F54 Gas Exchange
Interaction between ocean and atmosphere
in Aeolotron-Lab
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Summary

The experiment gives an insight into the basic mechanisms of the gas exchange between atmosphere and ocean. The exchange rate of carbon dioxide between air and water can be measured at the annular wind-wave facility using two different methods: conductivity and pH value measurements. The pH value is determined by the optical absorption spectroscopy and usage of pH indicators. Within this experiment following learning points are included:

1. Basic understanding of the exchange rate of gases between air and water:
   - the influence of wind, waves and surface films

2. Insights into chemistry of carbonates in the ocean:
   - the influence of pH value
   - does the carbon dioxide reactivity influence on the exchange rate?

3. Learning of modern (optical) measurement methods in environmental physics:
   - conductivity method versus absorption spectroscopy with a pH indicator
   - wave measurements

4. ... and of course, the computer-based experiment and evaluation.

The instruction may be rechecked periodically. If you notice an error, or you have a suggestion, please send an email with relevant notes to:

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1 Introduction

Ocean plays an important role in the global carbon cycle. In the Figure 1 natural flux (-70 GtC/y +70.6 GtC/y) and anthropogenic flux (-22.2 GtC/y +20 GtC/y) are added up to an every year net-intake flux which is equal to 1.6 GtC with more than ±20% of uncertainties (the information was taken from IPCC-report [12, S. 515]). If one makes a climate forecasts or wants to understand the uncertainties, it is important to understand the gas exchange process between ocean and atmosphere.

Figure 1: The Carbon cycle in 1990: IPPC (2007) [12, S. 515]

The gas exchange, i.e. the mass flow of a gas through the water surface, is determined on the one hand by deviation of the gas concentration on both sides of the interface from the state of equilibrium, and on the other hand by the velocity of the gas exchange. The transfer velocity of the gas exchange, also called transfer rate, depends primarily on the strength of the near-surface turbulence, which directly or indirectly depends on wind, waves, surface films, rain (and others).

The above mentioned estimates of global CO$_2$ fluxes are taken from empirical formulas, where the transfer velocity is gained by the parametrization with the wind speed. This wind speed parametrization is a pragmatic approach because wind measurements from buoys, ships and satellites are available globally. These parametrizations are very inaccurate. A major reason for this is in definition of the area which is nearby the surface. Here the first millimetre on both sides of the water surface is meant. It is essential for the gas exchange how thick the layer is, i.e. the layer that gas needs to diffuse through before it gets transported by turbulence. Wind has a strong influence on the boundary layer but its influence is more indirect. In this experiment, you may be able to experience, that at the same wind speed very various transfer velocities can be measured, and that it’s noticeable how the surface film influences on centimetre and millimetre waves.

To understand the gas exchange better, it is important to examine the physical mechanisms precisely and to learn about their significance for the gas exchange. In our group of Gas Exchange and Waves the laboratory experiments (also fields experiments from time to time) are conducted to study the physics of the processes of the gas exchange. The small circular wind-wave channel (for this practical experiment) was used from late 1970s till the end of the 1980s. Using this facility, the strong influence of surface films on the gas exchange and the transition from smooth to rough water surface

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$^1$GtC = Gigaton carbon
2 Physical basics

2.1 Gas exchange between air and water

2.1.1 Boundary layer

Commonly the transport of gases in fluids (as the transport of impulse and heat) can be divided in diffusive and turbulent parts. Mostly, far away from the interface the turbulent transport of large and small eddies is more effective than molecular diffusion. The eddies cannot penetrate the interface between two substances with different densities (as water and air). Therefore the maximal size of the eddies is limited by the distance to the interface. When the eddies are really small next to the interface, the viscosity is more significant and right next to interface diffusive transport is more effective than the turbulent transport. These areas of reduced turbulence are shown in the Figure 2a. As the diffusive transport is rather slow, the boundary layer that the gas needs to diffuse through, has a large resistance.

2.1.2 Transfer resistance and analogy to Ohm’s resistance

A simple illustration of the relative importance of the transport regimes and their associated transfer resistances for the concentration profile follows from the analogy to the series connection of resistors, see Figure 2b), which we wish to make use of in the following discussion. It is well known, that \( I = \frac{U}{R} \), where the voltage \( U \) corresponds to the difference in concentration \( \Delta c \) and the current \( I \) represents the net flow \( j \) of the gas through the surface interface. If one of the resistors has small resistance, only a small fraction of the voltage drops. Just as it is with the drop in the concentration of a zone with small transfer resistance. If the resistances \( R_2 \) and \( R_3 \) (in the zones of reduced turbulence) are much larger than the resistors \( R_1 \) and \( R_4 \) (see Figure 2b)), then the last ones can be neglected for determining the total resistance.
2.1 Gas exchange between air and water

The solubility in both cases is \( \alpha = 0, 5 \).

### 2.1.3 Film model

In practice it was found that the transfer resistance through the air side boundary layer for low soluble gases (e.g. \( \text{CO}_2 \)) can be neglected with respect to the resistance of the water-side boundary layer. One can speak in this case of water-side controlled gas exchange, or a water-side controlled tracer. If we consider the transfer resistance in the air space being neglectable to the water sided transfer resistance then we can assume constant concentration except in the boundary layer at the water side (see Figure 3). If we have only molecular diffusion (which is depth dependent) in the water side boundary layer, then the concentration in a stationary case depends linearly on the depth \( z \). This really simple description of the gas exchange is called Film model, which is shown in Figure 3. Even though we make the physically unrealistic assumption to have a flat and solid water surface and to have a small constant layer, this model is a good (because simple) starting point for the further discussion.

### 2.1.4 Net flow and transfer velocity

The net flow \( j \) of a gas through the water-side layer is given by the product of concentration difference \( \alpha c_a - c_w \) (see Section 2.1.5) and the transfer velocity \( k \) (see Section 2.1.6)

\[
j = k \Delta c = k \cdot (\alpha c_a - c_w).
\]

We assume for simplicity that there is no concentration gradient in the horizontal direction. Thus the net flow has only a non-zero constant \( z \)-component.
2.1.5 Driving concentration difference and solubility

In equation (1) there is a driving concentration difference through the interface $\Delta c = \alpha c_a - c_w$ (not a difference between air and water side concentrations $c_a - c_w$, but $\Delta c = \alpha c_a - c_w$ as the gas in the water possesses a certain solubility). The solubility $\alpha$ of the gas is the ratio of the concentrations in equilibrium.

$$\alpha \equiv \frac{c_w}{c_a}. \quad (2)$$

Direct at the surface there is a thermodynamic equilibrium between air-side concentration and water-side concentration, so at the interface the concentration curve makes a jump with the factor of $\alpha$ (see Figure 3). The solubility of CO$_2$ for different temperatures is presented in Figure 4. Last two columns of the table correspond to different concentration units. The calculation of the solubility in other units is explained, for example, in Sander [11].

2.1.6 Transfer velocity and transfer resistance

The transfer velocity $k$ (in $m/s$ unit) characterizes the velocity of the gas exchange and reflects fluid dynamic conditions at the water surface as equivalent to the conductivity of the conductors. The effective diffusion coefficient is $(D + K(z))$, where $D$ is the molecular diffusion constant and $K(z)$ is the depth dependent turbulence diffusion constant [10, Chapter 6.4.3, Equation (6.156)]. By inserting the effective diffusion coefficient in Fick’s first law, one can yield:

$$j = -(D + K(z)) \frac{\partial c}{\partial z}, \quad (3)$$

which can be written as the transfer resistance:

$$\frac{1}{k} = -\int \frac{1}{D + K(z)} dz, \quad (4)$$

or as the transfer velocity:

$$k = \frac{1}{-\int \frac{1}{D + K(z)} dz}. \quad (5)$$

The integral of the transfer velocity $k$ is relatively easy to measure, while $K(z)$ is difficult to access experimentally. But by integrating over different altitudes $[z_a...z_b]$, you can calculate the transfer resistance with known $K(z)$ for the different zones separately.

2.1.7 Transfer velocity and direction of the flux in film model

As mentioned before, the film model presents the turbulent intensity as a step function. Within the boundary layer we assume $K(z) = 0$ and outside the boundary layer $K(z) = \infty$. In the integral from $z = -\infty$ to $z = +\infty$ from equation (4) there is only one part left between $-\tilde{z} < z \leq 0$:

$$\frac{1}{k} = \int_{-\infty}^{-\tilde{z}} \frac{1}{D + \infty} dz + \int_{-\tilde{z}}^{0} \frac{1}{D} dz + \int_{0}^{+\tilde{z}} \frac{1}{D} dz + \int_{+\tilde{z}}^{+\infty} \frac{1}{D + \infty} dz. \quad (6)$$

The final transfer velocity is inversely proportional to thickness of the boundary layer $\tilde{z}$:

$$k = \frac{D}{\tilde{z}}. \quad (7)$$
2.1 Gas exchange between air and water

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**Figure 4:** Temperature dependence of the equivalent conductivity and solubility Jähne [6].
With a given concentration difference between air and water, the flux will increase if the boundary layer gets thinner. This result can also be obtained if you insert the concentration gradient through the interface \( \frac{\partial c}{\partial z} = \alpha c_a - c_w \) into the equation \( j = -D \frac{\partial c}{\partial z} \). The complete depth path described in the equation (6) also works with individual depth-profiles of \( K(z) \). The sign of \( j \) (the direction of the net flux) is directed towards the concentration difference. Two possible cases are indicated in Figure 3. In case a) the concentration \( c_w \) in water is larger than the equilibrium concentration \( \alpha c_a \). When the net flux is in the direction from the water side to the air side, then Evasion experiment takes place. In case b) the situation is opposite and the relation of the concentrations is \( c_w < \alpha c_a \). In this Invasion experiment the gas diffuses from the air side to the water side.

2.1.8 Important parameters for the gas exchange

![Parameters for gas exchange diagram](http://solas-int.org/resources/downloads/airseaflux.pdf)

Figure 5: Parameters for gas exchange. Source: McGillis [Link](http://solas-int.org/resources/downloads/airseaflux.pdf).

The gas exchange between ocean and atmosphere is influenced by direct and indirect factors. Figure 5 presents a brief overview of different factors. Waves have a big influence on the transfer velocity, because microscale breaking can significantly contribute to the near-surface turbulence. The bubble clouds can break larger waves (whitecaps) and therefore can have a significant effect. On the one hand gas exchange then takes place directly on the bubble surface, on the other hand the bubble clouds produce turbulence by its buoyancy. Both bubbles and small scale waves are strongly
affected by surface films, as this can significantly affects the hydrodynamic conditions. The wave field depends primarily on the wind, not only on the wind speed particularly, but also on the duration and sweep length (fetch) of the wind, and the wind direction. Figure 6 shows measured transfer rates, which are shown as a function of the wind speed. Even mono-molecular surface films have a significant effect on the wave field and thus indirectly on the gas exchange. At the different curves, which were measured with the addition of a surfactant (Triton X100), it can be clearly seen that the wind speed is not the only parameter to describe the transfer speed.

It is experimentally difficult to avoid the presence of surface films. Purified water itself contains some surfactants which over time accumulate into a film on the surface. The surface films in the laboratory experiment may be extracted from time to time with a skimmer (see Section 6.1.5). Through the use of a skimmer the additional turbulence may be generated and the water level in the channel decreases. Therefore, it is not appropriate to use the skimmer continuously. The surface needs to be controlled between skim operations by observation of the wave field. For this purpose, the response of the energy density of the wave field (mean squared slope mss) is measured by an optical method, see Section 6.2.

### 2.1.9 Influence of the choice of the gas exchange model

In the previous sections we limited ourselves with the simplest model for the gas exchange (Film model). There are other alternative models (you can find the description of them in Degreif [2, Chapter 2.5, p. 30ff] or Jähne [6, Chapter 2.3, p. 34ff]). However, models have influence on the Schmidt number scaling, which correlates the transfer velocity of a tracer A to the transfer velocity of another tracer B. For the film model the Schmidt number scaling is:

\[
\frac{k_A}{k_B} = \left( \frac{Sc_A}{Sc_B} \right)^{-1}
\]

, where the Schmidt number is defined as the ratio of the impulse diffusion constant and tracer’s diffusion constant. By the Schmidt number scaling the viscosity is shortened out, such that one gets the ratio of the tracers diffusion in equation (8). For the so-called surface renewal model, in which there are sporadic renewals of the water surface, the Schmidt number scaling is:
By comparison the scales one can see that the Schmidt number exponent is different for both models. Due to the different models the predictions for the transfer velocity by Schmidt number scaling are not equal to each other. It was shown experimentally and theoretically that the film model and the surface renewal model present the boarders between the real conditions [6, Kapitel 2.3, S. 34ff]. The dependence of the effective Schmidt number exponent on measurable properties (e.g. impulse transfer of wind to waves, energy distribution of the waves, turbulent dissipation of the kinetic energy, number and size distribution of bubbles in water) is an open question of current research.

In sum we can say that in this experiment the model representation of the gas exchange has no effect on the direct measurement of the transfer velocity of CO$_2$ (as long as the mass balance is right). For practical reasons, however, substitute tracers are often used, and the appropriate choice of a model is then important for the Schmidt number scaling. Until now there is no model which describes the gas exchange properly and considers all natural occurring conditions. Furthermore one cannot expect to get such a model, since there are many different parameters to consider. In order to test different models under various conditions, the laboratory experiments are need to be carried out.

3 Chemical basics

3.1 Overview of related chemical substances and names

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<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>auch bekannt als</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>Carbon dioxide</td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>Water</td>
<td></td>
</tr>
<tr>
<td>H$_2$CO$_3$</td>
<td>Carbonic acid</td>
<td></td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>Bicarbonate</td>
<td></td>
</tr>
<tr>
<td>H$^+$ (shortcut for: H$_3$O$^+$)</td>
<td>H$^+$-ion</td>
<td>Oxonium-Ion</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>Carbonate ion</td>
<td></td>
</tr>
<tr>
<td>OH$^-$</td>
<td>Hydroxide ion</td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>Hydroxide</td>
<td>Caustic soda</td>
</tr>
</tbody>
</table>

Table 1: Chemical symbols and names

3.2 Notation of the concentrations

In chemistry when it comes to concentration of different substances, it’s common to note it in square brackets. For example, [CO$_2$] denotes the concentration of CO$_2$. To keep the equations simple, in the part of the physical modelling of the exchange process the concentration of CO$_2$ in the air side and water side are noted as $c_a$ and $c_w$ respectively.

3.3 Law of mass action

The relationship between the concentrations of the products (final substances) and starting materials (precursors) of a chemical reaction is known as mass-action law. The law of mass action is:

\[
\text{The product of the concentrations of the final substances, divided by the product of the concentrations of the starting materials is constant in the chemical equilibrium.} [1, Seite 287 ff.]
\]

\[a\]

The encyclopedia [1] can also be found at Wind channel library at number 35.
3.4 \textit{pK-value and pH-value}

An example: The reaction

\[ A + B \overset{K}{\Longleftrightarrow} C + D \quad (10) \]

in equilibrium has a constant ratio of of the concentrations which can be described by

\[ K = \frac{[C] \cdot [D]}{[A] \cdot [B]} \quad (11) \]

, where \( K \) is the stoichiometric (i.e.: volume basis) dissociation constant. The dissociation constant for each chemical reaction is a characteristic constant that does not depend on the amounts and mixing ratios, but changes with the temperature and pressure \([1, \text{Seite 287 ff.}]\). An example of the temperature dependence of one of the major reactions in this experiment is shown in Figure 7.

\[ \text{pK-value and pH-value} \]

The equilibrium states of the chemical reactions can be described by products and quotients of concentrations using the law of mass action (see section 3.3). It is often useful to consider the logarithmic form of the mass action law. The products and quotients in this illustration transform to sums and differences. The negative logarithm of the dissociation constant \( K \) in the above example (equation (11)) is called the pK value:

\[
pK \equiv -\log_{10} K = -\log_{10} \left(\frac{[C] \cdot [D]}{[A] \cdot [B]}\right) = -\log_{10} ([C]) - \log_{10} ([D]) + \log_{10} ([A]) + \log_{10} ([B]) \quad (12)
\]

This is an analogy to the pH value, which is the negative logarithm of \([H^+]\).
The natural pH: water reacts with itself and form ions (autoprotolysis)

\[ H_2O + H_2O \leftrightarrow H^+ + OH^- \],

where \( H^+ \) is an abbreviation for \( H_3O^+ \). To the concentrations of ions in pure water:

\[ [H^+] \cdot [OH^-] = \text{konstant} = K_w \approx 1 \cdot 10^{-14} \text{mol}^2/\text{l}^2. \]

Therefore the \( pK_w \) value equals to \(- \log_{10}(10^{-14}) = 14\). The natural pH value occurs when the water is totally uncharged, i.e. when \([H^+] = [OH^-]\). The charge-neutral case can be written as \( pK = \text{pH} - \log_{10}[OH^-] = 2 \cdot \text{pH}\). This is the neutral case with pH value being equal to 7 (neutral pH). A solution with a pH < 7 is called as an acidic solution, for pH > 7 — alkaline solution.

### 3.5 Carbonate system

In the ocean carbon exists in three different organic forms. First one is a gas \( \text{CO}_2(\text{aq}) \) dissolved in water. Second one is hydrogen carbonate \( \text{HCO}_3^- \). And third one is carbonate ion \( \text{CO}_3^{2-} \).

The fourth form, namely the charge-neutral carbonated \( \text{H}_2\text{CO}_3 \), exists only in very small concentrations \( \frac{[\text{H}_2\text{CO}_3]}{[\text{CO}_2(\text{aq})]} \lesssim 0.3\% \). Here and for following the equations we note the sum of neutrally charged forms \( \text{CO}_2(\text{aq}) \) and \( \text{H}_2\text{CO}_3 \) as \( \text{CO}_2 \):

\[ [\text{CO}_2] \equiv [\text{CO}_2(\text{aq})] + [\text{H}_2\text{CO}_3]. \]

The equilibrium of carbonate system in water can be described as:

\[ \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons K_1 \text{HCO}_3^- + \text{H}^+ \overset{K_2}{\rightleftharpoons} \text{CO}_3^{2-} + 2 \text{H}^+ \]

It depends on the equilibrium condition only (not on the reaction path). Constants \( K_1 \) and \( K_2 \) in the equilibrium are the first and second dissociation constants for carbonic acid. The dissociation constants are [6, S. 68]:

![Figure 8: The percentage of the different inorganic carbon species CO2CO3^- and HCO3 as a function of pH value. Source: [9]](image-url)
3.6 Deionized water and sea-model water

Deionized water and sea-model water

For practical reasons, the gas exchange experiments are often carried out with deionized water. This so-called DI water has an advantage of lower level of calcification in the wind tunnel. Furthermore, the conductivity method for measuring the concentration of CO\textsubscript{2} in water (see Section 4.1) can only be performed initially with deionized water. When using deionized water, the gassing with CO\textsubscript{2} results in relatively low pH values, which is why, the water is always acid. The ocean, however, is slightly alkaline (pH = 8.2 ± 0.3 \cite{9}) and is rich of ions. One may of course ask whether the alkalinity and the presence of additional ions have a significant impact on the exchange rate of CO\textsubscript{2}. When CO\textsubscript{2} dissolves in sea water, [CO\textsubscript{2}\textsuperscript{−}] changes only slightly, since the system is buffered by CO\textsubscript{3}\textsuperscript{2−} ion. This influence can be modelled in practical experiment by adding to DI water the sodium hydroxide (NaOH) (about 10\textsuperscript{−4} mol/l for the facility we use). This solution will be called the sea-water model. Of course, the composition of our sea-water model is entirely different from real sea water, but at least the charge balance (see below) is in close reality.

3.6.1 Charge conservation

In addition to the mass action law, the charge balances play a crucial role. The charge balances are different for pure deionized water and the sea-water model.

**DI-Wasser:** According to the charge balance equation, the total charge of all ions supposed to be constant. In the deionized water there are no other ions except H\textsuperscript{+}, OH\textsuperscript{−}, HCO\textsubscript{3}\textsuperscript{−} and CO\textsubscript{3}\textsuperscript{2−}, therefore the charge conservation is:

\[
[H^{+}] = [OH^{-}] + [HCO_{3}^{-}] + [CO_{3}^{2-}] \quad \text{(19)}
\]

In acid case with pH < 7 this equation is simplified by negligible concentration of OH and CO\textsubscript{3}\textsuperscript{2−} (i.e. in acidic case) to:

\[
[H^{+}] = [HCO_{3}^{-}] \quad \text{for pH < 7} \quad \text{(20)}
\]

With this approximation and equation (17) it follows that the concentration of CO\textsubscript{2} is directly proportional to the square of the H\textsuperscript{+} concentration.

**Sea water model:** With approximately 10\textsuperscript{−4} moles of NaOH solution the charge conversation changes:

\[
[Na^{+}] + [H^{+}] = [HCO_{3}^{-}] + [OH^{-}] + \frac{1}{2} [CO_{3}^{2-}] \quad \text{(21)}
\]
Over a wide pH range, the concentration of \([\text{Na}^+]\) is considered to be constant, [14, S. 29]. In the alkaline solution, the excess of \(\text{OH}^-\) ions (from the NaOH adding) during the gassing of \(\text{CO}_2\) is converted to \(\text{HCO}_3^-\) ions [14, S. 96]. The gassing corresponds to a titration of NaOH solution with the weak acid \(\text{CO}_2\). The pH value decreases during the gassing and therefore simplifies the charge balance equation:

\[
[\text{Na}^+] = [\text{HCO}_3^-] \quad \text{for} \quad 6 \lesssim \text{pH} \lesssim 8
\]  

(22)

so \([\text{HCO}_3^-] \gg [\text{CO}_2] > [\text{CO}_2^-]\) (see Figure 8) and \([\text{Na}^+] \approx 10^{-4}\) molar \(\gg [\text{H}^+]\). Substituting (22) into (17):

\[
[\text{CO}_2] = \frac{1}{K_1} [\text{Na}^+] \cdot [\text{H}^+] \quad \text{in sea water model,}
\]  

(23)

i.e. that the sea-water model, the carbon dioxide concentration is directly proportional to \([\text{H}^+]\).

### 4 Methods for determination of \(\text{CO}_2\) concentration

#### 4.1 Conductivity method

For the gas exchange experiment with deionized water the conductivity method can be used. We take into account, that deionized water has negligible residual conductivity. The concentration of \(\text{CO}_2\) can be calculated by measuring the conductivity which is proportional to \(c_1^{1/2}\). It can be proved from chemical equilibrium equation:

\[
[\text{HCO}_3^-] \cdot [\text{H}^+] = K_1 \cdot [\text{CO}_2]
\]  

(24)

(see equation (18)) and the charge balance equation:

\[
[\text{H}^+] \cong [\text{HCO}_3^-],
\]  

(25)

at pH \(\lesssim 5.5\), i.e. considered here for the \(\text{CO}_2\) concentrations. The conductivity \(\Lambda\) is proportional to \([\text{H}^+]\) and from (24) and (25) follow the above-mentioned relation

\[
\Lambda \propto [\text{CO}_2]^{1/2}.
\]  

(26)

In deionized water, and for relatively high concentrations of \(\text{CO}_2\), the amount of bicarbonate ions (\(\text{HCO}_3^-\)), and carbonate ions (\(\text{CO}_2^-\)) with respect to the physically dissolved \(\text{CO}_2\) is negligible and therefore can be ignored for determining the transfer velocity.

The equivalent conductivity of \(\text{CO}_2\) is dependent on temperature, as shown in Figure 4 and 7 (right).

Equation (25) is not valid for the sea-water model case (with sodium hydroxide solution, see Section 3.6), as the concentrations of other ions (here: \([\text{Na}^+]\)) is large and can significantly contribute to the conductivity. The conductivity method can’t be easily applied to acids or bases [6, S. 73 ff.] and therefore is not used in the second part of the experiment. An alternative method uses the pH indicators. This will be explained in the following section.

#### 4.2 pH-indicator method

The pH value of the water can be measured using indicator dyes. With changes of the \(\text{CO}_2\) concentration in the water the pH value is changing as well, see Section 3.5. Therefore pH indicators can be used to measure the \(\text{CO}_2\) concentration.
4.2 pH-indicator method

Indicator dyes have the property of easily absorbing or releasing H\(^+\) ions and moreover changing their color. Here we denote the indicator molecule as HI. After the release of an ion H\(^+\), the indicator molecule is a negative ion I\(^-\). The balance of a highly dilute indicator solution:

\[
HI + H_2O \xrightleftharpoons{K_I} I^- + H^+ \tag{27}
\]
is described by the pK value of the indicator

\[
pK_I = -\log_{10} \left( \frac{[I^-] \cdot [H^+]}{[HI]} \right), \tag{28}
\]
and respectively

\[
K_I = \frac{[I^-] \cdot [H^+]}{[HI]}. \tag{29}
\]

To illustrate the use of the dye features, we consider an example, where molecules HI appear blue and molecules I\(^-\) yellow. The color of the solution of the indicator in the water depends on the ratio of concentrations of blue and yellow molecules, so depends on \([I^-]/[HI]\). The buffer point of the indicator is the condition when this ratio is equal to one, so these species have equal concentration:

\[
[HI] = [I^-] \quad \text{at buffer point}, \tag{30}
\]
and the solution in our example is getting green. Joining the equations (30) and (28), one can get:

\[
pK_I = -\log_{10} \left( \frac{[I^-] \cdot [H^+]}{[HI]} \right) = \text{pH} \quad \text{at buffer point}, \tag{31}
\]
, so at the buffer point the pH value is equal to pK\(_I\) value. When the pH value is smaller than pK value (it means there are more H\(^+\) ions), then the ratio \([I^-]/[HI]\) is getting smaller, so the blue HI molecules are dominant. When the pH value is larger than pK value there is the opposite case: the solution becomes yellow with large amount of I\(^-\) molecules.

This color example was chosen randomly. In general the absorption spectra of the HI molecules and I molecules differ in a defined manner. By absorption spectroscopy (Section 4.2.1) the ratio \([I^-]/[HI]\) can be determined, and thus the pH value as well.

The relationship between pH value and CO\(_2\) concentration is dependent on the composition of the water. Moreover, the indicator should be selected such that the pK value is closed to the pH value, so the measurement is sensitive to \([I^-]/[HI]\) change. This explains why in the different parts of the experiment different dyes are used. We distinguish the following two cases again, firstly, the deionized water model, and secondly, the sea-water model.

1. **Deionized water model:** The relation between the pH value and CO\(_2\) concentration for deionized water was discussed in the Section 4.1 for the conductivity method. In the deionized water the charge conversation law takes place \([HCO_3^-] = [H^+]\) (equation (25)). From the equations (16) and (29) follows:

\[
[CO_2] = \frac{[H^+]^2}{K_1} = \frac{K_2 \cdot [HI]}{K_1} \left(\frac{[HI]}{[I^-]}\right)^2, \tag{32}
\]

2. **Sea-water model:** The charge conversation in sea water model is \([Na^+] = [HCO_3^-]\) (see equation (22) and equation (23)):

\[
[CO_2] = \frac{K_2}{K_1} \cdot [Na^+] \cdot \frac{[HI]}{[I^-]} , \tag{33}
\]
, where \([Na^+]\) is assumed to be constant here.
4.2.1 Absorption spectroscopy with pH-indicator

In the previous section we discussed qualitatively how the color of an indicator dye solution may change by the pH value. The color change is achieved as a result of the fact that the indicator molecules HI and I⁻ have different absorption properties and by the pH value of the mixture their ratio is changed. To shorten the following equations we note the concentrations as following \([\text{HI}] \equiv c_1\) and \([\text{I}^-] \equiv c_2\). We know that \(c_1\) can increase only if \(c_2\) decreases as the total amount of the indicator is constant. In other words:

\[
c_1(t) + c_2(t) = c = \text{constant},
\]

so we can write \(c_2(t) = c - c_1(t)\) and vice versa.

Let us now consider the case of a strong acidic solution (pH \(\ll pK_1\)), which contains only HI molecules. Let \(\alpha_1 = \epsilon_1(\lambda) \cdot c_1\) be an absorption coefficient of HI, where \(\epsilon\) is the substance-specific molar natural extinction coefficient. After a fixed absorption path \(x\) in the solution, the irradiated spectrum \(I_0(\lambda)\) weakens according to the Lambert-Beer law:

\[
I(\lambda)_{\text{sauer}} = I_0(\lambda) \exp(-\alpha_1(\lambda) x) = I_0(\lambda) \exp(-\epsilon_1(\lambda) c_1 x) = I_0(\lambda) \exp(-\epsilon_1(\lambda) c x),
\]

where in the last step, the equation (34) is used and \(c_2 = 0\). In the second case, we consider a strong alkaline solution (pH \(\gg pK_1\)), where only I⁻ molecules contribute to the absorption with absorption coefficient \(\alpha_2 = \epsilon_2(\lambda) \cdot c_2\). The spectrum after a fixed path will be:

\[
I(\lambda)_{\text{alkalisch}} = I_0(\lambda) \exp(-\alpha_2(\lambda) x) = I_0(\lambda) \exp(-\epsilon_2(\lambda) c_2 x) = I_0(\lambda) \exp(-\epsilon_2(\lambda) c x),
\]

again with equation (34) and \(c_1 = 0\). During the experiment, the mixing ratio will change in time. The spectrum is therefore also time dependent:

\[
I(\lambda, t) = I_0(\lambda) \exp[-\epsilon_1(\lambda) c_1(t) x] \cdot \exp[-\epsilon_2(\lambda) c_2(t) x] = I_0(\lambda) \exp[-(\epsilon_1 c_1 + \epsilon_2 c_2) x].
\]

If we measure spectra \(I(\lambda)_{\text{alkaline}}\) and \(I(\lambda)_{\text{acidic}}\) at certain time points, we can for any time period of the experiment and for (almost) each wavelength \(\lambda\) calculate the following ratio:

\[
\frac{\ln(I_{\text{sauer}}) - \ln(I_{\text{alkalisch}})}{-\ln(I(t)) + \ln(I_{\text{sauer}})} = \frac{c_1}{c_2}.
\]

With the equation (34) we can calculate the desired ratio:

\[
\frac{[\text{HI}]}{[\text{I}^-]} = \frac{c_1}{c_2} - 1.
\]

With equations (32) for distilled water or (33) for the seawater model, the temporal behaviour of the CO₂ concentration in the water can be determined without explicit determination of \(I_0(\lambda), \epsilon_1, \epsilon_2, c\) or pH value.

In this experiment we use a digital spectrometer. It generally has a non-zero offset. Therefore, the dark spectrum needs to be measured and subtracted from all other spectra. The equations from (35) to (38) are valid for \(I = I_0 \cdot \exp(\ldots)\) and not for \(I = I_0 \cdot \exp(\ldots) + I_{\text{dark}}\). So you need to subtract the dark spectrum \(I_{\text{dark}}\) first.
Strictly speaking, the CO$_2$ concentration is determined by the foregoing constant factor. The factor is determined by the dissociation constant, and therefore a function of temperature (see for example Figure 7). Therefore it is difficult to specify the factors in the equations (32) and (33) precisely in order to determine absolute concentrations. However, this is not a particular problem, as long as the temperature varies only slightly during the experiment, then the factor is not a time-dependent quantity. In the following Section 5 we will see that in order to determine the transfer rate the temporal behaviour of the CO$_2$ concentration is sufficient to know (knowing their absolute value is not necessary).

5 Mass balance for determination of transfer velocity

To determine the transfer velocity the mass balance needs to be taken into account. In the mass balance for this experiment the mass flux of CO$_2$ between the air side and the water side of the channel is considered with the flushing of the air side with CO$_2$ free air. The fluxes will be modelled in following by a Box model. Hence there is a simple relation between the transfer velocity and time changes in CO$_2$ concentration in water.

5.1 Box model for evasion experiment with high flush rate

![Box model](image)

Figure 9: Box model of the gas exchange.

The wind channel consist of two boxes, see Figure 9. The first box is the water tank with volume $V_w$ and gas concentration $c_w$. The second box is the air space with volume $V_a$ and gas concentration $c_a$. Both boxes get in contact with each other by the water surface $A$. Within the boxes, the concentration is a constant over spatial dimension. That means that we consider that inside the air and water boxes everything is well mixed by turbulence processes. The water-side concentration of dissolved gases is changing only by gas exchange through the water surface. We want to use mass balance as easy as possible and consider just a special case. The coupled differential equations for the time variation of the concentrations in the general case can be found for example in Jaehne [6, Seite 59 ff.].

Here we consider the case of a so-called evasion experiments. So before the start of the experiment, the water is gassed with CO$_2$ and the airspace is free of CO$_2$. The net gas flow during the experiment therefore takes place from the water into the air side (evasion experiment). The airspace is flushed with CO$_2$-free air during the whole experiment. When the flush rate $V_a$ is sufficiently large, the temporal concentration increase in the air is negligible. Since we are flushing with CO$_2$-free air, the air concentration remains always small enough to provide a condition far from the equilibrium concentration, i.e. it is always

$$c_w \gg \alpha \cdot c_a,$$

(40)
where $\alpha$ is a solubility of CO$_2$ in water (see Section 2.1.5).

Under the above mentioned assumption the coupled differential equations are reduced to a simple
differential equation for the concentration in the water. The mass flow through the surface is:

$$V_w \cdot \dot{c}_w = k \cdot A \cdot (\alpha \cdot c_a - c_w),$$

(41)

where $k$ is a transfer velocity (see Section 2.1.6). With the equation (40) this further simplifies to:

$$\dot{c}_w = -k \cdot \frac{A}{V_w} \cdot c_w = -k \frac{h_{\text{eff}}}{c_w},$$

(42)

with the solution:

$$c_w(t) = c_w(0) \cdot \exp \left( -k \frac{h_{\text{eff}}}{t} \right)$$

(43)

The effective water level $h_{\text{eff}} = \frac{V_w}{A}$ can be different from the filling level in the water gutter of the
channel, for example, the volume of water in the pipes is also involved in the gas exchange and with
respect to the volume in the channel is not negligible. While $h_{\text{eff}}$ is not dependent on the time, the
transfer speed $k$ can be determined by the slope of the line in the graph $\ln(c)$ against $t$. An advantage
of this method is that it sufficient to measure the concentration $c$ only in relative units.

6 Experimental set-up

6.1 The small circular wind-wave channel

The experiment is carried out in a ring-shaped wind-wave channel with a diameter of one meter. The
channel consists of a stainless steel, which is filled with water and has a closed air volume.

6.1.1 Water gutter

The picture of water gutter is on the first page of this instruction. The water channel is annular with
an external radius of 30 cm and a width of 10 cm. The channel is about 10 cm deep and should be
filled to about 8 cm of water. The volume of water in the channel is approximately 12.6 liters. For
the experiments deionized water from the usual (house) pipe is used, which is additionally processed
with an ion exchange, and ideally has a residual conductivity of less than 0.05 $\mu$S/cm. The filling
level of the water gutter is determined during the experiment by means of a pressure sensor from the
hydrostatic pressure.

6.1.2 Air side

The volume of the air side is about 150 l. It’s flushed through the tubing system operated by flow
controllers with CO$_2$ free air by pure-airgenerator ([CO$_2$] $< 50$ ppm), see Figure 11 with known flow
rate (approximately 10 Liter/min). To equalize the pressure, air can escape again through a small
hole. By permanent flushing the air space of the channel the pressure is relative to the environment in
a slight overpressure, which prevents the air influx to be polluted with CO$_2$ or dust. CO$_2$ concentration
and temperature in the air space of the channel can be measured using commercial probes.

6.1.3 Wind generator

Four motorized rotor blades (wind-paddle) are used as wind generator, they cause circling of the air
in a horizontal direction. The wind speed can be controlled via the motor’s power. The wind speed
hardly depends on the distance to the water surface, and is therefore measured at (relatively arbitrarily
chosen) referent distance from the water surface by paddle anemometer.
6.1 The small circular wind-wave channel

Figure 10: Arrangement of some components of the experimental set up.
6 EXPERIMENTAL SET-UP

6.1.4 Gassing

Since we perform evasion experiments, a fairly high concentration of CO\textsubscript{2} is added to the water at the beginning of each experiment. This is done with an oxygenator connected to a CO\textsubscript{2} gas bottle. An oxygenator is an artificial lung, and it is usually used in medicine. Inside there is a membrane with very high surface area, which in our case separates the gas from water. On the gas side of the membrane (in our case with 100\% of CO\textsubscript{2}) an overpressure is applied. Water is pumped with a pump P2 along the other side of the membrane and absorbs CO\textsubscript{2}, which experiences little resistance across the membrane. Using a flow controller the flow rate of 60 millilitres per minute is set up. This volume flow is based on 1 bar pressure and temperature of 21 degrees C. The flow rate and the duration of the gassing can (and should) determine the number of moles that you aerate the water with. The flow controller supposed to be plugged in only during the gassing process, as the device without the presence of air pressure may be damaged.

6.1.5 Skimmer

Surface films have a strong influence on the wave field and thus indirectly on the gas exchange. In order to make the surface free of films, the skimmer need to be used. The skimmer is a suction device...
6.1 The small circular wind-wave channel

Figure 13: Circulation of the water (blue = Facility, rot = Bypass).

Figure 14: The absorption spectrometer.

with the possibility to suck out the water from the surface, as shown in Figure 12 a). To skim the surface, the skimmer is moved up such that the water in the small channel can only flow from the wind-facing side. One needs to hold the clamping holder from underneath the channel and push up the skimmer. Then turn the clamping holder again carefully to prevent damaging the seal and the thread of the facility. Do not hold the skimmer with the metal pipe, otherwise the fat from your skin can get into the water during next skimming process. Then the pump P3 is switched on and the valve is opened (in the tubing between the pump and the drain). After using the skimmer, it should be lowered back to the channel bottom and the valve between the pump P3 and outflow must be switched off (otherwise the channel will gradually leak though this way).

6.1.6 Water circulation

The water cycle is divided into the channel groove and attached pipe and tube system, see Figure 13. To gas the water the circulation goes through the oxygenator by using the pump P1, see section 6.1.4. In another circuit, operated by pump P2, the water is pumped through the spectrometer system and the conductivity sensor. For cleaning the surface of the water a skimmer is provided which is operated with a pump P3, see section 6.1.5.

6.1.7 Effective water height

As it was explained in the section 5.1, part of the water that takes part in gas exchange is in the pipe tubes. Therefore

\[ h_{\text{eff}} = \frac{\text{Volume in the pipes}}{\text{Volume of water gitter}} + \text{measured high level}. \]

(44)
The ratio of the volume in the tubing to the volume of water in the channel is [5]:

\[
\frac{\text{Volume in the pipes}}{\text{Volume of water gittet}} = 6.89 \pm 0.04 \text{ mm},
\]

when only pump P2 is operated, i.e. during Evasions experiments. Even with having only pump P2 working, circulation of the water in the lines of the gassing cycle also takes place because gassing and spectrometer circuit are interconnected. Therefore, the offset doesn’t increase significant if you forget to turn off the pump P1 during evasions experiment. The ratio from equation (45) with both pumps operating is \(7.1 \pm 0.2 \text{ mm} [5]\).

6.1.8 Injection

The injections of the indicator dyes as well as sodium hydroxide solution are made with syringes. Please ask your supervisor where and how the solutions can be injected.

6.1.9 Absorption spectrometer

The spectrometer is in the black-and-white box on the practical workplace and consists of a constant-current-powered LED, an 80 cm long glass tube with optical access from both sides and a commercial Spectrometer \(^2\), see Figure 14. The glass tube is slightly inclined, so that no air bubbles remain in the tube when the spectrometer pump draws air. If you still have this problem (look in the box, especially when it is unexpectedly dark in the spectrum figure), please contact your supervisor.

6.2 Wave slope measurements

The wave field in the wind tunnel is statistically recorded through so-called Laser Slope Gauge (LSG). The LSG consists of a laser, which is directed perpendicularly to the water surface, as well as a lens, focusing screen and camera below the channel, see Figure 15. At the surface the laser beam is deflected according to refraction Snell’s law. The angle of deflection is a function of the wave slope at one point. Through a window in the bottom of the channel, the deflected beam passes back into the air where it is imaged by a lens onto the screen. The position of the lens and the focusing screen is telecentric, so the focusing screen is exactly in the focal plane of the lens. Thus there is a clear relationship between the beam angle before the lens and the position of the point on the screen. The position on the screen is captured by a camera. So having the pixel position \([x, y]\)^T of the laser dot in the camera image, the wave slope \([s_x, s_y]^T = [\frac{\partial}{\partial x}, \frac{\partial}{\partial y}]^T h\) can be obtained, where \(h\) is the surface height at the position of the laser. Because of the telecentric arrangement of focusing screen and lens, the relationship is independent of the wave height, as shown in Figure 15 a. The conversion of beam deflection (in units of pixels) into the wave slope (unit in percentage) is performed using a calibration curve as was measured by Weber [13].

One of the easiest parameters to characterize the small-scale wave field is the mean square slope, short mss. The mean square slope is the sum of the variances of the two slope components. The variances are calculated in this case with time averaging, i.e.:

\[
mss = (s_x - \bar{s}_x)^2 + (s_y - \bar{s}_y)^2.
\]

It can be shown that the energy density of small-scale waves (capillary waves) is directly proportional to the mean squared gradient [8, S. 37–39]. The energy in the wave field can, for a given wind speed, be strongly influenced by surface films. A reduction over time of \(mss\) at constant wind speed is therefore an indication of the accumulation of surface-active substances on the water surface that form a film.

\(^2\)Ocean Optics USB2000
7 Questions

- What is the transfer velocity?
- How does the tracer gas go from the air side to the water side, or reverse? What is the role of turbulence and diffusion?
- How thick is the boundary layer between ocean and atmosphere under normal conditions?
- What factors influence on the turbulence close to the surface?
- How does the gas exchange differ in the presence of mono-molecular surfactant on the water?
- What is the Box model and what assumptions in the mass balance equation are made in this experiment?
- How can one obtain the transfer velocity from measuring the relative changes of gas concentration in the water side?
- How is it possible to neglect the air side tracer concentration?
- What parameters does the tracer conductivity depend on?
  - How important is that the following variables are constant during the gas exchange measurement?
1. temperature
2. water height in the channel ring
3. surface condition and wave roughness
4. air pressure
5. conditions of illumination
6. pH value

- What does autoprotolysis of water mean? What is the law of mass action?
- What happens with CO\textnormal{2} in water? Please explain Figure 8.
- What kind of water is used in the experiment? What is the difference from normal everyday-in-use water? Why do you still have a small conductivity of water used in the experiment?
- What is the equivalent conductivity? What ion has the highest equivalent conductivity? Do you have a clear explanation for this?
- What is the principle functionality of the absorption spectroscopy?
- What is a pH indicator? Do you know an example? Explain the term buffer point.
- Why are the different indicators used for the two parts of experiment?

8 Realization of the experiment

The experiment is divided in two parts. For both cases the CO\textnormal{2} transfer velocity is calculated. The first part is accomplished with clear water, in the second part sea-model water (described in Section 3.6) is used. You can find the experimental procedures in the following table.

You can start the experiment only if you were briefly informed about the general safety rules by your supervisor.

Your supervisor will show you what water taps and in which sequence need to be used to fill in or empty the channel. Be aware that if the taps and the valves operate in a wrong way, there is a risk you interfere with other experiments in the laboratory.

The supervisor will discuss with you all instruments in use and explain the data acquisition for the PC. It is done using the software Heurisko. The recording of the absorption spectra, wind speed, air temperature, water temperature, filling level, the CO\textnormal{2} concentrations in air, the wave slope, the air pressure and the conductivity is done using Heurisko-Skripts\textsuperscript{3}. The measurements are taken every 8 seconds (approximately). If you have questions regarding the Data recording your supervisor will be happy to help you.

The computer does all the work of the data tracking. The data points will receive a serial number (line number in the spectrometer image or first column in the output window and in the tabular output file). Your measurement protocol must necessarily note the time periods in which you perform operations during the experiment. It is recommended to write down the appropriate lines numbers.

8.1 Experimental procedures

The procedure is almost identical for both parts, please pay attention to the differences in the following table

\textsuperscript{3}Windm\textsuperscript{1}hle_Messung.ws
8.1 Experimental procedures

<table>
<thead>
<tr>
<th>Part 1 with Deionized water</th>
<th>Part 2 with Sea model water</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. The diode of the spectrometer is turned on with the flip switch at the power strip.</td>
<td></td>
</tr>
<tr>
<td>2. The pump for the skimmer and the bypass are closed. The skimmer is lowered and the water inlet to the channel is opened.</td>
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</tr>
<tr>
<td>3. Fresh water from the ion exchange needs to fill the channel till the filling level 8 cm (2 lines from the top). Your supervisor will show you what valve is supposed to be closed/opened. To be able to remove residual water and impurities in pipelines (bypass 1 and 2) from previous experiments, one should briefly open the bypasses during the filling processes. When the water level is about 4 cm, the conductivity measuring device can be turned on and tested together with the pump P2 to check whether the conductivity falls below 0.5 µS/cm. If this is not the case, one should drain off the water and fill it in again. This is needed when there are too many impurities in the tube system. CAUTION: It is important to turn off all the pumps before draining the water, so that no air is drawn into the spectrometer circuit.</td>
<td></td>
</tr>
<tr>
<td>4. Check that there are no air bubbles in the cuvette of the spectrometer or in the conductivity sensor. By switching the pumps P1 and P2 on and off, the air bubbles can be removed from most of the circuits. Tip: if only pump P2 is running the flow direction twirls around the spectrometer circuit. The conductivity probe should be lifted in order to get rid of the air bubbles in the pipes. Please ask your supervisor if the air bubbles can not be removed from the system. During further measurements the pump P2 should remain switched on continuously. Pump P1, however, should only be used during the gassing the water.</td>
<td></td>
</tr>
<tr>
<td>5. Open a Heurisko (Version 6.5.0), load the Workspace &quot;'Windmuehle_Messung.ws'&quot; and run it with the combination of STRG+R. By the program all the sensors will be read automatically and the data will be displayed in the output window. Make sure that all the sensors are working properly (firstly, that they are switched on and powered). Once data collection is started (next point), the window reacts slowly, as the program is occupied with the recording and preprocessing of data. Do not act too hectic with the windows, otherwise you risk a crash.</td>
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</tr>
<tr>
<td>6. The actual measurement can now be started by writing &quot;measure()&quot; in the command window of Heurisko and confirming with pressing ENTER button.</td>
<td></td>
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<tr>
<td>7. You need to record at least 5 lamp spectra with constant intensity without any dye.</td>
<td></td>
</tr>
<tr>
<td>8. For the sea-model water one need to add 2.5 ml of 1-mol of sodium hydroxide (NaOH) with a syringe.</td>
<td></td>
</tr>
<tr>
<td>9. Add indicator: 8 ml Bromocresol green-solution 0.8 ml Bromocresol purple-solution Is added by syringe. After that you need to wait until the water is well mixed. This can be recognized on real-time plot of the absorption spectrometer &quot;ispec&quot;. For more rapid mixing, the wind can be turned on (&lt;= 6 m/s). Note the start and end points of the injection. After adequate mixing the wind is turned off and wait until there are no waves and the water surface is smooth.</td>
<td></td>
</tr>
</tbody>
</table>
8 REALIZATION OF THE EXPERIMENT

<table>
<thead>
<tr>
<th>Part 1 with Deionized water</th>
<th>Part 2 with Sea model water</th>
</tr>
</thead>
<tbody>
<tr>
<td>10a) Start with the gassing the water. Plug the power supply for the flux controller Analyt-MTC into the socket. Turn on the pump P1. Then, turn on the main valve of the gas cylinder. Then turn on the silver valve. From this time point the gas flows through the flow controller into the oxygenator. Note the start time. The volume flow is controlled by the flow controller with rate 60 milliliters / minute. Check and record the volume flow. The pressure in the tube before the flow controller should be set up from 1 to 1.5 bar overpressure. This value can be read at the right pressure indication of the gas cylinder controller. In addition, the gas pressure is measured with a manometer and recorded automatically by the computer. (To be able to regulate the pressure, rotate the brass tap in the middle of the pressure regulator. The value will change only when gas is flowing.) (Continued 10 b))</td>
<td></td>
</tr>
<tr>
<td>10b) The conductivity initially rises fast and then rise slowly. At a conductivity of 8 $\mu$S/cm the process of gassing the water is completed.</td>
<td></td>
</tr>
<tr>
<td>The conductivity first drops quickly and then remains constant. Note the time interval from the start to the end of the gassing the water (the fast decrease of the conductivity). Then twice this time interval further is gas flushed. After this time, you should stop gassing the water.</td>
<td></td>
</tr>
<tr>
<td>Turn off the pump P1. Close the silver valve. Open the valve for a short time in the hose connection between the gas cylinder and flow controller until the moment, when the gas flow to the oxygenerator stops. Note this time. Also, connect the gas cylinder valve. Disconnect the power supply of the flow controller Analyt-MTC.</td>
<td></td>
</tr>
<tr>
<td>11 The wind is turned on and set to the desired wind speed value. The Evasion measurement begins:</td>
<td></td>
</tr>
<tr>
<td>1. Watch the timing of the spectrum and the conductivity sensor to decide how long you need to measure. The conductivity decreases steadily. If the conductivity value has dropped to approximately one quarter of the maximum value, then the Evasion measurement is completed.</td>
<td></td>
</tr>
<tr>
<td>1. Watch the timing of the spectrum, in order to decide how long you need to measure.</td>
<td></td>
</tr>
<tr>
<td>2. Observe the time profile of $mss$. During the experiment the surface films are formed. This reduces the energy and momentum input from the wind into the wave field, and as a result also reduces the transfer velocity. To measure the transfer speed at clean water surface, the skimmer should be used. This should be made at least once during the measurement, so you can see the difference in transfer process with and without the film.</td>
<td></td>
</tr>
<tr>
<td>3. Note the time points when you change something during the experiment, in particular, the time intervals for each skim process.</td>
<td></td>
</tr>
</tbody>
</table>
Part 1 with Deionized water

12 To determine a reference spectrum in the acid conditions, insert into the channel from 2 to 3.5 ml of the 1 molar hydrochloric acid (HCl) by using a small syringe. Wait until the spectrum does not change (view profiles of the spectral images). By further increasing the amount of HCl you can check if the spectrum changes. If that takes place, then the pH value dropped even further. The solution is not acidic enough. You need to continue adding HCl, but the total amount should not exceed 7 ml of a 1 molar solution. Write down each amount and timing of all additions. Note the time period, which is suitable for averaging (20 measurements) of the acidic reference spectrum.

Part 2 with Sea model water

13 Add from 5.2 to 5.5 ml of 1 molar sodium hydroxide (NaOH) using a small syringe in order to determine a corresponding alkaline reference spectrum. The amount of NaOH should be at least equal to the total amount of your HCl added previously. The pH-value of the water may be even smaller than pH-value before the addition of HCl as the $pK_i$ value of the indicator (depending on the remaining concentration of CO$_2$ at the end of the experiment). Again, you should test whether the indicator provides an appropriate reference spectrum (see previous point). Note the time period, which is suitable for the average value (20 measurements) of alkaline reference spectrum.

14 Turn off the diode for at least 5 measurements in order to record the dark spectra.

15 Then you can stop the measurement in Heurisko by pressing F4. The measured data are automatically saved in the folder “D:\Messungen\”. Write down the file name of your measurement that has been generated from the date and time of the measurements.

16 Remove the water through the outlet of the water channel and refill the channel again for cleaning purposes. During this procedure turn on the pump, but only if there is at least 4 cm water in the channel. Turn off the pump when the water level is going to be less than 4 cm, so that no air is drawn into the spectrometer circuit.

9 Data analysis

- Before the evaluation you should make sure you’ve saved your data once.
- The evaluation of the two parts of the experiment is done with the PC.
- All time profiles (wind, temperature, CO$_2$ concentration of the air side, ...) should be plotted. (Tip: You can use the measurement numbers instead of time in seconds, it simplifies the processing of the spectra).
- Indicate the time characteristics (time point or periods in which the gassing of the water took place, was the actual experiment started, reference spectrum was taken or skimming was used, etc.)
- Estimate the initial CO$_2$ concentration $c_0$ from the beginning of evasion experiment by using the duration, pressure and flow rate of the fumigation.
- Answer the question "At what time point during evasion experiment the inequality $c_a \ll c_{w}/\alpha$ is fulfilled for the Box model?". Consider the information at this time period to calculate the transfer velocity.
  - To answer the question, take $\Lambda^2 \propto c_{w}$ for deionized water or $\frac{[\text{H}]}{[\text{I}]} \propto c_{w}$ for sea-model-water. Think through how you can calculate the water side CO$_2$ concentration at each time
point of two evasion experiments using estimated above the initial concentration \( c_0 \). Plot the graph with \( c_w/\alpha \) dependent on time joint diagram with the air side measured absolute concentration \( c_a \) (in the same units, of course). If you make the y-axis logarithmic, you can take the distance between the curves as a direct answer to a question mentioned above (what time period to consider for transfer velocity calculation).

- For the deionized water model the transfer velocity \( k \) can be estimated from conductivity measurements. Note the time periods for which you do the fit. If the curve of conductivity measurement has kinks, you should average over the number of shorter time periods. Determine for the corresponding time ranges the mean values and standard deviations of the water level, the mean square slope \( mss \), wind speed and all the other variables that you think are important for the interpretation of the data.

- The preliminary analysis of the spectra of the pH−indicator method is done with the script Heurisko Windmuhle_Auswertung_Studenten.ws. The time ranges for the averaging of reference spectra (dark spectrum, lamp spectrum, acid spectrum, alkaline spectrum) can be specified at the beginning of the script according to your measurements. The procedure is explained step by step in the script. If you have any doubt, consult your supervisor. Get an idea of the quality of the data and select one or more appropriate wavelength ranges from the averaged \([HI]/[I−]\). For each script processing you will get the result in the form of several text tables, you can now proceed the data like the conductivity evaluation with a program of your own choice. Save or Print the plot of the reference spectra and the absorbance spectra. Note the selected time ranges and wavelength bins.

- Determine from the behaviour of \([HI]/[I−]\) the transfer velocity for different periods of evasions experiments, by analogy to the above described procedure for the evaluation of conductivity method. Consider the different relationships between the pH and the concentration of \( CO_2 \) for the two parts of the experiment.

- Determine the measurement error or temporal variations of all relevant data and their impact on the precision of the transfer velocity.

- Interpret your data and any deviations of the transfer velocity.

- Prepare the diagrams (reference spectra, time series, ...) in such a way that it is easy to obtain an overview of the experiment and it is easy to follow the choice of time period for the fits, or the choice of the wavelength range for the averaging of \([HI]/[I−]\).

- Save your final results and output files from the script Windmuhle_Auswertung_Studenten.ws.

References


