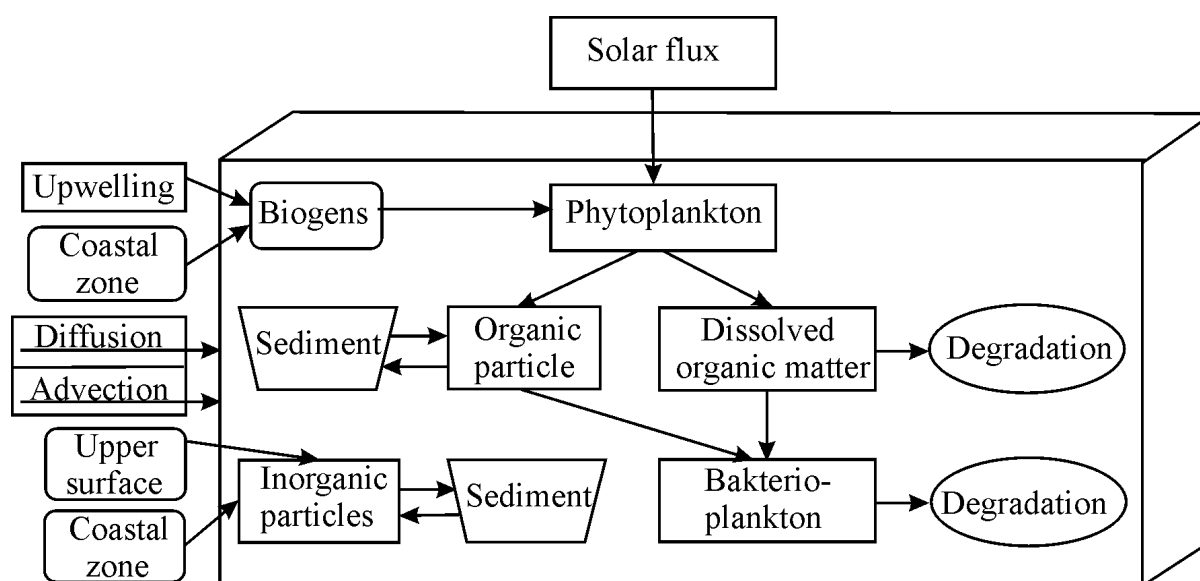
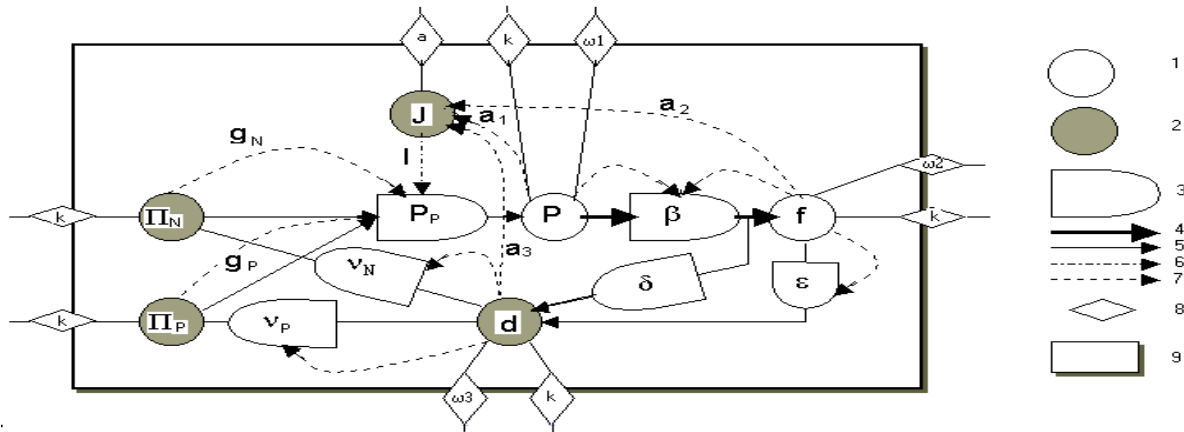


Figure 3. Scheme of dynamics of POP phase-carriers in sea water





**Figure 4.** Scheme of Lyapunov's model

Here: 1 - alive element of an ecosystem, 2 - lifeless element of an ecosystem, 3 - substance flux, 4 - trophic link, 5 - substance transfer, 6 - solar radiation energy, 7 - information link, 8 - transport between ecosystem cells, 9 - ecosystem cell, J - solar radiation,  $\Pi_N$  - nitrogen concentration,  $\Pi_P$  - phosphorus concentration,  $P_p$  - phytoplankton production, P - phytoplankton biomass, f - zooplankton biomass, d - detritus concentration, a - parameter of light absorption by water,  $a_1$  - parameter of light absorption by phytoplankton,  $a_2$  - parameter of light absorption by zooplankton,  $a_3$  - parameter of light absorption by detritus, k - coefficient of turbulent diffusion,  $\omega_1$  - parameter of phytoplankton sedimentation,  $\omega_2$  - parameter of zooplankton sedimentation,  $\omega_3$  - parameter of detritus sedimentation,  $\beta$  - Volterra coefficient for the consumption of phytoplankton by zooplankton,  $\delta$  - parameter of detritus formation as a result of zooplankton vital activity,  $\varepsilon$  - zooplankton mortality coefficient,  $v_N$  - coefficient of nitrogen release at detritus decomposition,  $v_P$  - coefficient of phosphorus release at detritus decomposition.

In this model it is supposed that processes take place without delay. The model calculates biomasses of phytoplankton and zooplankton, concentrations of phosphorus, nitrogen and detritus assimilated. Light in water media is absorbed by water, phytoplankton, zooplankton and detritus. Photosynthesis intensity is limited by the light flux and concentrations of nitrogen and phosphorus. Detritus is produced due to zooplankton vital activity. Phytoplankton is completely absorbed by zooplankton. Detritus particles are subjected to sedimentation. In addition all system elements are transported by turbulent diffusion in the vertical direction.

The equation set of Lyapunov's model is of the form:

$$\frac{\partial I}{\partial z} = -I(a + a_1P + a_2f + a_3d)$$

$$\frac{\partial \Pi_N}{\partial t} = -h_N P_p P + v_N d + \frac{\partial}{\partial z} \left( k \frac{\partial \Pi_N}{\partial z} \right)$$

$$\frac{\partial \Pi_P}{\partial t} = -h_P P_p P + v_P d + \frac{\partial}{\partial z} \left( k \frac{\partial \Pi_P}{\partial z} \right)$$

$$\frac{\partial P}{\partial t} = d P_p P - \beta P f + \frac{\partial}{\partial z} \left( k \frac{\partial P}{\partial z} \right) + \frac{\partial}{\partial z} (\omega_1 P)$$

$$\frac{\partial f}{\partial t} = \gamma_1 P f - \gamma_2 f^2 + \gamma_3 f d + \frac{\partial}{\partial z} \left( k \frac{\partial f}{\partial z} \right) - \frac{\partial}{\partial z} (\omega_2 f) - \varepsilon f$$

$$\frac{\partial d}{\partial t} = \varepsilon f - \mu d + \delta_1 P f + \delta_2 f^2 + \delta_3 f d + \frac{\partial}{\partial z} \left( k \frac{\partial d}{\partial z} \right) - \frac{\partial}{\partial z} (\omega_3 d)$$

Here the following notations in addition to mentioned above are used:  $\mu$  - parameter of detritus decomposition;  $\gamma_{1,2,3}$  - parameter of zooplankton nutrition;  $h_N$  - coefficient of

photosynthesis of nitrogen;  $h_p$  – coefficient of photosynthesis of phosphorus.

At a later time Lyapunov's model was supplemented with components of bacterioplankton and dissolved organic matter on account of their essential role in the process of energy and matter transfer in the described system.

A similar scheme of chemical-biological complex of the marine biogeocenosis is given in the work [Sergeev et al., 1979].

The model of transformations and transport of marine pollutants by bioprocesses is considered in the work [Kullenberg, 1982]. The scheme of bioprocesses is given in figure 5.

The model considers interactions of processes occurring in populations of phytoplankton, zooplankton, necton and benthos. In the benthos community organisms residing on the bottom surface (epifauna) and in the depth of sediments (infauna) are separated. The influence of detritus on the pollutant transport is noted. Processes of sorption and desorption of pollutant and suspended particles are considered.

### Models of phytoplankton dynamics

Phytoplankton plays the key role in functioning of biogeocenosis. Using solar energy it is the primary producer of organic carbon from dissolved inorganic matter. This property of phytoplankton is explained by the availability of chlorophyll in it which is capable of photosynthesis reactions. In phytoplankton community in the local biotope several hundreds of microorganism populations can exist. In different geographical zones there are sufficiently stable communities of phytoplankton organisms with clearly expressed succession\* [Monin, 1977]. In the geographical region under consideration (sea basin of the EMEP domain) located in the arcto-boreal and Arctic latitudes most common are organisms referring to diatom division (silicon algae) [Matishov, 1997].

\* succession - subsequent change in time of one biological processes by another, for example, alteration of phytoplankton organisms and bacteria.

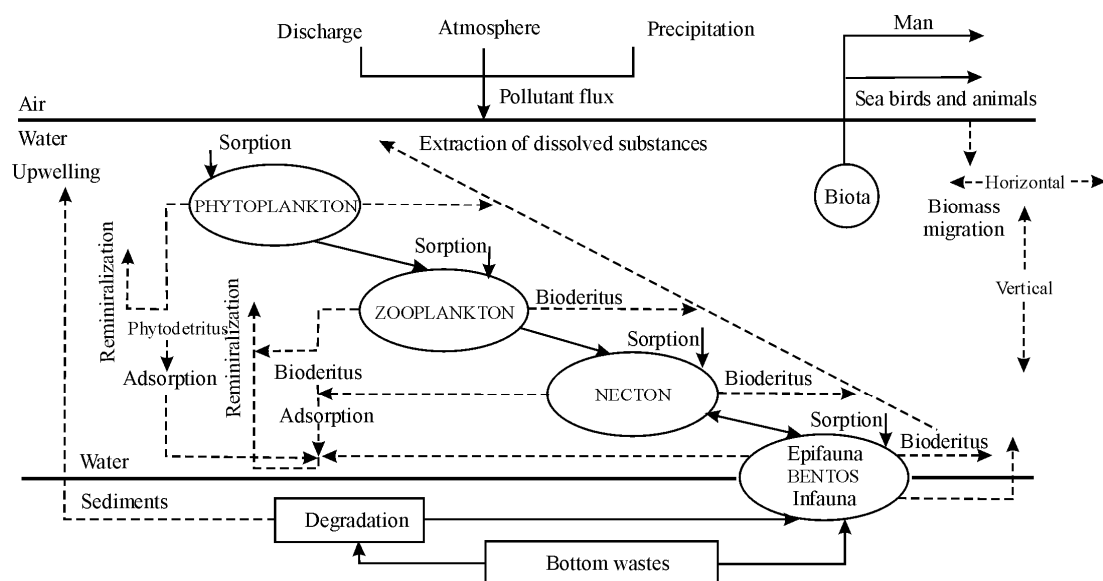


Figure 5. Transformation and transport of marine pollutants by bioprocesses



Photosynthesis rate can be restricted by illumination intensity and biogenic concentration. Without solar illumination, i.e. at the depths below 150 m, photosynthesis reactions cannot take place. Thus phytoplankton as POP phase-carrier can be considered in a sufficiently thin euphotic layer only.\* Biogenic elements arrive in the euphotic layer in pelagic regions as a rule from the lower layers thereby explaining an intensive evolution of phytoplankton in zones of upwelling [Carlos *et al.*, 1999; Ennet *et al.*, 2000]. The reproduction rate of phytoplankton is affected by some other parameters of the environment: water temperature, ist salinity, microelements availability etc. The maximum growth rate (at optimum illumination and sufficient availability of nutrient) can be represented by the dependence [Sergeev *et al.*, 1979]:

$$\mu_{max} = 5.35 \cdot 10^9 \cdot \exp(-6472 / T)$$

where  $\mu_{max}$  - maximum growth rate (1/day);  $T$  - water temperature ( $^{\circ}$ K).

Optimum illumination for photosynthesis process depends on specific biogeographical conditions. It can be different for different plant species. Moreover a specific taxon with time can adapt itself to available illumination due to enzyme reactions. Nevertheless it is supposed that for a certain phytoplankton under specific environmental conditions there is optimum illumination at which maximum phytoplankton growth rate is observed. The dependence of growth rate on illumination can be expressed in the following way:

$$\mu = a \cdot \mu_{max} \cdot I \cdot \exp(1 - a \cdot I)$$

where  $\mu$  - growth rate;  $\mu_{max}$  - growth rate at maximum illumination;  $I$  - illumination;  $a$  - empirical parameter [Sergeev *et al.*, 1979].

Mathematical models of phytoplankton evolution are numerous and diverse. This diversity can be connected with the sophistication of living organism system simulation and with the difference in specific biogeographical conditions of local biotope. An example of one-dimensional model with vertical distribution for the shelf zone can be found in the work [Sharples & Tett, 1994]. The equation for phytoplankton dynamics is:

$$\frac{\partial X}{\partial t} = \frac{\partial}{\partial z} \left( K_z \frac{\partial X}{\partial z} \right) + \mu X - GX^{\gamma} - w_s \frac{\partial X}{\partial z}$$

where  $X$  - phytoplankton concentration;  $K_z$  - vertical turbulent diffusion coefficient;  $\mu$  - plankton growth rate;  $G, \gamma$  - phytoplankton grazing coefficient by communities of the next link of the trophic chain;  $w_s$  - sedimentation rate of cells.

Limiting conditions for growth rate:

$$\mu = \mu_m \left( 1 - \frac{k_Q}{Q} \right) \quad \text{or} \quad \mu = q^{chl} (\alpha \bar{I} - r^B)$$

where  $\mu_m$  - maximum growth rate;  $Q$  - nutrient stock coefficient;  $k_Q$  - nutrient consumption coefficient;  $q^{chl}$  - factor of chlorophyll/organic carbon ratio;  $\alpha$  - coefficient of maximum growth rate;  $r^B$  - cell respiration rate.

Temperature dependences of maximum growth rate and respiration coefficient is represented by the relationship:

$$\mu_m = \mu_{m0} Q_{10}^{\mu} \frac{(T_0 - T)}{10} \quad r^B = r_0^B Q_{10}^r \frac{(T_0 - T)}{10}$$

where  $Q_{10}^{\mu}, Q_{10}^r$  - coefficients.

Cell sedimentation rate:

$$W_s = W_{sink} + W_{mig}$$

consists of gravitational sink rate  $w_{sink}$  and vertical migration rate  $w_{mig}$ .

\* - euphotic layer - the upper water layer with penetrating short-wavelength radiation

Dynamics of intracellular nutrient is described by differential equation:

$$\frac{\partial N}{\partial t} = \frac{\partial}{\partial z} \left( K_z \frac{\partial N}{\partial z} \right) + uX - GQN^\gamma - w_s \frac{\partial N}{\partial z}$$

where  $N$  - intracellular nutrient concentration;  $u$  - nutrient consumption rate determined by Michaelis-Menton formula:

$$u = \left[ u_m \left( 1 - \frac{Q}{Q_m} \right) \frac{S}{(k_u + S)} \right] (+\mu Q : \mu < 0 \quad +0 : \mu \geq 0)$$

$u = 0$  for  $S \leq S_{lim}$

where  $S$  - nutrient concentration;  $S_{lim}$  - limiting value of nutrient concentration.

Biogene concentration in its turn is determined by equation:

$$\frac{\partial S}{\partial t} = \frac{\partial}{\partial z} \left( K_z \frac{\partial S}{\partial z} \right) - uX + eGQN^\gamma$$

where  $e$  - coefficient of nutrient regeneration in the trophic chain.

Biogene flux from the bottom is prescribed by the ratio:

$$input = f_r (S_b - S_1) n \Delta t$$

where  $f_r$  - rate of *nutrient* input;  $S_b$  - nutrient concentration on the bottom;  $S_1$  - nutrient concentration in the near bottom layer.

For the solar radiation flux the equations are:

$$\frac{\partial I(z)}{\partial z} = -I(z)(\lambda_{PAR} + \varepsilon X_T(z))$$

$$I_{z=h} = F_{PAR} Q_S$$

where  $I$  - solar radiation flux;  $\lambda_{PAR}$  - coefficient of solar radiation flux reduction in water;  $\varepsilon$  - coefficient of solar radiation absorption by chlorophyll;  $X_T$  - chlorophyll concentration;  $F_{PAR}$  - solar radiation flux on the surface;  $Q_S$  - coefficient.

A local biological model for the upper layer of oceanic coastal zone is described in [Carlos *et al.*, 1999]. In this work equations of dynamics of nutrient  $N$ , phytoplankton  $P$ , zooplankton  $Z$ :

$$\frac{\partial N}{\partial t} + u_i \frac{\partial N}{\partial x_i} - (eZ - aP) - \frac{S^N}{h} = 0$$

$$\frac{\partial P}{\partial t} + u_i \frac{\partial P}{\partial x_i} - (aP - g_{zp}ZP - w_{sr}P) - \frac{S^P}{h} = 0$$

$$\frac{\partial Z}{\partial t} + u_i \frac{\partial Z}{\partial x_i} - (g_{zp}ZP - dZ - eZ) - \frac{S^Z}{h} = 0$$

where  $t$  - time;  $x_i$  - horizontal co-ordinates;  $u_i$  - horizontal components of the environment velocity;  $e$  - zooplankton excretion rate;  $a$  - rate of nutrient assimilation by phytoplankton;  $g_{zp}$  - grazing rate from zooplankton on phytoplankton;  $w_{sr}$  - phytoplankton sinking rate,  $d$  - zooplankton mortality;  $S^N$ ,  $S^P$ ,  $S^Z$  - intensity of sources/sinks of nutrient, phytoplankton, zooplankton caused by vertical fluxes of the environment and equal to  $\omega N^*$ ,  $\omega P^*$ ,  $\omega Z^*$ , where  $\omega$  - vertical velocity of the lower boundary of the considered layer;  $N^*$ ,  $P^*$ ,  $Z^*$  - concentrations of nutrient, phytoplankton, zooplankton at the lower layer boundary.

The assimilation rate of nutrient by phytoplankton is represented via light flux  $I$  and nutrient concentration following the equation:

$$a = \frac{v_m NI}{(k_n + N)(k_i + I)}$$

where  $v_m$  - coefficient of optimum photosynthesis rate;  $k_n$  - half-saturation constant for nutrient uptake;  $k_i$  - half-saturation constant for light flux intensity.

Similar biological model for one of the most productive region in the Atlantic ocean Georges bank is given in the work [Franks & Changsheng, 2001]. Bacterial component can inflict an essential impact on POP transport in the marine environment [Wallberg & Andersson, 1999]. In the light of modern concepts bacteria also play a leading role in the processes of energy and substance transfer from primary producers in trophic chains. First of all they are included to food ration of microzooplankton, second, they take part in demineralization of detritus, The refined

model of Lyapunov includes equations of bacterioplankton dynamics [Monin, 1977].

$$\frac{dl}{dz} = -al$$

$$\frac{\partial n}{\partial t} = -hP_p + vd + \eta \sum_{i=p1,b1,f1..f4,s1..s4} R_i + K \frac{\partial^2 n}{\partial z^2} + \beta \frac{\partial n}{\partial z}$$

$$\frac{\partial P}{\partial t} = \alpha P_p - R_p - \mu p - \sum_{j=f1..f4} C_{pj} + K \frac{\partial^2 P}{\partial z^2} - w_1 \frac{\partial P}{\partial z}$$

$$\frac{\partial b}{\partial t} = P_b - R_b - \mu b - \sum_{j=f1..f4} C_{bj} + K \frac{\partial^2 b}{\partial z^2} - w_2 \frac{\partial b}{\partial z}$$

$$\frac{\partial X_i}{\partial t} = u \sum_{j=p1,b1,f1..f4,s1,s2} C_{ji} - R_i - \mu_i X_i - \sum_{j=f2..f4,s1..s3} C_{ij}$$

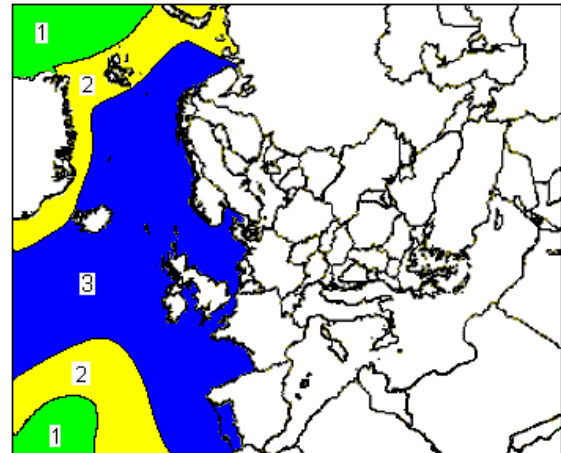
$$\frac{\partial d}{\partial t} = \sum_{i=f1..f4,s1..s3} (H_i + \mu_i X_i) - \sum_{i=f1..f4} Cd_i + K \frac{\partial^2 d}{\partial z^2} - w_3 \frac{\partial d}{\partial z}$$

where  $R$  - expenditures for exchange;  $\eta$  - coefficient of biogenic element release;  $X_i$  - biomass of the  $i$ -th zooplankton element ( $f1$  – protozoan;  $f2$  – microzooplankton;  $f3$  - small filtrators;  $f4$  - big filtrators;  $s1$  – Cyclopoida;  $s2$  – Calanoida;  $s3$  - Chaetognatha and Polychaeta);  $C_{ji}$  - coefficient of nutrition consumption of the  $j$ -th element by the  $i$ -th zooplankton element;  $b$  - bacterioplankton mass;  $\mu$  - mortality coefficient;  $H_i$  - coefficient of non-assimilated food.

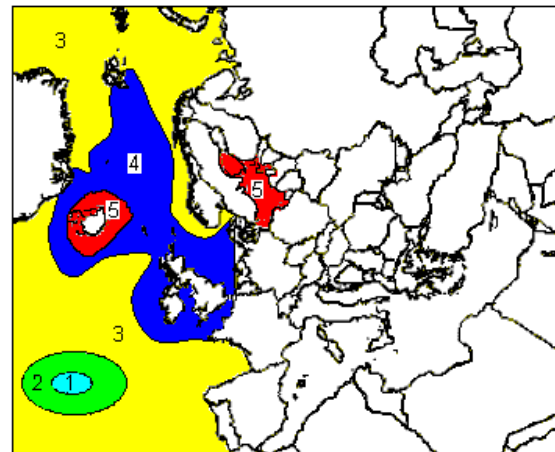
Notations of other parameters are similar to those of Lyapunov's model.

The simulated sea basin has sufficiently high phytoplankton population density (about  $10^3$ - $10^4$  cells/l) and it may be referred to mesotrophic waters. The distribution of cell numbers over the EMEP sea basin according to [Monin, 1977] is demonstrated in figure 6.

Figure 7 shows the distribution of mean annual primary production of organic carbon for the same water body.



**Figure 6.** The distribution of cell numbers over the EMEP sea basin within the layer of 1-100 m (cell/l)  
 1 –  $<10^2$ , 2 –  $10^2$ - $10^3$ , 3 –  $10^3$ - $10^4$



**Figure 7.** The distribution of mean annual primary production ( $\text{mg}/\text{m}^3/\text{day}$ ) in the EMEP water basin  
 1 –  $<100$ , 2 – 100-50, 3 – 150-250,  
 4 – 250-500, 5 –  $>500$

Vertical profiles of phytoplankton and biogenic concentrations measured (dots) and calculated at different experimental parameters (solid line) in the Georges bank region are given in figure 8 [Franks & Chen Changssheng, 2001].

Maximum values of bacterioplankton density as a rule are observed in the thermocline depth and they exceed by an order of magnitude the values observed above and below this layer. In mesotrophic waters the concentration of bacterium biomass is about  $10^2$  mg/m<sup>3</sup> with cell number about  $10^5$  cl/ml [Aiken & Bale., 2000]. In the succession process maximum values of bacterioplankton follows the phytoplankton maximum.

Concentrations values of bacterioplankton and its production during the blossom period and after this period in St.Laurentian Bay are presented in the work [Packard et al., 2000]. In the photic zone bioplankton concentration varied within the limits of  $2.79 \cdot 10^8$ - $16.5 \cdot 10^8$  cl/l, the production within 0.57-8.01 µg/l/day. The diagram of typical relative distribution of plankton organisms biomass in the upper mixed layer of the North Atlantic is demonstrated in figure 9 [Joint et al., 2001]. Summary data on plankton organism distribution over the EMEP water basin and adjacent regions taken from the literature are given in table 2.

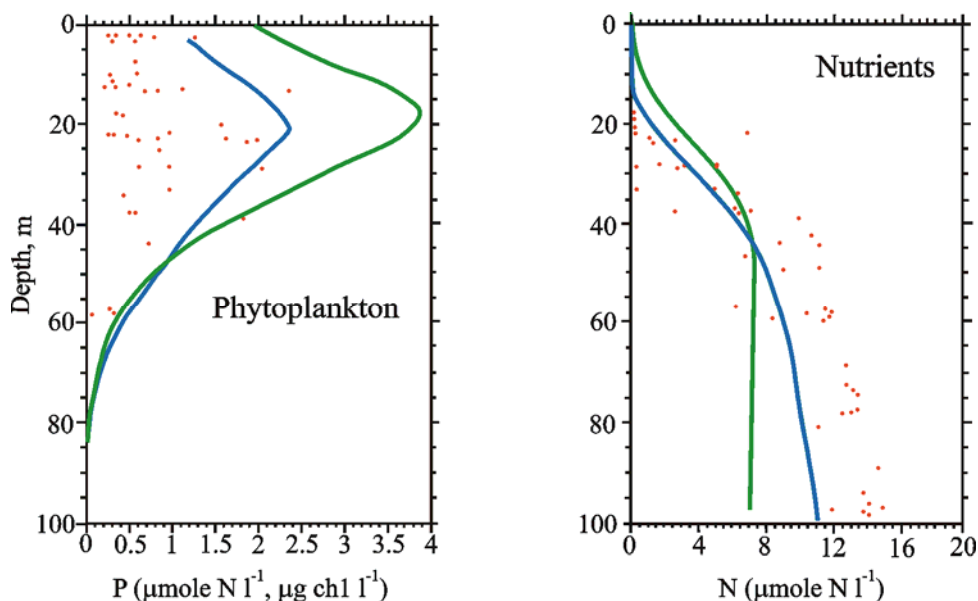
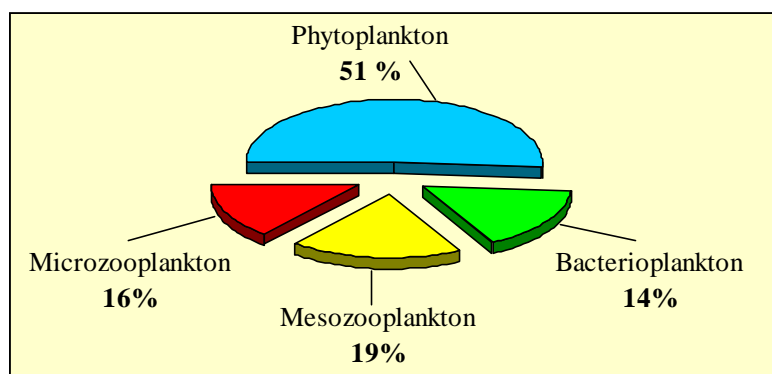


Figure 8. Vertical profiles of phytoplankton and biogenic concentrations in the region of Georges bank





**Figure 9.** Relative distribution of plankton organisms biomass in the upper mixed layer of the North Atlantic with co-ordinates 59°N, 20°W [*Joint et al.*, 2001]

**Table 2.** Summary data on concentrations of phase carriers in the EMEP water basin and adjacent region [ $\mu\text{M C/kg}$ ]

Reference	Latitude	Longitude	Depth, m	Phyto plankton	Bakterio plankton	POC	DOC	Notes
<i>I. Joint et al.</i> [2000]	59N	20W	0 - 20	2.90	0.82	13.24	75.00	Upper mixed layer
			0 - 35	2.92	0.84	11.65	75.17	Euphotic Zone
			0 - 100	1.28	0.56	8.15	77.75	Termocline
	37N	20W	0 - 20	0.78	0.42	4.01	90.21	Upper mixed layer
			0 - 35	0.50	0.44	4.33	88.83	Euphotic Zone
			0 - 100	0.57	0.36	4.54	87.42	Termocline
<i>A.S. Monin</i> [1977]	50N – 70N	40E – 40W	0 - 100	0.5 – 5.0				
<i>P.J.S.Franks et al.</i> [2001]	45N	66W	0 - 60	1 - 100				Georges bank
<i>P. Doyon et al.</i> [2000]	48N	62W	1 - 30	1 - 100				St.Laurentian Bay
<i>J. Aiken et al.</i> [2000]			1 - 100		0.1			Mesotrophic waters

## Model basic equations

Based on the short review of the literature data on marine biocenosis dynamics for modelling POP phase carriers we use the model built upon a simplified scheme of plankton evolution in biotope. Phytoplankton dynamics depending on the distribution of nutrient sources and solar radiation intensity in euphotic layer is described. Phytoplankton elevation leads to the concentration increase of bacterioplankton, detritus and dissolved organic compounds. Dynamics of zooplankton organisms is not considered in view of their less importance in POP transport processes. Fields of all the parameters are exposed to three-dimensional advection and three-dimensional turbulent diffusion. In the upper oceanic layer there is upper mixed layer. Below a set of differential equations used in the model are given.

### Equation of biogene concentration dynamics

In the description of nutrient dynamics it is assumed that there are sources of nutrient in the coastal zone and a known function of horizontal distribution in the depth adjacent to the euphotic zone.

$$\frac{\partial N}{\partial t} + u \frac{\partial N}{\partial x} + v \frac{\partial N}{\partial y} + w \frac{\partial N}{\partial z} = K_g \frac{\partial^2 N}{\partial x^2} + K_g \frac{\partial^2 N}{\partial y^2} + \frac{\partial}{\partial z} (K_z \frac{\partial N}{\partial z}) + S_N - k_{gr} P$$

$$N|_{z>h_{phot}} = N_{phot}(x, y)$$

$$S_N = S_{NO}, (x, y, z) \in Sh; \quad S_N = 0, (x, y, z) \notin S$$

where  $N$  - nutrient concentration;  $u, v$  - horizontal components of the environment velocity;  $w$  - vertical environmental velocity;  $K_g$  - horizontal turbulent diffusion coefficient;  $K_z$  - vertical turbulent diffusion coefficient;  $S_N$  - coastal sources of nutrient;  $S_h$  - neritic zone;  $S_{NO}$  - constants;  $k_{gr}$  - coefficient of nutrient consumption by phytoplankton;  $P$  - phytoplankton concentration;  $h_{phot}$  - photic zone depth;  $N_{phot}$  - known distribution of nutrient concentration in pelagic waters at depths adjacent to euphotic zone.

### Equation of phytoplankton concentration dynamics

Phytoplankton dynamics model describes the concentration growth following the scheme of Michaelis-Menton and concentration reduction with the formation of detritus and dissolved organic compounds represented by corresponding "decomposition" coefficients. The "decomposition" coefficients of phytoplankton parametrization mechanism of phytoplankton grazing by zooplankton with subsequent formation of detritus and dissolved organic matter. Light flux effect on the process of phytoplankton growth takes into account the availability of optimum flux observed at some depth below the sea surface. The phytoplankton concentration is limited by maximum and minimum.

$$\frac{\partial P}{\partial t} + u \frac{\partial P}{\partial x} + v \frac{\partial P}{\partial y} + w \frac{\partial P}{\partial z} = K_g \frac{\partial^2 P}{\partial x^2} + K_g \frac{\partial^2 P}{\partial y^2} + \frac{\partial}{\partial z} \left( K_z \frac{\partial P}{\partial z} \right) + k_P(N, R, z)P - k_{pro}P - k_d P$$

$$k_P(N, R, z) = k_N(N) \cdot k_R(R, z)$$

$$k_N(N) = k_{PN} \frac{N}{k_{mm} + N}$$

$$k_R(R, z) = R \cdot \exp\left(-\frac{abs(z - h_{eff}) - h_{eff}}{k_{att}}\right)$$

$$P_{min} < P \leq P_{max}$$

where  $k_p$  - function of nutrient consumption by phytoplankton in the photic zone;  $R$  - short-wavelength radiation flux on the upper surface;  $h_{eff}$  - coefficient of nutrient consumption by phytoplankton;  $k_{att}$  - coefficient of short-wavelength radiation flux attenuation;  $P_{max}$  - maximum possible phytoplankton concentration;  $P_{mix}$  - minimum possible phytoplankton concentration;  $k_{pro}$  - coefficient of detritus production by phytoplankton;  $k_d$  - coefficient of organic molecule production by phytoplankton.

### Equation of bacterioplankton concentration dynamics

In this model bacterioplankton is produced if detritus is available. It is considered that bacterioplankton is decayed with some intensity. However, the products of its decay are not taken into account. It is also assumed that bacterioplankton concentration cannot exceed some maximum value.

$$\frac{\partial B}{\partial t} + u \frac{\partial B}{\partial x} + v \frac{\partial B}{\partial y} + w \frac{\partial B}{\partial z} = K_g \frac{\partial^2 B}{\partial x^2} + K_g \frac{\partial^2 B}{\partial y^2} + \frac{\partial}{\partial z} \left( K_z \frac{\partial B}{\partial z} \right) + k_b O - k_{bd} B,$$

$$0 < B \leq B_{max}$$

where  $B$  - bacterioplankton concentration;  $k_b$  - coefficient of bacterioplankton growth on detritus;  $k_{bd}$  - bacterioplankton decomposition coefficient;  $B_{max}$  - maximum possible bacterioplankton concentration;  $O$  - concentration of organic particles.

### Equation of dissolved organic materials concentration dynamics

In the model dissolved organic compounds enter the marine environment as a result of parametrized process of plankton vital activity. In the equation the source of dissolved organic substances is proportional to phytoplankton concentration - primary producer. It is supposed that with time organic compounds are decomposed in the marine environment. Decomposition products are not considered. Sources of dissolved organic compounds are riverine runoff and washing from coasts. Maximum concentration of dissolved organic compounds is prescribed by constant  $D_{max}$ .



$$\frac{\partial D}{\partial t} + u \frac{\partial D}{\partial x} + v \frac{\partial D}{\partial y} + w \frac{\partial D}{\partial z} = K_g \frac{\partial^2 D}{\partial x^2} + K_g \frac{\partial^2 D}{\partial y^2} + \frac{\partial}{\partial z} \left( K_z \frac{\partial D}{\partial z} \right) + k_d P - k_{degD} D + S_D$$

$$D < D_{max}$$

$$S_D = S_{D0}, (x, y, z) \in Sh; \quad S_D = 0, (x, y, z) \notin S$$

where  $D$  - concentration of dissolved organic compounds;  $u, v$  - horizontal components of environmental velocity;  $w$  - vertical environmental velocity;  $K_g$  - coefficient of horizontal turbulent diffusion;  $K_z$  - coefficient of vertical turbulent diffusion;  $k_d$  - coefficient of phytoplankton decay into organic molecules;  $k_{degD}$  - coefficient of organic molecule degradation;  $P$  - phytoplankton concentration;  $S_D$  - source intensities;  $S_{D0}$  - constant.

### Equation of organic particle concentration dynamics

Concentration dynamics of organic particles is defined by an equation representing organic matter sources presenting detritus, particle sedimentation, coastal sources of riverine runoff, tidal events and coastal runoff as well as organic matter fluxes from the bottom. The concentration of organic particles is limited by some maximum value  $O_{max}$ .

$$\frac{\partial O}{\partial t} + u \frac{\partial O}{\partial x} + v \frac{\partial O}{\partial y} + w \frac{\partial O}{\partial z} = K_g \frac{\partial^2 O}{\partial x^2} + K_g \frac{\partial^2 O}{\partial y^2} + \frac{\partial}{\partial z} \left( K_z \frac{\partial O}{\partial z} \right) + k_{pro} P - w_{sedO} O + S_O$$

$$\frac{\partial O}{\partial z} \Big|_{z=H} = F_{OB} - (w_{sedO} O) \Big|_{z=H}$$

$$O < O_{max}$$

$$S_O = S_{O0}, (x, y, z) \in Sh; \quad S_O = 0, (x, y, z) \notin S$$

where  $O$  - concentration of organic particles;  $u, v$  - horizontal components of environmental velocity;  $w$  - vertical environmental velocity;  $K_g$  - coefficient of horizontal turbulent diffusion;  $K_z$  - coefficient of vertical turbulent diffusion;  $k_{pro}$  - coefficient of phytoplankton decay into organic particles;  $w_{sedO}$  - sedimentation rate of organic particles;  $H$  - bottom

depth;  $P$  - phytoplankton concentration;  $S_O$  - organic particle sources;  $S_{O0}$  - constant;  $F_{OB}$  - organic particle flux from the bottom.

### Equation of inorganic particle concentrations

Equation for inorganic particle concentrations is similar to that of organic particle dynamics. The difference is in the follows: no sources depending of phytoplankton concentration are available, on the upper surface there is a particle flux defined by deposition to the sea surface from the atmosphere.

$$\frac{\partial I}{\partial t} + u \frac{\partial I}{\partial x} + v \frac{\partial I}{\partial y} + w \frac{\partial I}{\partial z} = K_g \frac{\partial^2 I}{\partial x^2} + K_g \frac{\partial^2 I}{\partial y^2} + \frac{\partial}{\partial z} \left( K_z \frac{\partial I}{\partial z} \right) + S_I - w_{sedI} I,$$

$$\frac{\partial I}{\partial z} \Big|_{z=0} = F_{IS},$$

$$\frac{\partial I}{\partial z} \Big|_{z=H} = F_{IB} - (w_{sedI} I) \Big|_{z=H},$$

$$I < I_{max},$$

$$S_I = S_{I0}, (x, y, z) \in Sh; \quad S_I = 0, (x, y, z) \notin Sh,$$

where  $I$  - concentration of inorganic particles;  $u, v$  - horizontal components of environmental velocity;  $w$  - vertical environmental velocity;  $K_g$  - coefficient of horizontal turbulent diffusion;  $K_z$  - coefficient of vertical turbulent diffusion;  $F_{IS}$  - inorganic particle flux on the surface;  $F_{IB}$  - inorganic particle flux on the bottom;  $I_{max}$  - constant;  $H$  - bottom depth.

### Equation of POP concentration dynamics

In accordance with the assumptions on the equilibrium of processes of POP phase redistribution between different carriers and in the solution, for POP total concentration in the marine environment the following equation is used:

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} + v \frac{\partial C}{\partial y} + w \frac{\partial C}{\partial z} = K_g \frac{\partial^2 C}{\partial x^2} + K_g \frac{\partial^2 C}{\partial y^2} +$$

$$+ \frac{\partial}{\partial z} (K_z \frac{\partial C}{\partial z}) - K_{degG} C_G - K_{degO} C_O - K_{degI} C_I -$$

$$- K_{degP} C_P - K_{degD} C_D$$

$$C = C_G + C_O + C_I + C_P + C_D$$

$$C_O = k_{dissO} C_G O \quad k_{dissO} = k_{CO} \cdot k_{OW} / \rho_O$$

$$C_I = k_{dissI} C_G I \quad k_{dissI} = k_{CI} \cdot k_{OW} / \rho_I$$

$$C_P = k_{dissP} C_G P \quad k_{dissP} = k_{CP} \cdot k_{OW} / \rho_P$$

$$C_D = k_{dissD} C_G D \quad k_{dissD} = k_{CD} \cdot k_{OW} / \rho_D$$

For the gas-phase flux through the water-air interface the following expression is used [Strukov *et al.*, 2000]:

$$F_G |_{z=0} = Pr \cdot C_{pr} + \alpha_1 (C_a / K_H - C_G |_{z=0})$$

$$((1 - \alpha_2) D_\mu / \delta + \alpha_2 K_H h_f + F_{dr})$$

$$\delta(U_a) = \delta_0 \cdot \exp(-0.15 \cdot U_a)$$

$$\alpha_1 = 1.75 - 0.75 \cdot \exp(-0.18 \cdot U_a)$$

$$\alpha_2 = 1 - \exp(-0.01 \cdot U_a)$$

$$F_O |_{z=H} = -w_{sedO} C_O O \quad F_I |_{z=H} = -w_{sedI} C_I I$$

where  $C$  - POP total concentration in all the phases;  $C_G$  - POP concentration in the "gas"-phase;  $C_O$  - POP concentration in the phase bound with organic particles;  $C_I$  - POP concentration in the phase bound with inorganic particles;  $C_P$  - POP concentration in the phase bound with phytoplankton;  $C_D$  - POP concentration in the phase bound with dissolved organic matter;  $u, v$  - horizontal components of environmental velocity;  $w$  - vertical environmental velocity;  $K_g$  - coefficient of horizontal turbulent diffusion;  $K_z$  - coefficient of vertical turbulent diffusion;  $O$  - organic particle concentration;  $I$  - inorganic particle concentration;  $P$  - phytoplankton concentration;  $D$  - concentration of dissolved organic matter;  $k_{CO}$  - organic carbon relative content in organic particles;  $k_{CI}$  - organic carbon relative content in inorganic particles;  $k_{CP}$  - organic carbon relative content in phytoplankton;  $k_{CD}$  - organic carbon relative content in undissolved organic matter;  $k_{OW}$  - coefficient of octanol-water

equilibrium concentration;  $\rho_O$  - density of organic particles;  $\rho_I$  - density of inorganic particles;  $\rho_P$  - density of phytoplankton;  $\rho_D$  - density of dissolved organic matter;  $w_{sedO}$  - sedimentation rate of organic particles;  $w_{sedI}$  - sedimentation rate of inorganic particles;  $H$  - bottom depth;  $F_G$  - gaseous component flux;  $F_O$  - POP flux with organic particles;  $F_I$  - POP flux with inorganic particles;  $Pr$  - precipitation intensity;  $C_{pr}$  - POP concentration in precipitation;  $C_a$  - POP atmospheric concentration at the reference height;  $K_H$  - Henry's law coefficient;  $D_\mu$  - coefficient of molecular diffusion in water;  $h_f$  - surface foam degradation rate,  $\delta_0$  - coefficient;  $U_a$  - module of wind speed at the reference height;  $F_{dr}$  - POP flux from the atmosphere at dry deposition of atmospheric particles.

## Experimental results

To test the model efficiency numerical experiments were carried out. In these experiments the equations of pollutant dispersion in the ocean were considered as a part of the MSCE-POP long-range transport model [Shatalov *et al.*, 2000]. Like in the previous report PCB-153 was selected as a pollutant since it is present in the particulate and gaseous phase in a sufficient quantity. Oceanic velocity fields, synoptic parameters and emission source intensities were taken from data for 1996. In multiannual experiments (10-20 years) annual variations of 1996 were repeated. The problem formulation was slightly simplified: organic and inorganic particles were considered together, to cut down the computation time bacterioplankton was not considered. The model parameters were chosen in such a way that POP mean concentrations in dissolved and particulate phase were of the same order of magnitude. This assumption can be made proceeding from some results of concentration measurements in sea water of different pollutant phases [Schulz-Bull *et al.*, 1998]. The

aim of the experiment was to test the model description of the transport of pollutant different phases, the effect of model parameters on pollutant phase partitioning, dynamics of establishment of pollutant and pollutant-carriers fields and concentration intra-annual variations. Figure 10 shows plots of POP mass dynamics in different phases for a given experiment. The plots evidence that dynamics of pollutant mass is equilibrated during the period of 10 years. Although POP mass on plankton is relatively small due to the availability of a carrier (plankton) in the thin upper surface layer, in view of particulate matter formation the consideration of plankton is important. Dynamics of POP mass on plankton is actually equilibrated during the first year. Annual variations of model parameters is explicitly reflected in dynamics of all POP phases in the considered system.

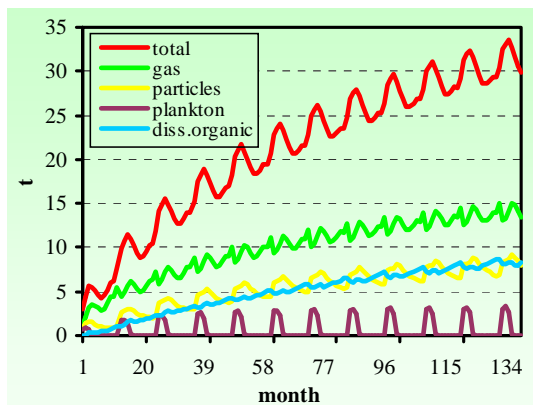


Figure 10. POP mass variation on different carriers

Spatial distribution of POP total mean monthly concentration in the upper oceanic layer at the equilibrium state is demonstrated in figure 11. POP distribution field is similar to fields obtained in previous experiments with a simplified model of POP transport in the ocean [Strukov *et al.*, 2000]. The highest concentration is observed near continental POP sources in the region of the North Sea, in

some regions of the water basin the concentrations are lower.

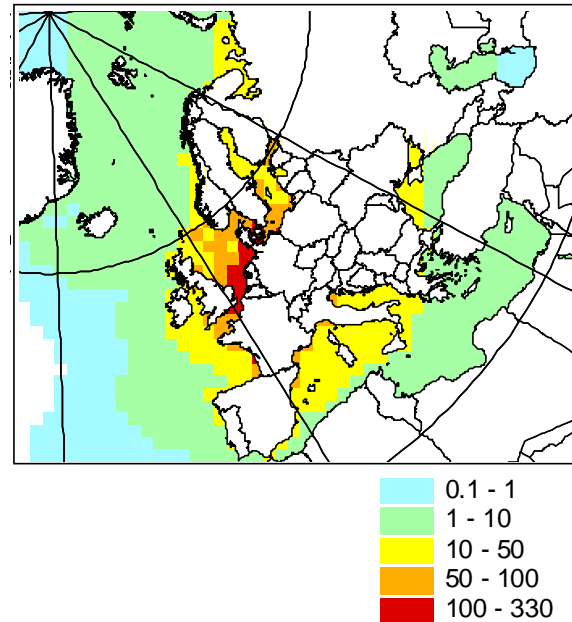


Figure 11. POP total concentration in the upper layer in January, ng/m<sup>3</sup>

Characteristic annual dynamics of POP concentrations in different phases in one of the points of the North Atlantic (with coordinates 60°N, 30°W) is given in figure 12. The figure shows POP concentration variation associated with plankton (the 4th plot). The highest values of POP concentration connected with this phase are reached during spring months. It happens because of elevated concentrations of the phase-carriers (phytoplankton) during this season (“spring blossom”). Subsequent to POP maximum concentration connected with phytoplankton comes the maximum of POP concentration connected with particles (the 3d plot). In this experiment the particle source is phytoplankton. This fact can explain the alteration of POP concentration maxima connected with plankton and particles. The reduction of phase-carriers concentration in

the second half of the year leads to the increase of the dissolved phase concentration as a result of the phase redistribution (the 2d plot).

Preliminary results of the numerical experiment indicate the importance of POP partitioning between different phases. Numerical experiments point out that general pattern of POP distribution over the EMEP water basin is similar to that described in [Strukov *et al.*, 2000] where the diversity of POP phases was neglected. A detailed consideration of the effect of POP phase redistribution will be possible after the refinement of bioprocess parameters and the model of inorganic particles. However, the experimental results allow to draw a conclusion about the necessity of separate

description of dynamics of POP different phases in the sea environment. It is quite evident for water reservoirs with high density of primary bioproducers such as regional seas, coastal zones, upwelling regions. The consideration of POP phase redistribution is also necessary for the determination of pollution concentration in sediments and benthos organisms.

The numerical experiment results demonstrate the model efficiency. The model application to the determination of concentrations of different POPs in sea waters will be possible after series both of experiments with individual model subsystems (plankton, particles, dissolved organic matter) and with the entire model.

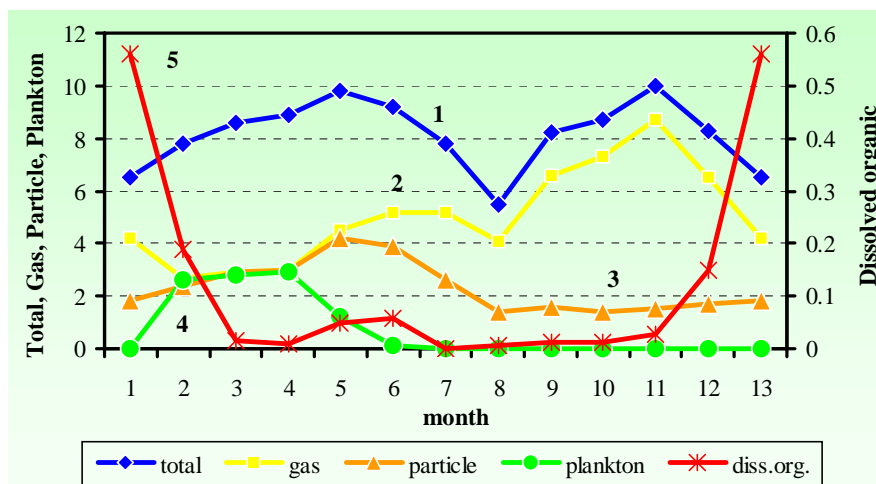


Figure 12. Annual dynamics of POP different phases in the upper layer of the Northern Atlantic, ng/m<sup>3</sup>

## Conclusions

- The technical note suggests the first version of a mathematical model of POP transport in the marine environment with allowance made for dynamics of POP redistribution between different states (in the water solution and associated with different carriers: particles and dissolved organic compounds). Model of dynamics of POP carriers includes such components as phytoplankton, bacterioplankton, detritus, inorganic particles, dissolved organic compounds.
- The developed model of POP transport in the marine environment has been integrated into the EMEP multicompartment POP transport model.
- Numerical experiments carried out with the multicompartment POP transport model allow us to conclude that the introduction of POP redistribution in the marine environment can essentially influence POP concentration in the environmental compartments. These processes are most pronounced in water basins with high density of primary bioproducers: coastal and upwelling zones, regional seas. High level of concentrations of POP carriers near the sea surface can considerably enhance POP gaseous flux from the atmosphere to water. The consideration of POP redistribution processes is also necessary for the determination of pollutant concentrations in sediments and benthos organisms.
- For better understanding of POP transport in the marine environment further investigations will be carried out:
  - evaluation of parameter variations in model of POP carrier dynamics taking into account peculiarities of regions studied and model spatial resolution;
  - consideration of POP dynamic redistribution: adsorption on particles and dissolved organic compounds from the water solution and reverse processes (desorption);
  - parametrization of the process of POP exchange between sea water and bottom sediments;
  - study of model sensitivity to POP redistribution in the marine environment.

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