

# TRANSPORT PHENOMENA

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## AT INTERFACES

In environmental fluid mechanics, the most common type of interfaces are those formed between air and water (gas-liquid interface) and those formed between sediments and water (solid-liquid interface).

The chemical and physical processes occurring at such interfaces are very similar, and lead to boundary fluxes of mass, momentum and energy (read heat).

Boundary exchange of mass, momentum and energy plays a central role in many environmental processes such as:

- transfer of greenhouse gases ( $\text{CO}_2$ , methane) in surface waters
- atmospheric exchange of oxygen with hypoxic\* water bodies
- desorption\*\* of dissolved toxics (e.g. PCBs) from inland and coastal water bodies

\* Aquatic hypoxia occurs when the oxygen dissolved in water becomes reduced in concentration up

to a point that it becomes detrimental to aquatic organisms living in the environment.

A water body is defined hypoxic when the concentration of dissolved oxygen is between 1% and 30% of the saturation level.

When concentration is below 1%, the system is defined anoxic (or noxic).

A "healthy" aquatic system should be characterized by concentrations of dissolved oxygen above 80% of the saturation level.

\*\* DESORPTION is the process of releasing a substance from or through a surface

PCBs (Polychlorinated biphenyl) are organic chlorine compounds that are extremely toxic (comparable to dioxin) and hardly degradable

To examine transport phenomena at an interface, we will focus on the process of transferring a substance that can be dissolved in the water phase (or, in more general terms, in a liquid).

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This process is relevant for all air-water processes listed at page 1, but also for transfer of metals, salts, nutrients and organic compounds at a sediment-water interface.

The transfer of such substances at the interface gives rise to a net mass flux  $J$ , which can have diffusive and advective contributions: the diffusive contribution is typically controlled by equilibrium chemistry, whereas the advective contribution may depend on many processes (the most important being turbulence).

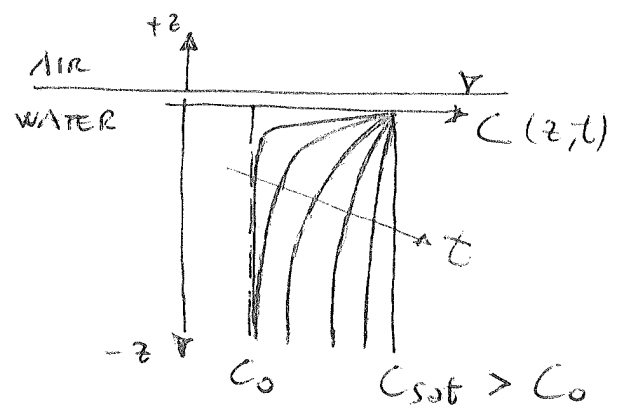
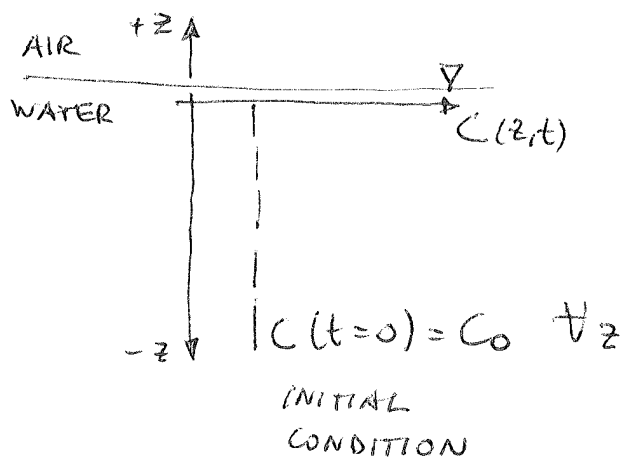
From a modelling point of view, the mass flux  $J$  represents a boundary condition that the governing transport equations in each phase must satisfy in order to be solved (either analytically or numerically) in a correct way.

As a boundary condition,  $J$  must be predicted somehow: the difficulty of predicting the magnitude of  $J$  stems from the fact that  $J$  depends on the physico-chemical properties of the

transferred substance, as well as on the hydrodynamic conditions in each phase. 4

### ● BOUNDARY EXCHANGE OF A SUBSTANCE INTO A STAGNANT WATER BODY

To start looking at boundary exchange, we consider first a simple, idealized situation in which the substance is dissolved into a stagnant water body:



The initial condition is given by a uniform concentration of the substance:  $C(t=0) = C_0 \quad \forall z$ .

The interface is then instantaneously exposed to an infinite source of the substance coming from the air side.

If  $C_0 < C_{sat}$ , then the substance will be transferred at the interface and will dissolve into the water body until the entire water body reaches

the saturation concentration,  $C_{sat}$ .

L5

The dissolution reaction is very fast and so the concentration at the surface goes from  $C_0$  to  $C_{sat}$  almost immediately once the source of substance is applied. In the remaining of the water body, however, the increase of concentration from  $C_0$  to  $C_{sat}$  takes longer, as shown in the schematic at page 4.

In the simplified case we are considering, the governing transport equation for concentration:

$$\frac{\partial C}{\partial t} + u_j \frac{\partial C}{\partial x_j} = D \frac{\partial^2 C}{\partial x_j^2} + R_c$$

Simplifies to:

$$\boxed{\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2}} \quad [1]$$

since  $u_j = 0 \forall j$  (water is at rest and advection can be neglected) and  $\partial C / \partial x = \partial C / \partial y = R_c = 0$ .

Boundary and initial conditions for  $C$  are:

$$\boxed{BC} \quad C(z = -\infty, t) = C_0 \quad ; \quad C(z = 0, t) = C_{sat}$$

→

$$\boxed{\text{IC}} \quad C(z, t=0) = C_0 \quad \forall z$$

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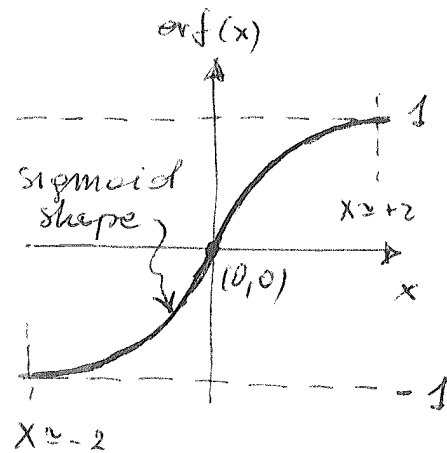
The solution of eqn. [1] with such BCs and IC reads as:

$$\boxed{\text{[2]}} \quad C(z, t) = C_0 + (C_{\text{sat}} - C_0) \left[ 1 - \operatorname{erf} \left( -\frac{z}{\sqrt{4Dt}} \right) \right]$$

where erf = Error Function :

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-y^2} dy$$

$$= \frac{1}{\sqrt{\pi}} \int_{-x}^{+x} e^{-y^2} dy$$



The minus sign inside the error function is included because we are assuming a negative value for  $z$  as we move downward.

From eqn. [2], we can derive an expression for the flux exchanged at the boundary by using Fick's law :

$$\boxed{J = -D \cdot \frac{\partial C}{\partial z} \Big|_{z=0} = -D \cdot \frac{(C_{\text{sat}} - C_0)}{\sqrt{\pi Dt}} = -(C_{\text{sat}} - C_0) \sqrt{\frac{D}{\pi t}}}$$

Since :

$$\frac{\partial C}{\partial z} = \frac{\partial}{\partial z} \left\{ C_0 + (C_{sat} - C_0) \left[ 1 - \operatorname{erf} \left( -\frac{z}{\sqrt{4Dt}} \right) \right] \right\}$$

$$= -(C_{sat} - C_0) \frac{\partial}{\partial z} \left[ \operatorname{erf} \left( -\frac{z}{\sqrt{4Dt}} \right) \right]$$

$$= -(C_{sat} - C_0) \frac{\partial}{\partial z} \left[ \frac{2}{\sqrt{\pi}} \int_0^x e^{-y^2} dy \right] \Bigg|_{x = -\frac{z}{\sqrt{4Dt}}}$$

where  $dx = -\frac{1}{\sqrt{4Dt}} dz$ . One gets :

$$\frac{\partial C}{\partial z} = -\frac{2}{\sqrt{\pi}} (C_{sat} - C_0) \cdot \left( -\frac{1}{\sqrt{4Dt}} \right) \frac{\partial}{\partial x} \left( \int_0^x e^{-y^2} dy \right)$$

$$= \frac{C_{sat} - C_0}{\sqrt{\pi Dt}} \cdot e^{-\left(\frac{z}{\sqrt{4Dt}}\right)^2} \cdot e^{-x^2}$$

At  $z=0$  :  $e^{-(-)^2} = 1$  and  $\frac{\partial C}{\partial z} \Big|_{z=0} = \frac{C_{sat} - C_0}{\sqrt{\pi Dt}}$  ✓

In the simple case of stagnant water, one can also compute the characteristic thickness  $\delta$  of the mixing layer, which coincides with the concentration

boundary layer  $\delta_z$  over which concentration changes from  $C_0$  to  $C_{sat}$  :

$$\delta = \delta_z = \sqrt{2Dt}$$

where this expression comes from the boundary layer theory applied to the Stokes boundary layer (evolving in time).

Note that the quantity  $\sqrt{D/\pi t}$  is expressed in  $m/s$  and therefore is equivalent to a velocity.

Indeed :

$$K \triangleq \sqrt{\frac{D}{\pi t}}$$

TRANSFER VELOCITY  
OF SUBSTANCE  
ACROSS THE SURFACE



$$J_z = -K \cdot (C_{sat} - C_0)$$

BOUNDARY  
EXCHANGE  
FLUX

- BOUNDARY EXCHANGE OF A SUBSTANCE INTO A TURBULENT WATER BODY

A more realistic situation in which boundary exchange can occur is the one with a turbulent motion of the water body below the interface.



The turbulent motion has two main effects:

1. it limits the growth of the mixing layer thickness  $\delta$  (namely of the concentration layer  $\delta_c$ ). This implies that the concentration gradient  $\partial C / \partial z$  below the interface will increase, namely that the boundary exchange flux will increase.
2. it increase the effective diffusivity such that the coefficient in Fick's law is not just  $D$  but has an additional turbulence-induced contribution. This implies again that the boundary exchange flux will increase.

However, these two effects are due to the large-scale motions in the bulk of the flow. Near the interface three-dimensional turbulent motions cannot exist and molecular diffusion is still important as rate-limiting process that prevents the transfer rate from growing indefinitely large.

NOTE: For many gas-liquid systems, the largest effects on the boundary exchange come from

the motions on the liquid side. This because of the following reasons:

1. Molecular diffusivity in liquids is 3 to 4 orders of magnitude smaller than in gases, which causes the concentration gradient to be much larger on the liquid side.
2. Many systems involve the transfer of a species that is poorly soluble in the liquid phase (e.g.  $CO_2$ ,  $O_2$ ,  $H_2$  or  $CH_4$  in water)

Therefore, the concentration/mixing boundary layer lies mainly on the liquid side and this explains why motions on the liquid side affect boundary exchange much more than those on the gas side.

Going back to the prediction of  $T_e$  for the present case, the effect of turbulence can be summarized in terms of the following three expectations:

- E1) turbulence prevents  $\delta$  from growing arbitrarily large, so that an average thickness of the concentration/mixing layer can be expected

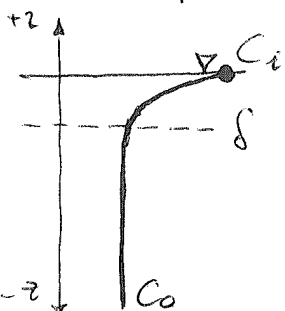
E2) As a consequence of E1, an average transfer rate and, hence, an average boundary exchange flux can be expected.

E3) The transfer rate can be limited on either side of the interface by the specific chemical or hydrodynamic conditions in that side.

Based on these expectations, the prediction of the boundary exchange flux  $J_2$  still requires the definition of a suitable transfer velocity  $K$ .

The simplest expression available for  $K$  was derived by Lewis & Whitman in 1924. They hypothesized that, even if the fluid is in turbulent motion below the interface, a thin film of fluid moving in laminar condition existed adjacent to the interface.

This laminar film provided the main resistance to mass transfer, and the resulting model does not account for turbulent motions reaching the interface. The expression for  $K$  reads as:



$$K = \frac{D}{\delta}$$

LEWIS - WHITMAN  
MODEL

where  $\delta$  is the mixing layer constant thickness, assumed to be constant.

Note that, in this model,  $K \propto D$  while it was  $K \propto D^{1/2}$  in the "stagnant" case: experiments in stirred tanks showed that the  $D^{1/2}$ -dependence is more correct and, therefore, the Lewis-Whitman model needs refinement.

Another weakness of the model is that it does not provide any physical insight about how to predict  $\delta$ , which must be determined empirically.

An improvement of the L-W model was granted by the so-called FILM RENEWAL MODEL, which provides a physical mechanism that controls the boundary layer thickness and, therefore, allows to formulate a predictive expression for  $\delta$ .

In the film-renewal model, the boundary layer can grow in time until turbulence suddenly replaces the water contained in the boundary layer. When this happens, the boundary layer is re-created and the thickness starts growing again.

This process repeats itself periodically, and the renewal frequency is a function of the turbulent characteristics of the flow. 13

Assuming that the renewal is instantaneous (namely  $\delta$  grows undisturbed over a certain time interval  $\Delta t$ , then renewal occurs and  $\delta$  grows over from the beginning over a subsequent interval  $\Delta t$ , and so on), it is possible to determine  $J_z$  analytically.

The governing transport equations, the initial and the boundary conditions are exactly the same as in the "stagnant" case. Therefore also the expressions for  $C(z, t)$  and for  $J_z$  are the same, with the difference that these expressions are only valid from  $t=0$  to  $t=t_R$  where  $t_R$  is the time between two successive renewal events.

The mean value of the boundary exchange flux between successive renewals can be found by taking the time average of  $J_z$ :

$$\bar{J}_z = \frac{1}{t_R} \int_t^{t+t_R} J_z(t) dt$$

$$= \frac{1}{t_R} \int_t^{t+t_R} - (C_i - C_o) \sqrt{\frac{D}{\pi t}} dt$$

$$= - (C_i - C_o) \sqrt{\frac{4D}{\pi t_R}}$$

where  $C_i$  is the concentration of the substance at the interface (e.g.  $C_i = C_{sat}$ ).

The renewal frequency is  $f_R = t_R^{-1}$  so:

$$\bar{J}_z = - (C_i - C_o) \sqrt{\frac{4D \cdot f_R}{\pi}} \Rightarrow K = \sqrt{\frac{4D \cdot f_R}{\pi}}$$

FILM RENEWAL MODEL

where  $f_R$  is the main model parameter (which depends on the characteristics of the turbulent flow).

Two estimates for  $f_R$  can be given, recalling that turbulence is characterized by a range of spatial scales from the largest (known as INTEGRAL SCALE) to the smallest (KOLMOGOROV SCALE):

• small-scale estimate of  $f_R$  :

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the time between renewals  $t_R$  is taken equal to the Kolmogorov time scale :

$$\tau_K = \sqrt{\frac{\nu}{\epsilon}}$$

where  $\epsilon$  is the energy dissipation rate, which can be estimated as :

$$\epsilon = \frac{v_*^3}{h} = \frac{\text{friction velocity } (= \sqrt{\frac{\tau_w}{\rho}})}{\text{depth of the shear layer}}$$

This yields :

$$t_R = \tau_K = \sqrt{\frac{\nu \cdot h}{v_*^3}} \Rightarrow f_R = \sqrt{\frac{v_*^3}{\nu \cdot h}}$$

It can be demonstrated that  $v_* = \bar{v} \sqrt{\frac{f}{8}}$ , so :

$$f_R = \sqrt{\frac{\bar{v}^3}{\nu \cdot h} \left(\frac{f}{8}\right)^{3/2}} \quad (*)$$

where  $\bar{v}$  is the mean flow velocity and  $f$  is the friction coefficient of the flow.

Based on  $(*)$ , the transfer velocity can be written as :

$$K = C' \frac{\bar{v}^{3/4}}{h^{3/4}}$$

Small-scale estimate

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where  $C' = \sqrt{\frac{4D}{\pi \cdot \nu^{3/2}} \cdot \left(\frac{f}{8}\right)^{3/4}}$  is a constant that depends on the fluid properties, represented by  $\nu$ , on the physico-chemical properties of the transferred substance, represented by  $D$ , and on the type of boundary layer that forms below the interface, represented by  $f$ .

For an air-water interface:  $C \sim 0(10^{-1} \div 10^0) \frac{\text{cm}}{\text{s}}$

• large-scale estimate of  $f_R$ :

the time between renewals  $t_R$  is taken equal to the INTEGRAL TIME SCALE:

$$Z_I \triangleq \frac{v_*}{h}$$

↓

$$f_R = \frac{h}{v_*} + v_* = \bar{v} \sqrt{\frac{f}{8}} \Rightarrow$$

large-scale estimate

$$K = C'' \bar{v}^{-1/2} \cdot h^{1/2}$$

where  $C'' = \sqrt{\frac{8\sqrt{2} \cdot D}{\pi \cdot f}}$  is another constant, only dependent on  $D$  and  $f$ .



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Experimental evidence is not conclusive, but seems to agree better with the small-scale estimate  $K \propto \bar{v}^{3/4}$ , which would mean that film renewal is governed by the small-scale turbulent eddies in the flow.

The boundary transfer models described so far cannot take into account two further complications that arise because of the fact that the air-water interface is a moving boundary.

One complication arises when wind generates shear directly at the interface. In the film renewal model, shear is generated by the turbulent events that renew the surface (these events being generated at the channel bed) but wind-generated shear is not accounted for.

Wind-generated shear, however, generates motions at the interface that can strongly affect (and greatly increase) the transfer rates, particularly in oceans and lakes.

The second complication arises when the surface

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of the interface is characterized by waviness, breaking and hydrodynamic instability. These processes greatly increase boundary transfer by "disturbing" the mixing/concentration boundary layer within which boundary exchange occurs.

In particular, breaking waves entrain air and carry air bubbles deep into the fluid upon folding on themselves. These bubbles then dissolve as they rise back towards the surface, thus increasing the concentration of dissolved gas.

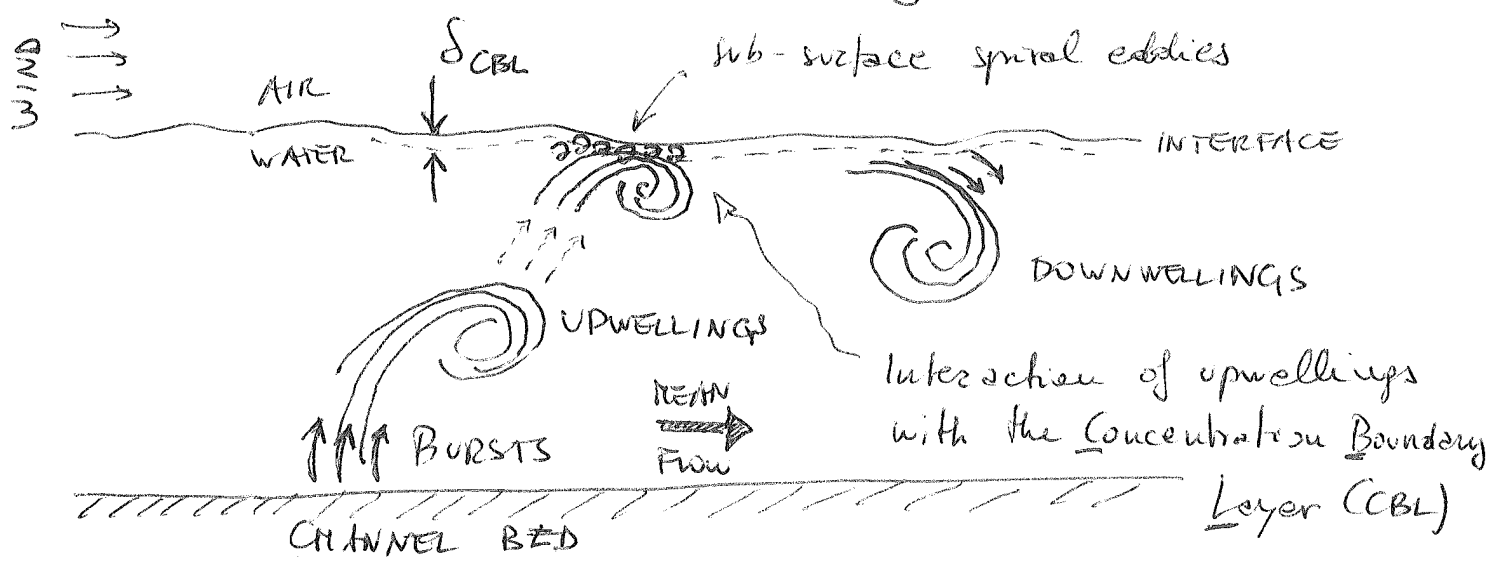
Wave breaking begins when the interfacial shear rate is sufficiently large, with a dramatic increase of interfacial transfer rate observed for wind speeds exceeding 3 m/s as measured 10 m above the interface.

Such dramatic increase is due to the onset of small waves of approximate length  $\sim 10$  cm, known as MICRO-BREAKING WAVES.

These micro-breaking waves introduce new mechanism of turbulence generation at the interface and, therefore, determine a physical situation characterized by multiple time scales. In such situation, the film-renewal theory fails to provide reliable estimates of the transfer rates, because it relies only on global turbulence properties.

Clearly, the next theoretical step to handle the above-mentioned complications is to relate boundary exchange directly to local turbulence properties, namely to the actual turbulence characteristics near the air-water interface.

The physical picture envisioned for developing such relation is the following:



Since the CBL is very thin ( $\delta_{CBL}$  is very small) compared to the depth of the water layer, the derivative in the vertical direction ( $z$ ) is much larger than the derivative in the horizontal directions ( $x; y$ ). /20

Therefore, considering a coordinate system embedded on the interface, the transport equation for the substance transferred through the interface may be simplified as:

$$\frac{\partial C}{\partial t} + w' \frac{\partial \bar{C}}{\partial z} = D \frac{\partial^2 C}{\partial z^2}$$

provided that a flow region near the interface is considered (deep in the water layer, these simplified form of the equation would not be accurate). Note that:

- $C$  = instantaneous concentration of the transferred substance (dissolving in water)
- $\bar{C}$  = time-averaged concentration of the transferred substance
- $w'$  = fluid velocity fluctuation normal to the interface

Applying a series expansion, one can find: [21]

$$w'(z) \cong \cancel{w'(z_{\text{interface}})} + \frac{\partial w'}{\partial z} \cdot (z - \cancel{z_{\text{interface}}}) + \frac{1}{2} \cdot \frac{\partial^2 w'}{\partial z^2} (z - \cancel{z_{\text{interface}}})^2 + \dots$$

$w' \cong \frac{\partial w'}{\partial z} \cdot z$

←  $z = \text{distance from the interface}$

where  $\frac{\partial w'}{\partial z}$  is the vertical velocity gradient very near to the air-water interface: This gradient may change in time and with the distance parallel to the interface, and is also dependent on the characteristics of the turbulent flow.

Near the surface,  $\partial w' / \partial z$  is different from zero due to continuity:

$$\frac{\partial w'}{\partial z} = - \overbrace{\left( \frac{\partial u'}{\partial x} + \frac{\partial v'}{\partial y} \right)}^{\text{SURFACE DIVERGENCE } (\nabla_{2D})} \neq 0$$

where  $u'$  and  $v'$  are the fluid velocity fluctuations in the streamwise and spanwise directions, respectively. Therefore:

$w' \cong - \nabla_{2D} \cdot z$

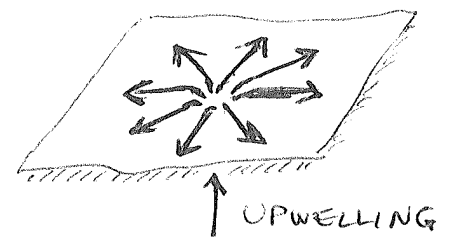
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and :

$$\frac{\partial C}{\partial t} - \nabla_{2D} \cdot z \frac{\partial C}{\partial z} = D \frac{\partial^2 C}{\partial z^2}$$

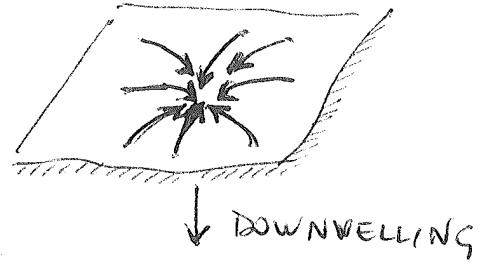
The physical meaning of  $\nabla_{2D}$  is the following :

$$\nabla_{2D} > 0 \quad ( \partial w' / \partial z < 0 \Rightarrow w' < 0 )$$



Fluid flows toward the interface and interface-parallel motions diverge

$$\nabla_{2D} < 0 \quad ( \partial w' / \partial z > 0 \Rightarrow w' > 0 )$$



Fluid flows away from the interface and interface-parallel motions converge

The transport equation for C indicates that an estimate of  $\nabla_{2D}$  is needed in order to determine the transfer rate associated with the boundary exchange across the surface.

Skipping the derivation, it can be shown that

the transfer rate of substance across the interface can be expressed as  $K \approx (D \cdot \nabla_{2D})^{1/2}$  or:

$$\frac{K \cdot Sc^{1/2}}{\langle u \rangle} \approx Re_t^{-1/2} \cdot \nabla_{2D}^{1/2} \quad (1)$$

for the case of an unstressed interface at high Schmidt number:

$$Sc \triangleq \frac{\nu}{D} = \frac{\text{momentum diffusivity}}{\text{mass diffusivity}}$$

In eq. (1), which is expressed in dimensionless form,  $\langle u \rangle$  is the mean fluid velocity and  $Re_t = \langle u \rangle h / \nu$  is the Reynolds number of the turbulent flow on the water side.

Eq. (1) can be extended to the case of deformed interface with curvature  $\kappa = -\bar{\nabla} \cdot \vec{m}$ , where  $\vec{m}$  is the normal unit vector to the interface:

$$(2) \quad \frac{K \cdot Sc^{1/2}}{\langle u \rangle} \approx C \cdot Re_t^{-1/2} \cdot \left[ (\nabla_{2D} - 2w' \bar{\nabla} \cdot \vec{m})^2 \right]^{1/4}$$

where  $C \sim O(1)$  is a proportionality coefficient,

And the term  $-2w' \nabla \cdot \vec{m}$  represents surface [24]  
dilatation produced by the deformation of the  
interface.

Eq. (2) in dimensional form reads as:

$$K \approx G \cdot \left[ D \left( \nabla_{2D} - 2w' \nabla \cdot \vec{m} \right) \right]^{1/2}$$

In practice, the surface divergence, which has the dimensions of an inverse time scale ( $s^{-1}$ ), takes the place of the time between renewals  $t_R$  adopted in the film-renewal model, with the advantage that  $\nabla_{2D}$  can be measured (or computed) more easily than  $t_R$ .

One popular expression for  $\nabla_{2D}$  was provided by Banerjee (1990):

$$\nabla_{2D} = 0,3 \left( 2,83 \text{Re}_t^{3/4} - 2,14 \text{Re}_t^{2/3} \right)^{1/4}$$



SURFACE  
DIVERGENCE  
MODEL FOR  
K (FOR  
UNSHEARED  
INTERFACE)

$$\frac{K \cdot Sc^{1/2}}{\langle u \rangle} \approx \text{Re}_t^{-1/2} \cdot \left[ 0,3 \left( 2,83 \text{Re}_t^{3/4} - 2,14 \text{Re}_t^{2/3} \right)^{1/4} \right]$$

(3)



Note that eq. (3) predicts:

$$K \propto Re_t^{-1/2} \text{ for small } Re_t$$

in agreement with the large-scale estimate of  $t_R$  adopted in the film-renewal model (see page 16 of these notes), whereas:

$$K \propto Re_t^{-1/4} \text{ for large } Re_t$$

in agreement with the small-scale estimate of  $t_R$  (see page 16, again).

In addition, eq. (3) does not require the calculation of the friction factor (which, on the contrary, is required in the film-renewal model).

The equations for  $K$  written so far are valid for the case of unsheared interface. If the interface is sheared (like in the case of a wind blowing on the gas side), then the following relation has been proposed by Banerjee (1990):

$$K \cdot Sc^{1/2} = 0,108 - 0,158 U_*$$

where  $U_*$  is the friction velocity associated to the

interfacial shear stress. This expressions has L26  
been derived in the absence of wave breaking,  
yet turns out to be rather accurate also in the  
case of small microbreaking waves.

### SEDIMENT-WATER INTERFACE

Unlike the air-water interface, which is generally confined to an abrupt transition from one side to the other, the sediment-water interface is very difficult to define due to its multi-phase nature and to the range of complex physical and chemical processes that control the interface dynamics.

To describe a sediment-water interface, two important quantities are used:

- Porosity ( $m$ ), which is the volume of water ( $V_w$ ) contained in a unit volume of sediment mixture:

$$m = V_w / V_m \quad \text{Porosity}$$

This parameter ranges between 0.1 and 0.9 in the sediment bed (which is equivalent to a porous medium), whereas it is  $\geq 0.99$  in the

water column above the sediment bed, where sediments are suspended (i.e. not deposited).

- SETTLING VELOCITY ( $V_{\text{settling}}$ ), which is the terminal fall velocity of the sediment in a quiescent liquid.

The interface between the sediment bed (where sediments are deposited) and the water column (where sediments are suspended) can then be defined as the ensemble of points where the porosity  $n$  becomes small enough that the settling velocity  $v_s$  goes to zero due to the contact with other sediment particles (thus forming a relatively fixed bed load).

There are several important physical and chemical processes that control boundary exchange and transfer rates through the sediment-water interface. Besides advection and diffusion (that can be both molecular and turbulent), the following physical processes (that do not involve chemical transformation) and chemical/biological processes matter:

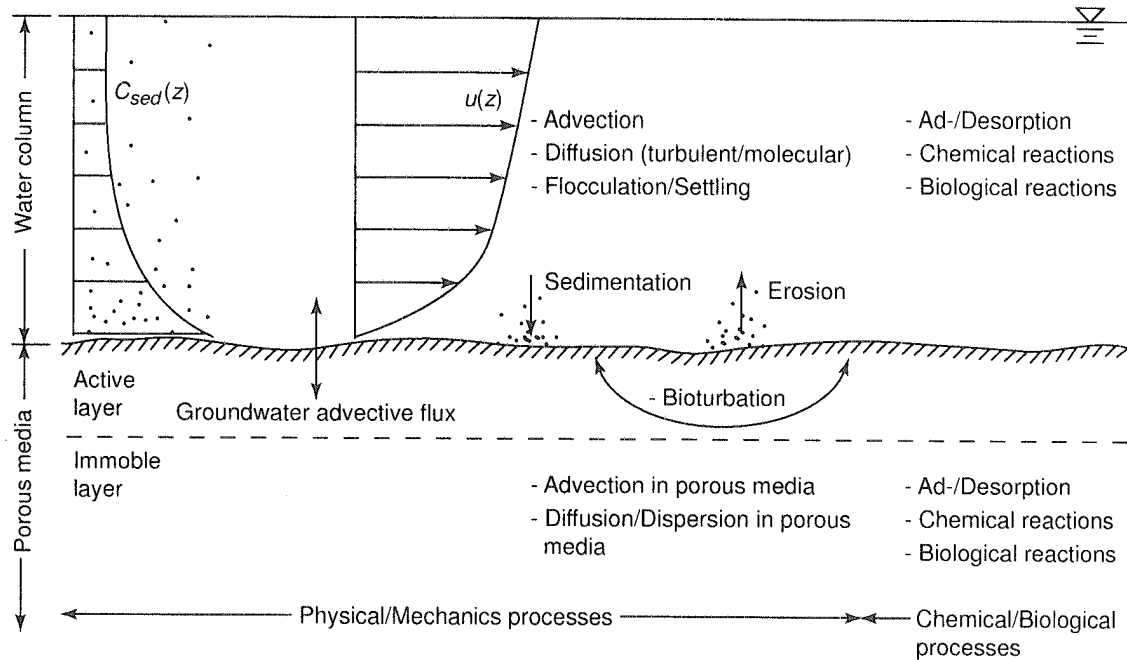


Fig. 5.5. Schematic of processes occurring at the sediment-water interface, in the water column and in the sediment bed (porous media).

- **Erosion:** erosion is the process by which sediment is lost from the sediment bed and entrained into the water column.

Within the sediment bed, or porous media, further transport processes are at work. For species in the liquid phase, the processes of advection, diffusion, and dispersion are active throughout the porous media. For the sediment particles, physical transport occurs only in the upper active layer due to the process of bioturbation:

- **Bioturbation:** bioturbation is the name given to the mixing of sediment caused by animals living in the sediment (mostly worms). These animals move sediment as they dig. Two important classes of worms mix the sediment differently. In the one case, sediment is eaten at the base of the active layer and moved up to the surface. In the other case, sediment is removed from the surface and carried down to the bottom of the active layer. The net movement of sediment is often modeled by an enhanced diffusion process, where we use bioturbation diffusion coefficients.

Through the combination of all these transport processes, chemical species move in and out of the water column and the porous media.

Through transformation processes, chemical species move in and out of the solid and liquid phases and, also, change to other species. We have already discussed chemical and biological transformation reactions. These reactions occur both in the water column and in the porous media. They can also occur in either the liquid phase, the solid phase or at the interface.

Processes at the sediment interface are particularly important for the transport of chemicals through these multi-phase systems:

- **Adsorption/desorption:** the chemical processes of adsorption and desorption control the distribution of certain chemicals between the solid and liquid phases. Due to complex chemical/physical processes, some molecules have an affinity for sticking to the solid phase (often due to electrical charge interaction). That is, some molecules would rather stick to a sediment particle than remain dissolved in the surrounding fluid. The behavior of most organic compounds and heavy metals is controlled by sorption chemistry.

Because sorption is a dominant process occurring at the sediment-water interface, it is discussed in more detail at the end of this section.

As discussed in Gschwend (1987), the processes at the sediment-water interface (at the bottom of a lake or channel) depend on the energetic state of the water body. Beginning with laminar conditions (as in a deep lake) and progressing to increasingly energetic, turbulent conditions (as in reservoirs, estuaries, and streams), the progression is as follows. With no motion, exchange occurs due to direct sorption exchange and diffusion of dissolved species from the pore water. Next, the system begins to flow, allowing the advective and dispersive flux of groundwater flow. Bioturbation, which may always be present, adds energy by actively mixing the sediments. As the water column begins to flow, sediments can be pushed along the top layer of sediments in a process called bed-load transport. Finally, with an energetic water column, erosion begins, sediment is carried up into the water column, and suspended transport (advection of sediment in the water column) becomes important. Hence, the transport of species associated with sediment is a complex problem dependent on the chemistry of the species and the mobility of the sediment.

### 5.3.1 Adsorption/desorption in disperse aqueous systems

Ignoring the complex problems that lead to the transport of sediment, we focus in this section on the exchange at the solid/liquid interface of a mixed solution of suspended sediment particles in a dispersed (large  $n$ ) system. An important process controlling the distribution of many toxins in sediment-laden solutions is adsorption/desorption. Defined above, this process causes a large fraction of the sorbing compound to attach to the sediment particles. Hence, sorption controls the concentration of dissolved contaminant, and causes much of the contaminant to be transported with the sediment.

Figure 5.6 illustrates the situation. Sorbing compounds include most polar and non-polar organic compounds and heavy metal ions. To describe the situation quantitatively, we define two concentrations. First, the concentration of substance  $A$  that is dissolved in solution is designated  $C$  and is defined as

$$C = \frac{M_{\text{dissolved}}}{V_w} \quad (5.35)$$

having normal concentration units. Second, the non-dimensional sorbed-fraction concentration,  $C_s^*$ , is defined as

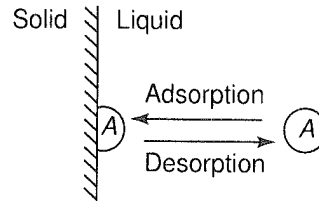


Fig. 5.6. Schematic of the adsorption/desorption process for the molecule  $A$ .

$$\begin{aligned}
 C_s^* &= \frac{M_{\text{adsorbed}}/V_w}{M_{\text{sediment}}/V_w} \\
 &= \frac{M_{\text{adsorbed}}}{M_{\text{sediment}}}
 \end{aligned}
 \tag{5.36}$$

These equations are valid only for highly dispersed systems, where  $nV \approx V$ .

Because sorption kinetics are very fast, we can usually assume that equilibrium exists between the adsorbed and desorbed fractions. Based on experiments, the following simple type of equilibrium relationship has been proposed:

$$C_s^* = \frac{\Gamma C}{K + C} \tag{5.37}$$

which is called the Langmuir equation. The coefficient  $K$  is a constant with units of concentration; the coefficient  $\Gamma$  is a non-dimensional constant, called the Langmuir isotherm, which gives the asymptotic value of  $C_s^*$  as  $C$  becomes large. Figure 5.7 plots the Langmuir equation for  $\Gamma = 1$  and  $K = 1$ . For most toxins in the environment,  $C \ll K$ , and we can simplify the Langmuir equation to

$$C_s^* = \mathcal{P}C \tag{5.38}$$

where  $\mathcal{P}$  is the partition coefficient with units  $[L^3/M]$ . Typical values of  $\mathcal{P}$  are between  $10^3$  to  $10^6$  l/kg.

In order to avoid the confusion caused by  $C_s^*$  being non-dimensional, a dimensional concentration of adsorbed contaminant is convenient to define. From the density of the sediment  $\rho_s$  and the porosity, the dimensional adsorbed concentration is

$$\begin{aligned}
 C_s &= C_s^* \rho_s \left( \frac{1-n}{n} \right) \\
 &= K_D C
 \end{aligned}
 \tag{5.39}$$

where  $K_D$  is a non-dimensional distribution coefficient. It is important to note that  $\mathcal{P}$  is a purely physico-chemical parameter; whereas,  $K_D$  also depends on the sediment concentration and physical characteristics (through the porosity and density, respectively).

## Summary

This chapter introduced the processes that result in boundary exchange of chemical species. The general issue in describing boundary exchange is in determining the net boundary flux  $\mathbf{J}$ . Once

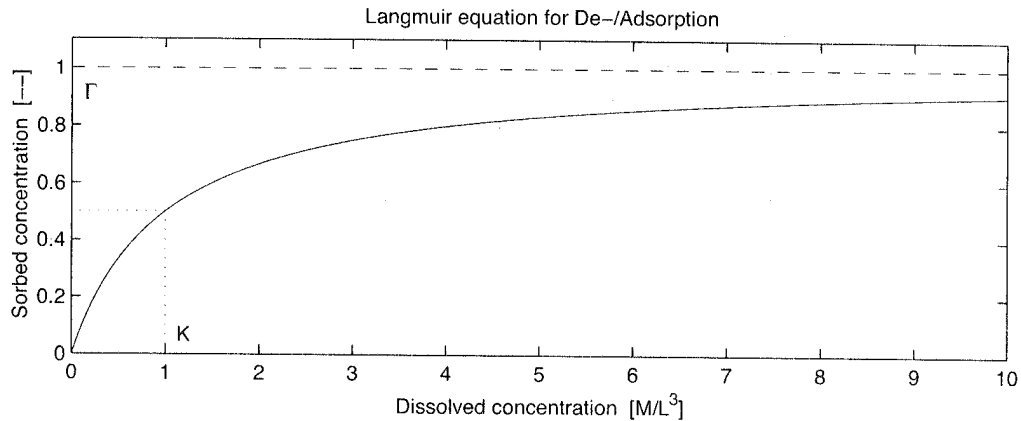


Fig. 5.7. Langmuir equation for de-/adsorption with  $\Gamma = 1$  and  $K = 1$ . Note that  $C_s^*$  is  $1/2$  at  $C = K$ .

### Example Box 5.3:

#### Naphthalene partitioning.

Consider the partitioning of the organic toxin naphthalene, the smallest of the polynuclear aromatic hydrocarbons (PAHs). We wish to find the fraction of dissolved to adsorbed naphthalene,  $f_d$ . Using (5.38), this fraction is given by

$$f_d = \frac{C}{C + C_s^*} = \frac{1}{1 + \rho_s \left( \frac{1-n}{n} \right) \mathcal{P}}$$

For naphthalene  $\mathcal{P} = 10^3$  l/kg. Typical sediment has a density of  $2600$  kg/m<sup>3</sup>. For a mixture with  $n = 0.99$ ,  $f_d = 4\%$ .

We can see that  $f_d$  is always large for low concentrations  $C$  by looking at the range of expected  $K_D$ . From above

$$K_D = \rho_s \left( \frac{1-n}{n} \right) \mathcal{P}.$$

Making the following order-of-magnitude estimates

$$\begin{aligned} \rho_s &= 10^3 \\ (1-n)/n &= 10^{-3} \\ \mathcal{P} &= 10^3 \text{ to } 10^6 \end{aligned}$$

$K_D$  ranges from  $10^3$  to  $10^6$ ;  $f_d$  ranges from  $10^{-3}$  to  $10^{-6}$ . Therefore, we can assume that a large fraction of the contaminant is present in the sorbed state.

If we manage to eliminate the source of a toxic contaminant that is also sorbed to the sediments, then the sediment bed itself will start to release its sediment load into the water column water, creating a new source (see Exercise 5.3). Unfortunately, because  $f_d$  is so large, the sediment load is large, and it takes a long time before the water column is free from this sediment source of the contaminant.

that flux is known, boundary exchange becomes a boundary condition on the governing transport equation. The solution for  $\mathbf{J}$  in a stagnant water body was used to develop two descriptions of exchange in turbulent water bodies. The Lewis-Whitman model, the simplest model, assumes the concentration boundary layer between phases has a constant depth. The film-renewal model assumes that turbulence constantly refreshes the fluid in the concentration boundary layer, and that the renewal rate derives from turbulent eddy characteristics. The exchange at the air-water interface was discussed in more detail, with examples for volatile chemicals and oxygen aeration. The sediment-water interface was described qualitatively, and the sorption chemistry at the sediment-water interface was described in more detail.