

## **Projet RenovRisk - TRANSFERT – Livrable 3 – L3.3.2-A : Données issues de l’acquisition (bilan des carbonates)**

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# 1. Authors Informations

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# 2. Files descriptions

## 2.1. Naming convention

The data are compiled in a ZIP-file containing 3 directories and 27 CSV files. The directories correspond to the years of field investigations on 4 digits YYYY, in each directory the files are named according to the **date\_** (YYYYMM\_, year and month), the **station name\_** and the **parameters measured**.

Examples:

- 202104\_offshore\_biogeochemprobes.csv: biogeochemical measurements realized at the offshore station, in April 2021

- 202110\_TDE\_currents.csv: currents measurements (hydrodynamics) realized on the TDE station in october 2021.

## 2.2. Descriptions of the fields in the files

### 1. Files containing currents (hydrodynamics) data on the reef flat

Field name	Unit	Definition
time	yyyy/MM/dd HH:mm:ss	time vector
speed	m/s	depth-average current speed
dir	decimal degrees (°)	depth-average current direction
depth	m	sea water height above sensor

Missing data (NaN) are linked to the quality control mentioned below.

### 2. Files containing Biogeochemprobes data on the reef flat

Field name	Unit	Definition
time	yyyy/MM/dd HH:mm:ss	time vector

do_raw_mgL	mg.L <sup>-1</sup>	raw dissolved oxygen concentration
do_calib_mgL	mg.L <sup>-1</sup>	dissolved oxygen concentration calibrated
do_calib_mmolm3	mmol.m <sup>-3</sup>	dissolved oxygen concentration calibrated
do_smooth_mmolm3	mmol.m <sup>-3</sup>	smoothed dissolved oxygen concentration calibrated
temp	°C	Temperature
temp_smooth	°C	smoothed Temperature
sal		Salinity
sal_smooth		smoothed Salinity
PAR	μmol.m <sup>-2</sup> .s <sup>-1</sup>	Photosynthetically active radiation
ph_raw	total hydrogen ion scale	raw pH measurements
ph_calib	total hydrogen ion scale	pH measurements calibrated
ph_smooth	total hydrogen ion scale	smoothed pH measurements calibrated

### 3. Files containing Biogeochemical data offshore

Field name	Unit	Definition
time	yyyy/MM/dd HH:mm:ss	time vector
do_raw_mgL	mg.L <sup>-1</sup>	raw dissolved oxygen concentration
do_calib_mgL	mg.L <sup>-1</sup>	dissolved oxygen concentration calibrated
do_calib_mmolm3	mmol.m <sup>-3</sup>	dissolved oxygen concentration calibrated
do_smooth_mmolm3	mmol.m <sup>-3</sup>	smoothed dissolved oxygen concentration calibrated
ph_raw	total hydrogen ion scale	raw pH measurements
ph_calib	total hydrogen ion scale	pH measurements calibrated
ph_smooth	total hydrogen ion scale	smoothed pH measurements calibrated

### 4. Files containing Biogeochemical data on the reef flat

Field name	Unit	Definition
time	yyyy/MM/dd HH:mm:ss	time vector
ta	μmol.kg <sup>-1</sup>	Total alkalinity
dic	μmol.kg <sup>-1</sup>	Dissolved inorganic carbon concentration
omega	Ω <sub>aragonite</sub>	aragonite saturation state of seawater
pco2	μatm	partial pressure of CO <sub>2</sub>

### 5. Files containing Biogeochemical data offshore

Field name	Unit	Definition
time	yyyy/MM/dd HH:mm:ss	time vector
do	mmol.m <sup>-3</sup>	dissolved oxygen concentration
ph	total hydrogen ion scale	pH measurements
ta	μmol.kg <sup>-1</sup>	Total alkalinity
sal		Salinity

## 3. Methodology

### 3.1. Measurements

#### 1. Dates and locations

Data collection was performed on February-March 2020, October 2020, April 2021, October 2021 and June 2022.

Measurements and water sampling were performed offshore (55.238, -21.106) and at three sites on the reef flat: Livingstone (LIV) (55.23772, -21.09962), Toboggan (TOB) (55.222, -21.08137) and Trou d'Eau (TDE) (55.2403, -21.10157).

On the reef flat, autonomous measurements and water sampling were performed at three sites over three periods to characterize the spatial and temporal variability of physical and biogeochemical parameters.

Measurements of light, temperature, salinity, currents, and water chemistry were carried out at Toboggan and Livingstone in February 2020 (summer) for 4 and 2 days respectively, at Bodega in March 2020 (summer) for 3 days, at Livingstone in October 2020 (winter) for 4 days, at Trou d'Eau in April 2021 (summer) for 15 days, at Livingstone, Toboggan and Trou d'Eau in October 2021 (winter) for 5, 3 and 2 days respectively and Toboggan in June 2022 (mid-season) for 3 days. Offshore measurements of temperature, salinity and water chemistry were performed in April and October 2021.

## 2. Physical variables measurements

A bottom-mounted ADCP (Nortek Aquadopp Profiler) was deployed on the reef flat and programmed to record 2-min average current speed and direction, every 5 minutes over a vertical profile with cells size of 10 cm. ADCP was associated with a pressure sensor to record instantaneous depth every 10 and 5 minutes offshore and on the reef flat, respectively.

Salinity was recorded during sampling offshore using a miniCTD (Valeport) with an accuracy  $\pm 0.01$ . Salinity and temperature were measured every 15 minutes on the reef flat using a JFE Advantech ACTW-USB probe, with accuracies  $\pm 0.01$  and  $\pm 0.1^\circ\text{C}$ , respectively.

Downwelling planar photosynthetically active radiation (PAR) was measured on the reef flat using a Compact LW (Alec-Electronics) recording during 10 seconds every 15 minutes.

## 3. DO, pH<sub>T</sub> and TA measurements

DO was measured every 15 minutes offshore and on the reef flat using YSI 6920 V2-2 probes equipped with optical O<sub>2</sub> sensors, with an accuracy  $\pm 0.1 \text{ mg.L}^{-1}$ . The pH<sub>T</sub> (total hydrogen scale) was measured every 15 minutes using a SAMI<sup>2</sup>-pH probe (Sunburst Sensors) on the reef flat, with an accuracy  $\pm 0.003$  pH units, and a SeaFET<sup>TM</sup> V2 probe (Sea-bird Scientific) offshore, with an accuracy  $\pm 0.02$  pH units.

Water samples were collected with a Niskin bottle for DO and pH<sub>T</sub> and TA analysis. On two occasions, an automated water sampler (AquaMonitor, GreenEyes) was used to collect TA samples only, at Trou d'Eau in April 2021 and Toboggan in June 2022. Samples collected for DO and pH<sub>T</sub> analysis were used to check the calibration of the probes. Water samples for analysis of TA were immediately filtered in the field using Whatman GF/F filters. Water samples for pH<sub>T</sub> and TA analysis were poisoned with mercuric chloride, following Dickson and Goyet (1994). In total, 31 offshore samples were collected, 15 during the warm season and 16 during the cold one. Reef flat samples were collected at shortest possible time intervals and at different times over the day course. During each one of the sampling periods, more than 10 DO and 15 pH<sub>T</sub> samples were collected.

DO was measured using the Winkler method according to Aminot and K  rouel (2004). pH<sub>T</sub> was measured on the total hydrogen ion scale at 25  C using the potentiometric method described by Dickson and Goyet (1994) and using a 905 Titrand Metrohm titrator with a combined pH electrode 6.0253.100. The electrode was calibrated using TRIS (T36) buffers provided by A. Dickson, Scripps Institution of Oceanography. The slope of the electrode was checked each day of measurements with NBS buffers of pH = 4.01, pH = 7.01 and pH = 10.01 (Hanna instruments). pH<sub>T</sub> was calculated according the following equation:

$$pH_T = pH_{TRIS} + \frac{E_{TRIS} - E_{SAMPLE}}{\text{electrode slope}}$$

with E the potential difference across the electrode. The precision of the analysis is  $\pm 0.01$  pH units (Dickson, 2010). TA was measured in triplicate using an automated potentiometric titration (905 Titrand Metrohm) and calculated from the second inflection point of the titration curve. To approximate the ionic strength of seawater, the acid titrant was 0.01 mol.L<sup>-1</sup> HCl in NaCl. The HCl concentration was checked each day of measurements using a CRM provided by A. Dickson, Scripps Institution of Oceanography. The precision of the analysis in triplicate measurements is  $\pm 2 \mu\text{mol.kg}^{-1}$ .

## 3.2. Data processing

### 1. Pressure and currents

The current meter was fixed on the bottom at a depth of about 1 m. Current measurements are made in cells 10 cm vertical. A minimum number of 5 cells is thus usable in the water column, once subtracted from the mounting height

of the instrument (10-29 cm depending on the site), the blanking region of 10 cm above the instrument and surface echo effects that remove 1-2 cells below the surface. The data obtained are time series of vertical profiles of speeds, current directions and water pressure.

A quality control on all the measurements was carried out in order to filter the cells for which certain data are not valid and are likely to introduce errors in the estimation of the currents on the vertical. These filters select usable data by taking into account (1) invalid depths, i.e. those near the surface and in the atmosphere, (2) the positioning of the instrument, (3) the intensity of the acoustic signal, (4) known speed values of the Reunion reefs: < 20 cm.s<sup>-1</sup> and 50 cm.s<sup>-1</sup> for the vertical and horizontal speeds, respectively, and (5) echoes due to potential obstacles along the acoustic beams.

Vertical current profiles were depth-averaged every 5 minutes. Water flowing in shallow water is not constant on a vertical profile so depth-average current speed and direction is estimated according Soulsby (1997).

## 2. Biogeochemistry

Data from the probes were smoothed to solve problems of noise filtering (Sharma et al., 2015). The smoothing procedure was the locally weighted scatterplot smoothing (LOWESS) method (Cleveland, 1979) on a 6 hours window (semidiurnal tide). This method led to the most consistency between raw and smoothed data ( $r^2 > 0.97$ ).

## 3. Carbonate system

Dissolved inorganic carbon (DIC) concentrations, partial pressure of CO<sub>2</sub> ( $p\text{CO}_2$ ) and aragonite saturation state of seawater ( $\Omega_{\text{aragonite}}$ ) were estimated with the Matlab program CO<sub>2</sub>SYS (van Heuven et al., 2011) using as input data laboratory TA measurements and *in situ* pH<sub>T</sub>, temperature and salinity from the probes (the temperature recorded by the SeaFET™ V2 and the JFE Advantech ACTW-USB probe for offshore and reef flat samples, respectively). Typical values of phosphate (0.1  $\mu\text{mol.kg}^{-1}$ ) and silicate (3  $\mu\text{mol.kg}^{-1}$ ) for open ocean and the reef flat of La Saline fringing reef were used (Cuet et al., 2011). The constants  $K_1$  and  $K_2$  were from Leuker et al. (2000) as recommended for best practices by Dickson et al. (2007).

### 3.3. Calibration informations

The pH and DO measurements were calibrated with the discrete bottle samples. pH samples were measured at 25°C. For the calibration pH at *in situ* temperature have been estimated with the Matlab program CO<sub>2</sub>SyS (van Heuven *et al.*, 2011).

**Offshore measurements** environment relatively constant so probes (DO and pH) were calibrated with samples by adding the mean difference between samples and probes at the same time.

#### April 2021

DO (calibrated) ( $\text{mg.L}^{-1}$ ) = DO + 0.14

pH (calibrated) = pH + 0.003

#### October 2021

DO (calibrated) ( $\text{mg.L}^{-1}$ ) = DO + 0.42

pH (calibrated) = pH + 0.029

**Reef flat measurements:** Probes (DO and pH) were calibrated with samples by linear regression.

#### February-March 2020 (same deployment):

DO (calibrated) ( $\text{mg.L}^{-1}$ ) = 1.0631 \* DO + 0.0362 ( $r^2 = 0.99$ )

No pH samples for calibration.

#### October 2020:

Mean of three calibrated probes:

DO1 (calibrated) ( $\text{mg.L}^{-1}$ ) = 1,0297 \* DO1 + 0,0066 ( $r^2 = 0.99$ )

DO2 (calibrated) (mg.L<sup>-1</sup>) = 0,967 \* DO2 + 0,1513 (r<sup>2</sup> = 0.99)  
DO3 (calibrated) (mg.L<sup>-1</sup>) = 0,9873 \* DO3 + 0,1348 (r<sup>2</sup> = 0.99)  
No pH measurements.

#### April 2021

DO (calibrated) (mg.L<sup>-1</sup>) = 1.0062 \* DO (r<sup>2</sup> = 0.99)  
pH (calibrated) = 0.9903 \* pH + 0.068 (r<sup>2</sup> = 0.98)

#### October 2021

DO (calibrated) (mg.L<sup>-1</sup>) = 1.098 \* DO + 0.029 (r<sup>2</sup> = 0.98)  
pH (calibrated) = 0.9993 \* pH (r<sup>2</sup> = 0.93)

#### June 2022

DO (calibrated) = 1.106 \* DO - 0.136 (r<sup>2</sup> = 0.99)  
pH (calibrated) = 0.9994 \* pH (r<sup>2</sup> = 0.98)

### 3.4. Data-specific informations

- pH was not measured at Livingstone in October 2020
- For reef flat salinity at Trou d'Eau – Apr 2021 and Livingstone- Oct 2021, very low salinities (<34.8) were considered as not natural because no rain event occurred during the field.
- At Toboggan – Jun 2022, pH time series is shorter because of a sensor failure. Recording started on 15/06/2022 at 06:00:00.
- Low reef flat TA compared to offshore waters are discussed in the publication associated with this dataset.

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## 5. Cited References

- Aminot, A., Kérouel, R., 2004. Hydrologie des écosystèmes marins: paramètres et analyses, Ed. Ifremer.
- Cleveland, W.S., 1979. Robust Locally Weighted Regression and Smoothing Scatterplots. *Journal of the American Statistical Association* 74, 829–836.
- Cuet, P., Atkinson, M.J., Blanchot, J., Casareto, B.E., Cordier, E., Falter, J., Frouin, P., Fujimura, H., Pierret, C., Susuki, Y., Tourrand, C., 2011. CNP budgets of a coral-dominated fringing reef at La Réunion, France: coupling of oceanic phosphate and groundwater nitrate. *Coral Reefs* 30, 45–55. <https://doi.org/10.1007/s00338-011-0744-4>
- Dickson, A.G., Goyet, C., 1994. Handbook of methods for the analysis of the various parameters of the carbon dioxide system in seawater, Version 2. Oak Ridge National Lab., TN (United States). <https://doi.org/10.2172/10107773>
- Dickson, A.G., Sabine, C.L., Christian, J.R., 2007. Guide to Best Practices for Ocean CO<sub>2</sub> measurements. Technical Report. PICES Special Publication 3. pp. 191. (ISBN 1-897176-07-4)
- Lueker, T.J., Dickson, A.G., Keeling, C.D., 2000. Ocean pCO<sub>2</sub> calculated from dissolved inorganic carbon, alkalinity, and equations for K<sub>1</sub> and K<sub>2</sub>: validation based on laboratory measurements of CO<sub>2</sub> in gas and seawater at equilibrium. *Marine Chemistry* 70, 105–119. [https://doi.org/10.1016/S0304-4203\(00\)00022-0](https://doi.org/10.1016/S0304-4203(00)00022-0)
- Sharma, S., Swayne, D.A., Obimbo, C., 2015. Automating the Smoothing of Time Series Data. *J Environ*

Anal Toxicol 05, 1000304. <https://doi.org/10.4172/2161-0525.1000304>

Soulsby, R., 1997. Dynamics of Marine Sands. A manual for practical applications, Thomas Telford Publications. ed.

van Heuven, S., Pierrot, D., Rae, J.W.B., Lewis, E., Wallace, D.W.R., 2011. MATLAB program developed for CO<sub>2</sub> system calculations. ORNL/CDIAC-105b. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S Department of Energy, Oak Ridge, Tennessee. [https://doi.org/10.3334/CDIAC/otg.CO2SYS\\_MATLAB\\_v1.1](https://doi.org/10.3334/CDIAC/otg.CO2SYS_MATLAB_v1.1)