Measurement of mass transfer coefficients of pollutants across the atmospheric air-sea interphase

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The rate of transfer of pollutant loads from the atmosphere to the sea water depends, among other physicochemical parameters on the mass transfer coefficient of each pollutant across the air-sea interphase, and the change of this coefficient with temperature. The knowledge of the exact values of the mass transfer coefficient for the various pollutants homogeneously dissolved in the atmosphere (carbon monoxide, nitrogen oxides, sulfur oxides, hydrocarbons, etc.) permits the calculation of the absorption rate of these substances by the sea water, and therefore of the depletion rate of the air from the above substances.

The new technique of Reversed-flow gas chromatography, developed in our laboratory, is employed. This technique has no far successfully been applied to various physicochemical measuremetns and three reviews on it have been published[1-3], together with a book[4].

A very simple experimental set-up is used, consisted of a slightly modified gas chromatograph. The sea water is placed at the bottom of a diffusion column (1 m X 4 mm I.D.), and the interphase is fed with the pollutant by gaseous diffusion, whereas pure air (as carrier gas) passes through another column, perpendicularly connected to the previous column at a remote distance from the gas-liquid boundary. This arrangement resembles very much to the actual natural process of movement of the air pollutants to the sea surface.

By repeatedly performing flow reversals of short duration (15-60 s), extra chromatographic peaks (sample peaks) are obtained. These are narrow and symmetrical, their height h from the baseline as a function of time being given by the equation

$$h = \frac{N_2}{1+1.801 V_G'/V_G}\left[(1+\frac{Z}{Y})\exp(-\frac{X+Y}{2}t_o)\right.$$
$$\left.+(1-\frac{Z}{Y})\exp(-\frac{X-Y}{2}t_o)\right]$$

where X, Y and Z are functions of the diffusion coefficient D of the pollutant in the air, its overall mass transfer coefficients K_G and K_L, in the gas and the liquid phase, respectively, and its partition coefficient K between the two phases in contact.

By analyzing the experimental data with the help of the above equation, one can determine accurately in a single experiment lasting only a few hours, both overall mass transfer coefficients of the pollutant under study across the air-sea interphase, together with the relevant partition coefficient. The mathematical equations have been derived from the solution of a system of partial differential equations, under given initial and boundary conditions.

References

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Modeling for estimation of input of toxic metals into a bay

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ABSTRACT

Marinas with their services and small shipyards pollute marine environment with toxic metals. Most often such marinas are situated in bays. It is interesting therefore to determine the rates of sedimentation and flashing rates of such toxic elements and to determine their actual input. Our aim is to demonstrate the usefulness of mathematical models in solving this problem. A case of Punat Bay is analyzed. This is a small bay with the area of 2.5 km**2, on the island Krk (Northern Adriatic). The total input of Pb, Cu and Zn is determined from current measurements, measurements of these metals in water and muddy sediment of the Bay.

A. Currents. Tidal currents are measured and reconstructed by a standard two-dimensional model. Monte Carlo methods are used to determine the clearance of the bay due to tidal current. A component of residual current which influences the clearance has been identified. This component is caused by underwater wells. The strength of wells is determined by two different models with practically the same result. The total wash-out due to two considered currents is estimated.

B. Metals. Concentrations in water have large fluctuations and it is necessary to take samples in time sequences to determine mean values and fluctuations of concentrations. Because of small concentrations of such metals in water it is difficult to determine their concentrations in samples, so that an extensive sampling was abandoned. However, concentrations in muddy sediment of the Bay are high enough and have been easily determined by X-ray spectroscopy. In addition, content of a metal in the muddy sediment results from an accumulating process so that the fluctuations of concentrations are less pronounced than in water. By using transport models the extinction constants are determined for three considered metals, and consequently the rates of sedimentations are estimated.

C. Inputs. Inputs are calculated from the rates of flashing and sedimentation by using the transport model and topography of the Bay.

Since the source of a toxic metal is diffuse and cannot be easily estimated in a direct way, we propose here the estimation of input based on clearance mechanisms of a bay by the following procedure. Clearance mechanisms are analysed by mathematical models. Concentrations in sediments are used for fitting parameters and then concentrations in water are used for scaling. Since the input is equal to the output caused by all clearance mechanisms, it can be estimated from the obtained models.

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