



Gas-transfer in streams and rivers

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Transport processes through the gas-liquid interfaces are of paramount importance in a number of areas of industrial engineering, such as chemical and mechanical engineering, and for geophysical and environmental systems. In such systems, gaseous pollutants may be directly exchanged between air and water in either direction across the air-water interface. Gas fluxes being transferred can be upward to the air or downward to the water depending on the substances involved. Thus, *gas transfer* is a two-way process involving both gas absorption, i.e. air to water, and volatilization, i.e. water to air, across an air-water interface, for a volatile or semi-volatile chemical. In the environmental fluid mechanics field, for processes at the free surfaces of terrestrial water bodies, early interest related the absorption of atmospheric oxygen in natural waters. This process is also termed as atmospheric reaeration. Since dissolved oxygen (DO) is commonly considered as the main indicator of aquatic ecosystem health, reaeration is one of the most relevant source of DO in the water bodies, whose DO level are depleted by natural causes or the discharge of organic matter. The volatilization of many chemicals, such as mercury, PCBs, PAHs and pesticides, has been widely recognized as an important process determining the transport, fate, and chemical loadings of these contaminants in the atmosphere and in large water bodies, such as lakes, estuaries and oceans. Also, the assessment of volatilization rate of environmentally important compounds of low molecular weight such as benzene, chloroform, methylene chloride, and toluene from rivers and streams contaminated by spills or industrial discharges has been subject of continuing interest. Therefore the estimation of both reaeration and volatilization rate is a key issue in the application of a modeling framework of dissolved oxygen balance or of contaminant transport and fate.

More recently, the exchange of moisture, carbon dioxide (CO₂) and other greenhouse

gases between the atmosphere and the oceans or the lakes have become important because of their impact on global warming. It is estimated that approximately 30-40 per cent of man-made CO₂ is taken up by the oceans, but these estimates are significantly affected by the uncertainties in the prediction of gas-transfer rate at the air-water interface.

Despite the significant theoretical, laboratory, field and numerical studies, research efforts have not yet achieved a complete understanding of gas-transfer process. Also, predictive models currently available are not yet able to predict its rate in all the environmental and hydrodynamic conditions. In the hydraulic and environmental engineering field several empirical equations have been long proposed to estimate both reaeration and volatilization rates, but recent studies have demonstrated that these equations cannot have a general application. Therefore, intensive researches are currently carried on to gain insight into the complex mechanisms of gas-transfer and to develop a physically sound and reliable predictive equation of gas-transfer rate.

First of all, we can define *gas-transfer* as an *interphase mass-transfer process* that occurs at the air-water interface if a non-equilibrium condition between the air phase and the water phase exists for a chemical. The equilibrium or non-equilibrium condition generally depends on chemical potential of the considered species within the phase involved, which is related to concentration, which is simpler to be measured. Thus, the transport of material between phases is controlled by the gradient in concentration across the interface, which represents the *driving force* of the gas-transport process. As a result of this gradient, a flux of the chemical moves through the air-water interface. Also, this flux should be related to the characteristics of transport processes near the air-water interface. These processes can occur at the molecular scale and are also affected by turbulence because the flow in the atmosphere and in the water body is turbulent. Thus, a first qualitative assessment of gas-transfer process would lead to state that a gas-transfer flux J_{g-t} [ML⁻²T⁻¹] driven by concentration gradient could be generally expressed using Fick's law as:

$$J_{g-t} = - \left(D_m + D_t \right) \cdot \frac{dC}{dz} \quad (1)$$

where D_m and D_t are, respectively, the molecular and *turbulent* or *eddy* diffusion coefficient [L²/T] and dC/dz is the concentration gradient of the species being transferred, where z is the vertical coordinate. Notably, the gas being transferred is assumed to be distributed uniformly in the bulk fluid. Also, the magnitude of the eddy diffusion coefficient D_t in the natural environment is usually many times larger than molecular diffusivity D_m .

Equation (1) points out that gas-transfer process depends on the physicochemical char-

acteristics of the substance being transferred and on the interaction between turbulence in the atmosphere and/or in the water body, on one hand, and the air-water interface, on the other. The latter feature introduces a second critical point that is related to the relative importance of the gas-phase, i.e. the atmosphere, and of the water-phase, i.e. the water body, on gas-transfer process. It is likely that sometimes one phase can prevail and transport processes occurring within this phase should be better investigated to gain insight into gas-transfer process. Third, another critical point is expected to be related to where the turbulence is produced, i.e. whether close to the air-water interface or far from it, since the interplay between turbulent motions and the interface should be different.

The previous short discussion suggests to divide the subject and to organize the chapter as follows. Section 2 explains how the physicochemical characteristics of the substance being transferred affect gas-transfer process and they can control which phase governs the process. Section 3 provides a discussion on how turbulence generally interacts with the air-water interface for a substance being controlled by the water phase. This discussion highlights that a more detailed approach requires to consider separately conditions where turbulence is produced far from the air-water interface, that is an unshared interface, and where turbulence is produced close to the interface, that is a shared interface. Thus, Section 4 deals with the gas-transfer at an unshared air-water interface. First of all, dimensional analysis of gas-transfer process is presented to achieve a robust theoretical framework where suitable modelling efforts can be developed. After then, classical and more recent modeling approaches starting from Lewis-Whitman two films theory are discussed. Both approaches based on *global* and *local* properties of turbulence are presented. Moreover, results from both laboratory and field studies together with those coming from numerical simulations are also considered to elucidate physical features of the gas-transfer process and to assess models performances. Finally, conclusive remarks are drawn also highlighting the areas where future research would be useful.